SIXTH FRAMEWORK PROGRAMME
PRIORITY FP6-2002-INCO-MPC-1
Integrating and strengthening the European Research Area,

Specific Measures in support of International Cooperation (INCO)

PROMET

DEVELOPING NEW ANALYTICAL TECHNIQUES AND MATERIALS FOR MONITORING AND PROTECTING METAL ARTEFACTS FROM THE MEDITERRANEAN REGION

CONTRACT n° 509126

Final Report

REPORTING PERIOD FROM: **01/11/2004** TO **30/04/2008**

PROJECT START DATE: **01/11/2004** DURATION : **42 Months**

Project Coordinator Name: Dr. Vasilike Argyropoulos
Project Coordinator Organisation Name: Technological Educational Institution of Athens

1. Project Execution

1.1 Statement of the Problem and PROMET's Objectives

Technological innovation is considered as the key element to economic development in the Mediterranean region that requires cooperation. To this end, the project known as PROMET represents an endeavour which brings together specialists and end users in the field of preservation of cultural heritage so as to develop innovative strategies to protect, preserve, and interpret the material culture made of metals, which is in museums of the Mediterranean basin.

To fulfil this curatorial mission, a good knowledge of the composition and manufacturing techniques of the finds of the collections is necessary. This information is of primary importance for improving the archaeological/historical data of the collection and for conducting a survey of the metallic collections to allow the set up of a coherent conservation and restoration policy.

Taking into account environmental data and the degradation mechanisms, the curator will need to develop and implement a coherent conservation plan. In some cases, the plan shows that conservation-restoration work must take place because of the presence of active corrosion on a metal object. At the end of the conservation treatment, a protection coating must be applied to slow down the exchange between the metal and the corrosive media. With the application of these protective coatings, a maintenance programme must be set up to prevent the degradation of the coating and to determine the time between two applications.

Unfortunately, most of those methods cannot be easily pursued because of the lack of qualified persons in the institutions; consequently it is difficult to have a coherent conservation and restoration policy since, except for large institutions, the curator has to hire a conservator-restorer (C-R) as well as search for funds.

Good knowledge of the composition of the ancient metals can be a decisive factor for their preservation, because some alloys are more sensitive to changes in the environment than others. Thus, it is often important to perform early diagnostic analysis to identify the mechanisms that lead to the degradation of collections.

Jointly, the partners of PROMET developed new strategies to monitor the corrosion of metal objects using the state-of-the-art portable techniques of Laser- induced breakdown spectroscopy (LIBS) and micro-X-ray Fluorescence (μ-XRF). Scientific studies are providing other and newer ways to obtain information about these unique collections from the past. At the same time, conservation scientists developed and tested new materials, corrosion inhibitors, coatings, and PVD and PECVD barrier films as alternative ways of better protecting metals collections, ways that are safer, more effective, reversible, and longer-lasting.

Survey and damage assessment

The only way to establish and to promote a proper conservation strategy for the Mediterranean region is to develop prototype portable diagnostic and/or monitoring systems and protection methods, to identify each specific degradation factor for the many museum collections of precious metals, iron and copper alloys, and then carry out the preservation.

Condition surveys and reports were developed for PROMET project and damage assessment reports were written for these museum collections.

The collections studied in the PROMET project are collections of different metals.

Archaeological collections

A1. Silver alloy collection from the Egyptian Museum of Cairo
A2. Copper alloy and iron collection from the Archaeological Museum of Ancient Messene, Greece
A3. Silver alloy Coins from the National Roman Museum, Italy

A4. Copper alloy collection from the Museum of Umm Qais, Jordan
A5. Copper alloy collection from the Rabat Archaeological Museum of Morocco
A6.Iron alloy collection from the villages of Calatrava la Vieja and El Saucedo, Spain
A7.Copper and iron alloys collection from excavations in the Syrian Arab Republic
A8.Copper alloy and iron collection from the Van Museum in Eastern Anatolia, Turkey

Historical collections

H1.Silver alloy collection from the Museum of Technology of Athens, Greece
H2.Silver Abbasid coins from the Museum of Jordanian Heritage
H3.Steel Armour of the Knights from St. John, Grand Masters Palace, Malta

Non-destructive analytical techniques

Prototype portable techniques, such as Laser-induced breakdown spectroscopy (LIBS) and micro X-ray Fluorescence (µ-XRF) are excellent analytical tools for identifying the characteristics of metal artifacts as well as the different metal degradation factors. These non-destructive techniques were developed for PROMET, given the difficulty to be granted permission to remove bulk materials for destructive analysis or even to transport them to a lab for scientific examination. Advanced analytical methods were used to survey collections of archaeological or historical metal objects in *situ,* making it possible to pinpoint conservation needs without any risk of damaging the artifacts.

Corrosion inhibitors and protective coatings

Another major innovation for this project was the search for new, safe, and effective corrosion inhibitors and coatings for the protection of cultural property made of metals. Safe corrosion inhibitors do exist, and new chemical agents were developed and/or validated to use on artificially- or naturally-aged metal reference alloys and, then, real metal objects. These include: Linear saturated sodium carboxylates; Azoles and natural extracts from Moroccan plants; Salts of linear aliphatic organic acids, derived from vegetable oils and extracts (for example, cactus); Commercially available and safe corrosion inhibitor additives for synthetic waxes and varnishes.

Furthermore innovative plasma processes for the deposition of barrier films and for suitable cleaning of the artifacts were investigated, such as Plasma Enhanced Chemical Vapour Deposition (PECVD) of SiO_2-like thin films associated to a cleaning pre-treatment in hydrogen plasma. The SiO_2-like coatings are transparent and characterised by high chemical and thermal stability, good dielectric properties, and low gas permeability.

Quality Assurance of PROMET's deliverables

Testing and evaluating the innovative approach, monitoring tools, protection materials on real collections throughout the Mediterranean region is essential to ensure the quality of the tools, materials, and products produced and/or tested for this project. Furthermore, the PROMET deliverables were also tested and evaluated for by the end-users, namely museum and conservation-restoration professionals in order to assure their applicability to real situations.

Just as the changing climate represents a global concern, the environmental impact on heritage preservation has a global character, and partnerships across Europe and the Mediterranean are essential to maximise the impact of the state-of-the-art research and development within the intensified global economy. European partners collaborated together with Mediterranean partners within PROMET's consortium to develop the latest technologies and examples of effective heritage planning. PROMET offered challenging cases for the preservation of cultural property made of metals requiring international co-operation to build on their own best practices for viable solutions within their countries.

For a greater impact of the research results of PROMET, one needs to consider the sustainable development of culture heritage in the field of preservation.

In the framework of the EC 6th Framework Programme that supported the PROMET project financially, several innovative methods and materials for the conservation of ancient metals have been explored, achieving interesting results worth being implemented through future actions: (i) innovative portable instruments have been developed as prototypes for diagnostic tools to be optimised in order to satisfy the market and unskilled operator requirements; (ii) low toxic organic inhibitors, green inhibitors and thin barrier films produced via environmentally friendly plasma based techniques have to be evaluated for longer exposure times in different environments.

The exciting work and study experience carried out in the PROMET project leaves a permanent sign in the PROMET Internet portal www.promet.org.gr (currently with 185 registered users representing 38 countries worldwide), an integrated information system allowing communication, control and exchange of information between the partners, European and Mediterranean Museum and Conservation Institutions, that constitutes a tool for:

(i) Updating the identification of the demand of C-Rs and researchers concerning the reliable methods and materials for the conservation, management and exhibition of ancient metal objects in the Euro-Mediterranean basin;

(ii) Maintaining a database dedicated to the description of exemplary degradation cases as well as to literature information dedicated to the conservation materials and methods and to the exhibition, management, and storage of safe conditions.

(iii) Providing information on the organisation of thematic workshops, actions of co-operation for solving specific conservation problems related to the moving, management, exhibition and storage of ancient metals collections with the choice of safe environmental conservation conditions and materials with the ultimate goal of increasing the knowledge and encouraging sharing of each member's capabilities.

The past and future efforts of all the participants of the project will contribute to extend the life of the witnesses of human metallurgical activities that allowed humankind to produce wonderful artifacts.

Contractors Involved:

Role*	**Partic. no.**	**Participant name**	**Participant short name**	**Country**
CO	1	Technological Educational Institution of Athens	TEI	Greece
CR	2	Foundation for Research & Technology- Hellas	FORTH-IESL	Greece
CR	3	Heritage Malta	HM	Malta
CR	4	Department of Metallurgy and Material Engineering, University of Malta	DMME	Malta
CR	7	SVUOM Ltd	SVUOM	Czech Republic
CR	8	National Institute of Laser Enhanced Science	NILES	Egypt
CR	9	The Laboratory of Research on Historic Monuments	LRMH	France
CR	10	Laboratory for Material Analysis	Demokritos	Greece

		Institute of Nuclear Physics. NCSR Demokritos		
CR	12	Institute of Archaeology and Anthropology	YU-FAA	Jordan
CR	13	Royal Scientific Society	RSS	Jordan
CR	14	Politecnico di Torino, Dipartimento di Scienza dei Materiali ed Ingegneria Chimica	POLITO-SMIC	Italy
CR	15	Consiglio Nazionale delle Ricerche, Instituto per lo Studio dei Materiali Nanostrutturati	CNR-ISMN	Italy
CR	16	National Technical University of Athens, School of Chemical Engineering	NTUA	Greece
CR	17	Consejo Superior de Investigationes Cientificas, Centro National des Investigaciones Metalurgicas	CSIC-CENIM	Spain
CR	18	National Research Center, Physical Chemistry Department	NRC-EC	Egypt
CR	19	Egyptian Museum	EM-MC	Egypt
CR	20	Jordan University of Science and Technology, Faculty of Computer and Information Technology	JUST	Jordan
CR	22	IBN TOFAIL University- Faculty of Science, Department of Chemistry	IBN-DC	Morocco
CR	23	EGE University, Department of Protohistory and Near Eastern Archaeology	EGE-PNEA	Turkey
CR	24	Ministry of Culture, General Directorate of Antiquities & Musuems	MC-DAM	Syrian Arab Republic
CR	25	University of Aleppo, Department of Materials Engineering	ALP-ME	Syrian Arab Republic

*CO = Coordinator
CR = Contractor

1.2 Innovative Portable Systems: Micro-XRF and LIBS (Workpackage 2)

The successful conservation of ancient objects relies to a large extent on the knowledge of a) the physical and chemical nature of the constituent materials and b) the extent of their transformation through time and under the influence of environmental or burial conditions.

A particularly attractive aspect of modern analytical technology is mobility. Over the past few years, research efforts have resulted in compact, mobile instruments that can be transported and operated beyond the standard scientific laboratory environment, namely in the conservation laboratory, in the museum or even at the archaeological/historical site, offering unique opportunities for the study of valuable objects at their location. An additional issue of high importance is that such mobile analytical techniques enable also analysis to be carried out directly on the objects, thereby eliminating the need for sampling. And this can be done in a practically non-invasive manner.

a) Micro-XRF spectroscopy:

Basic research was focused at first in the original design and optimization of the micro-XRF probe characteristics, implementing the experience of previous developed successful commercial prototypes and in-house at Demokritos developed milli-beam spot XRF spectrometers. The hardware integration resulted to a compact size flexible spectrometer head enabling accurate targeting of the analysis spot, visualization and recording of the spots analyzed, whereas the possibility to map the investigated area in short measuring time added a significant analytical potential to the spectrometer. A systematic study of the analytical performance of the micro-XRF spectrometer was undertaken next, regarding the analytical description of its elemental excitation response, spatial resolution and analytical sensitivity. Optimized analysis protocols were developed and validated through various experimental methodologies towards an accurate, precise compositional analysis of the alloys composition overcoming problems that arise either from their heterogeneity (in many cases) at the micrometer scale or Bragg spectral interferences.

As a next step the micro-XRF spectrometer was evaluated in terms of its analytical performance to identify corrosion products developed on the alloys surface. Artificially corroded copper and silver coupons produced by the PROMET partner P7, CNR-ISMN to simulate the composition and degradation phenomena of archaeological alloys, were measured exploring various experimental (single spots analysis, line or area elemental mapping) or analytical methodologies (the variation of the intensity ratio of two characteristic X-rays of the same element with low and high energy, respectively). Since the coupons were characterized prior by SEM-EDX and XRD techniques by partner CNR-ISMN, the comparison with the micro-XRF results offered a solid basis to identify and document the analytical capabilities of the technique.

The five (5) in-situ analytical campaigns of DEMO group at Ancient Messene (twice, September of 2005 and 2006), Malta (October 2006), Syria (October 2007) and Jordan (November 2007) were served as unique opportunities to apply and assess the analytical performance of the micro-XRF spectrometer (and in two cases of another milli-XRF device) in the analysis of various museum metal collections (including all types of metal alloys; iron, copper, silver and gold metals), tackling successfully conservation, authenticity and technological related issues. In the framework of the in-situ analytical campaigns DEMO collaborated closely with partners TEI , FORTH, HM, MC-DAM, ALP-ME, YU-FAA, RSS, and POLITO

During Ancient Messene and Malta campaigns the results of the micro X-Ray Fluorescence (micro-XRF) spectrometry were critically compared with those of the milli-XRF analysis, whereas at ancient Messene, Syria and Jordan the Demokritos group together with FORTH, tested and assessed the real-time and combined use of µXRF and LIBS on original artifacts.

The two portable, non-destructive analytical techniques, LIBS (Laser Induced Breakdown Spectroscopy) and micro-XRF were applied for the first time in the characterization of copper alloy corrosion layers. The combined application of LIBS and micro-XRF techniques on corroded metal alloys was assessed as quite complementary and very promising.

Analytical methodologies were developed, studied and optimized to overcome two major problems regarding the micro-XRF analysis of metal alloys; the heterogeneity that it is appeared very often (depending on the type of the alloy) at the micrometer scale and the interfering presence of diffraction peaks in the XRF spectrum. Experimental tools such as: a) The implementation of line and area scans to obtain in reasonable measuring time (1x1 mm^2, 50 µm step, 10s/step,~1.5h) distribution maps of various elements, b) The analysis of corroded area versus corrosion free surface, c) The utilization of optimized filtered excitation and d) The variation of the K/L or L/M elemental intensity ratios in single spot, line or area scan measurements provide accordingly numerous of analytical results such as: a) The spatial distribution of individual elements or iidentification of the spatial coexistence of different elements, fingerprints of certain corrosion products or of manufacture (gilding or surface finishing) techniques b) Estimation on a semi-quantitative basis of the elements enriched or depleted from the surface c) Identification of the presence of certain minor to trace elements that may support provenance and manufacture studies of the metal and d) Rough estimation of the depths that a certain element is located, namely, on the surface, near surface (~2-10 µm) or below ~10 µm. The experimental tools and the results obtained proved to help significantly towards the non-destructive identification of corrosion products based on either the spatially resolved co-existence of fingerprint elements (at the range of 100 µm), or of single element distribution maps, this information supported by the intensity contrast between the corrosion layer and the bare alloy or/and from the competition of the element low and high energy characteristic X-rays (if both detected). These experimental approaches are considered as state of the art methodologies proposed and applied for the first time by the Demokritos work within PROMET.

A significant state of the art contribution of DEMO within PROMET was the development of a novel analytical approach to describe the X-ray lens transmission efficiency and thus to predict more accurately the exciting spectral distribution in the micro-XRF analysis. More specifically, a theoretical model was developed based on a published description for the tube emission spectrum and on a transmission efficiency expressed as polynomial of 5^{th} degree versus energy. Measured and theoretically predicted characteristic K- or L- line intensities emitted by a large set of pure single element or compound targets (1.5 - 25 keV) with infinite or very small thickness, were compared through a X^2 minimization procedure utilizing the coefficients of the transmission efficiency function as fitted parameters. The agreement between fitted and experimental values at the convergence minimum was equal to 10-15%. The developed model was next validated in reproducing concentrations of ten NIST and BAM SRM glasses with deviations less than about 10%-15%. The state of the art advantage of the proposed analytical approach is that it does not require removal of the X-ray lens from the micro-XRF setup configuration and thus it can be adapted in commercial micro-XRF spectrometers supporting crucially the quantification process in micro-XRF analysis.

The synergistic and combined real time application of micro-XRF and LIBS spectrometers is presented also for the first time by DEMO and FORTH partners within PROMET framework as a state of the art development. The analysis of a micro-spot being successively ablated by LIBS pulses may reveal and elucidate the elemental stratigraphy of a corrosion layer, whereas in addition the µ-XRF technique evaluated the micro-destructive aspect of the LIBS irradiation supporting this way the optimization of the LIBS instrumental and operational parameters for minimum risk.

The in-situ analytical campaigns of the micro-XRF spectrometer assessed extensively the analytical performance of the spectrometer in “real” conditions, away from the controlled conditions of the laboratory environment.

Despite the dissemination of the micro-XRF spectroscopy to the market and in particular to the museums and conservation diagnostic laboratories (as it is indicated by the availability of relevant commercial instruments), from the published up to now bibliography it seems that its full potential had not been exploited. In the case of metal artifacts, in particular, micro-XRF analysis faces challenging analytical problems referring to the possibility of identifying the elemental composition of surface distributed corrosion products supporting thus the characterization of their mineralogical composition. These topics were successfully addressed within PROMET framework by Demokritos. In addition, improving the methodological and quantitative aspects of the micro-XRF analysis, Demokritos work showed that important information may be revealed regarding the manufacture techniques and composition of raw materials and associated trace elements supporting the archaeometallurgical research and conservation strategy of a metal collection.

The PROMET analytical campaigns offered unique – internationally - experience and knowledge regarding the *in-situ* application of the non-invasive micro-XRF analysis. Analytical possibilities were explored, difficulties were identified and the complementarity of the technique was also assessed. It should be highlighted, however, the most important contribution in the research field of the DEMO work within PROMET; the fact that in close collaboration with conservation scientists the micro-XRF analysis encountered practical problems related to the routine conservation work revealing its importance as a first elemental screening analysis that provides insight into the manufacture and the preservation state of archaeological and historical metal artifacts.

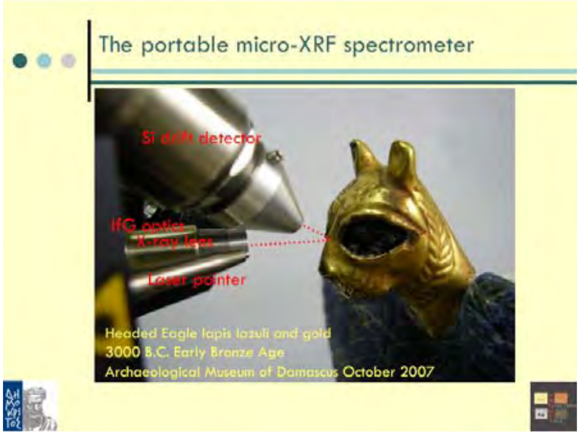
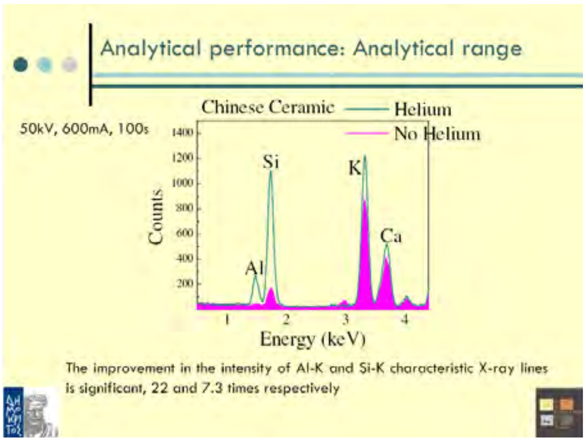
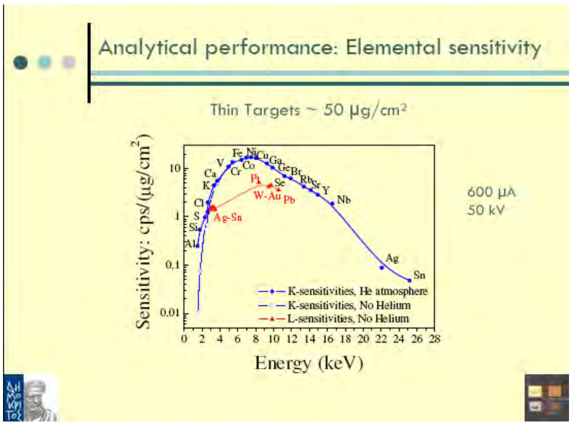


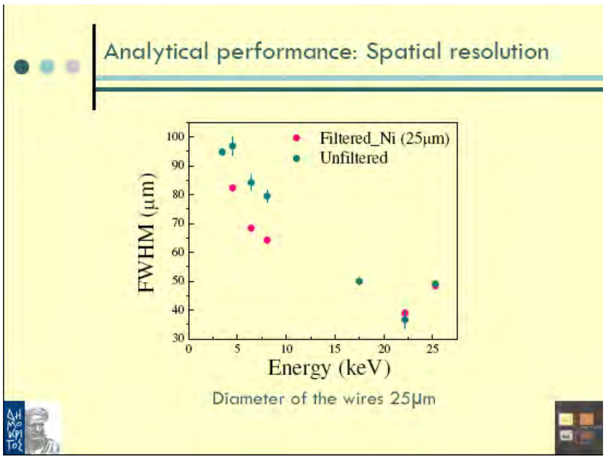
Photo of the micro-XRF measuring probe, designed and customized for Demokritos specifications (“open’ geometry), including the X-ray lens with 2 cm focal distance, a silicon drift detector and a ccd color camera for visual inspection of the analysis spot supported by a laser pointer.



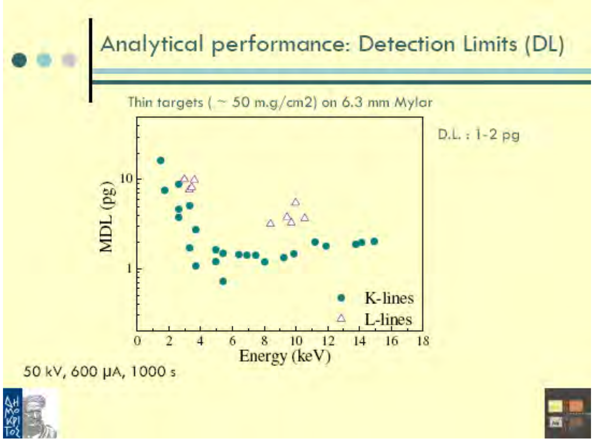
(a)



(b)

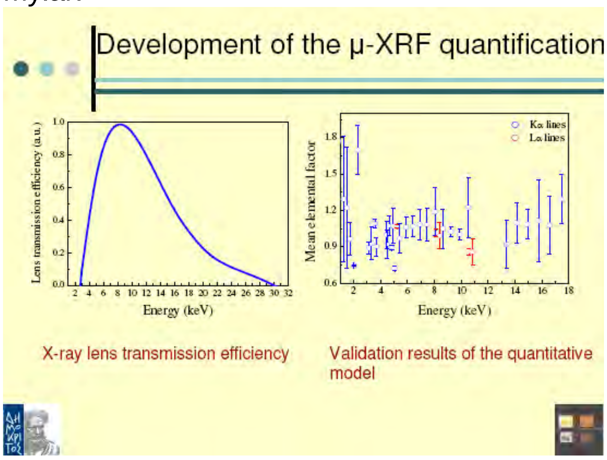


(c)



(d)

Graphs that present elements of the work related to the characterization of the analytical performance of the micro-XRF spectrometer (a) the implementation of a nozzle and He atmosphere in front of the X-ray detector improves the detectability of low atomic number elements. The graph shows the comparison of two µ-XRF spectra of a chinese ceramic reference material (IAEA) acquired in He and air atmosphere, respectively. (b) Elemental excitation response of the µ-XRF spectrometer, measured in terms of the fluorescent intensity per unit mass of a large number of infinitely thin targets. Under optimum opearional conditions intensities from 10 to about 10000 cps may be attained in the full energy region (1.5-26 keV) per 1 micro-g/cm^2 of pure material (c) Spatial resolution of the µ-XRF spectrometer measured my scanning the focal plane with a thin wire (diameter of 25 µm) and deducing the Full Width at Half Maximum (FWHM) of the intensity distribution versus position. The filtered excitation was produced by means of a Ni filter with 25 µm thickness and (d) Minimum Detectable Limit's (MDL's) for the µ-XRF spectrometer expressed in absolute mass (pg) determined by means of infinitely thin targets deposited on 6.3 µm mylar.

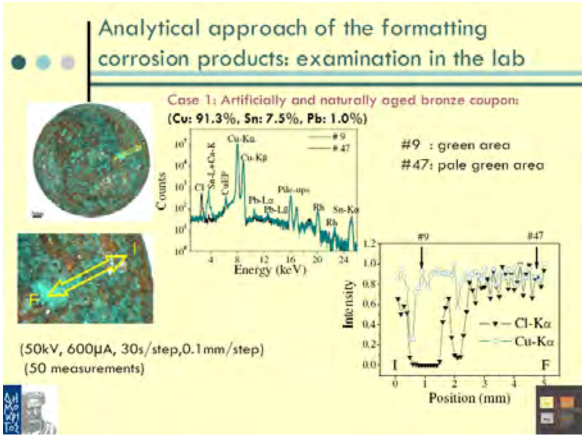


A new quantification analytical procedure was developed by Demokritos group within PROMET framework. The proposed method was presented in the European X-Ray Spectrometry Conference 16-20th June, 2008, Cavtat, Croatia, as a poster presentation. It is consisted of different steps: First, the characteristic X-ray intensities of a large set (about fifty) of infinitely thin and thick pure targets were measured. Then, the corresponding theoretical intensities were generated by the fundamental parameter equation. Experimental and theoretical intensities were compared through a non-linear least squares (X^2) minimization with fitted parameters the coefficients of a fifth-degree polynomial, assumed to describe analytically the energy dependence of the X-ray lens transmission efficiency. The results showed that the percentage differences between fitted and experimental values of the characteristic X-ray intensities (from thin and thick pure targets) were about 10-20% or less at the convergence minimum.

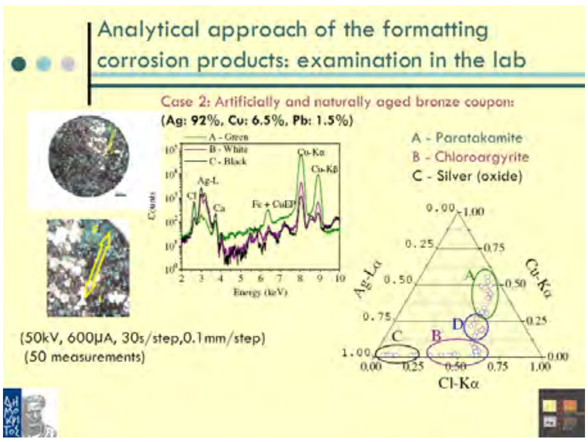
The developed quantification model was validated in reproducing elemental concentrations of ten NIST and BAM standard reference glasses. For each element, the ratio of the measured concentration with respect to the nominal one was served as a quantity to assess the accuracy of our procedure. The factor is expressed as follows:

$$K_i \equiv \frac{c_i}{c_{i,nominal}}$$

The mean value of Ki factor from all samples versus the characteristic X-ray energy is presented in the right figure of the slide, exhibiting variations mostly at the order of ±10%.

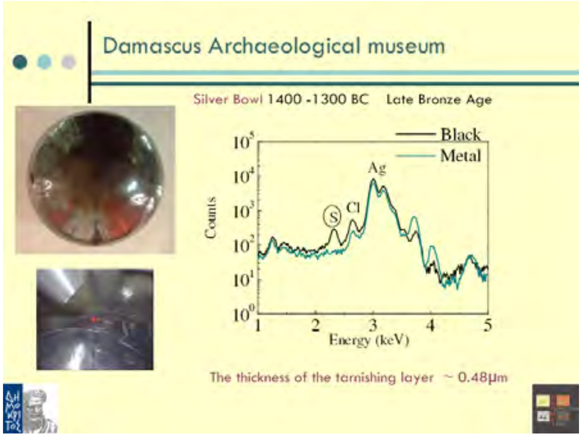


Micro-XRF analysis of a copper coupon (CNR128), with typical composition Cu: 91.3%, Sn: 7.5%, Pb: 1.0%. The line scan parameters were: Tube voltage 50 kV, Tube current 600 μA, length of the scanned area=5mm, step size= 0.1mm, measurement time/step=30 s. In the magnified photo the scanned area is shown including areas mainly with green or light-pale green color. The variation of the Cu-Kα and Cl-Kα characteristic X-ray intensities is in association with the colors observed, namely, Cu and Cl coexist in the light-pale green area, whereas in the green one Cu and Sn, respectively. Two micro-XRF spectra, representative of the two areas suggesting the possible presence of paratacamite (#47, high Cu, Cl) and of malachite together with minor amounts of cassiterite (#9, high Cu, Sn-L).are compared and presented in the slide.

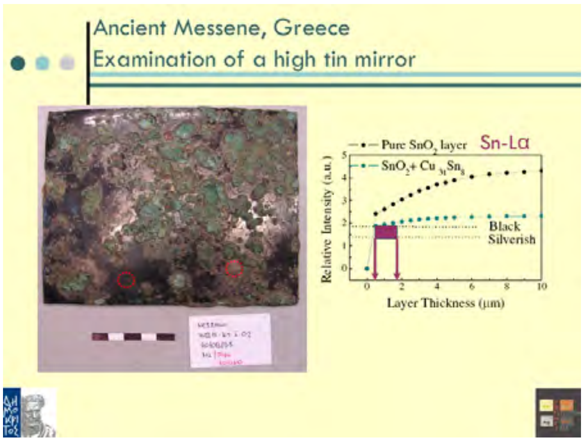


Results of the Micro-XRF analysis of a silver coupon (CNR-92), with typical composition Ag: 92%, Cu: 6.5%, Pb: 1.5%. The line scan parameters were: Tube voltage 50 kV, Tube current 600 μA, length of the scanned area=5mm, step size= 0.1mm, measurement time/step=30s. In the slide the scanned area is shown including white, black and green areas. The ternary plot presents normalized (to unity) Cu-Kα, Ag-Lα and Cl-Kα characteristic

X-ray intensities deduced from the micro-XRF spectra acquired across the line scan spots. Four regions can be identified: A) High Cu, Cl, low Ag, B) High Ag, Cl, low Cu, C) High Ag, low Cu, Cl and D) High Cl and medium Cu, Ag suggesting the presence of paratacamite (?) (A, green spots), chlorargyrite (B, white spots), silver oxide (C, black spots) and a mixture of more than one compounds in region (D).

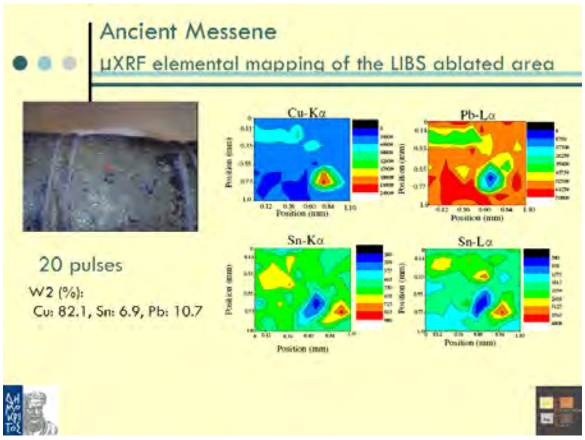


Micro-XRF analysis of a silver bowl (Late Bronze Age, 1400 -1300 BC, #402_25) engraved with geometric patterns at the National Museum of Damascus. The micro-XRF spectra (50kV, 600μA, 30 sec) from the black and the bare surface of the alloy are compared in the figure. The presence of S, Cl and of increased Cu content, together with the fact that actually there is no observable difference in the intensities of Ag-L (and Ag-K) X-ray intensities, characterizes the black shiny appearance of the silver alloy surface, the so-called silver tarnishing (Ag_2S). The estimated thickness of the tarnishing layer is 0.48μm in accordance with literature data. The sensitivity of the microXRF spectrometer enables probing of tarnishing thicknesses down to the few tens of nanometers offering thus early warning.

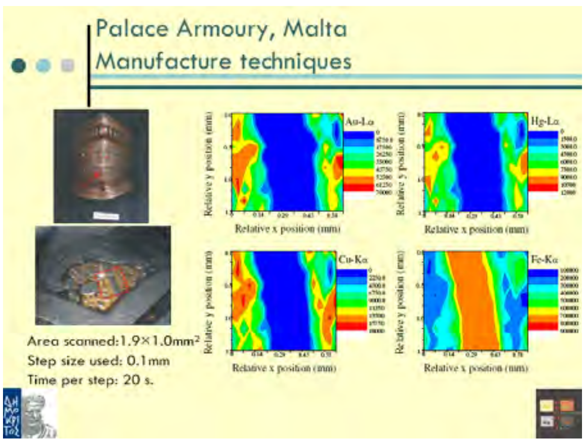


Assuming that on the silverfish area of a high tin bronze mirror (Ancient Messene), a thin composite layer of tin oxide plus a copper-tin phase has been grown with a black color, simulations were performed to deduce the thickness of the black layer. As experimental data, the relative intensity enhancement of Sn-Lα was utilized. The calculations indicate that, while the tin oxide layer at the silverfish areas is less than 1 μm, the thickness of the black area is from 1-3 μm.

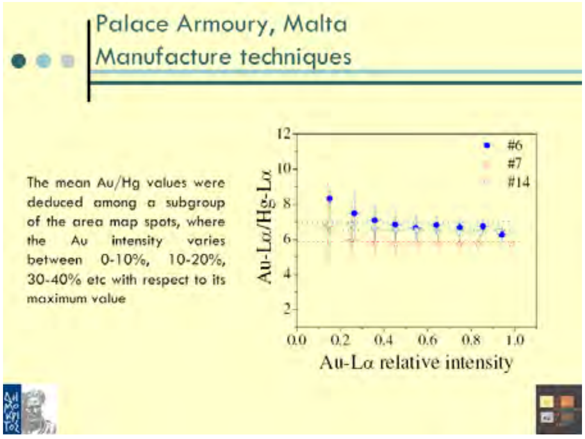
The head of the micro-XRF spectrometer coupled together with the LIBS unit for performing a dynamic mode of analysis. a: Object (Scraper, S2), b: Si-drift X-Ray detector (Bruker-AXS), c: Polycapillary X-ray lens (IfG), d: X-ray source (Bruker-AXS), e: LIBS unit (probe head).



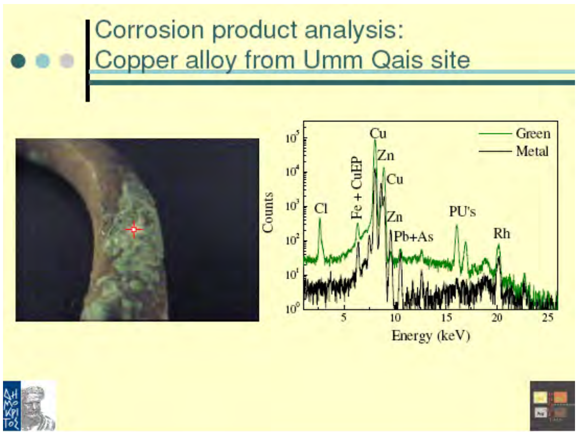
Micro-XRF analysis on the LIBS ablated area at Ancient Messene, Greeece. Object analyzed: Savrotiras W2 (n. 5256) found in the Asklepieion complex, in the Temple of Demeter dated in the 4th c. BC. The exciting X-ray beam scanned the light- green colour corroded surface that also includes the LIBS crater. Copper intensity on the surface is consistent and it is clearly higher in the core of the crater. The opposite phenomenon is observed for lead. The size of the LIBS crater was found to be 120 X 120 µm^2 (approx.). The micro-XRF elemental mapping provide a direct contrast of the elemental profile between the surface and ablated (core metal) area, respectively.



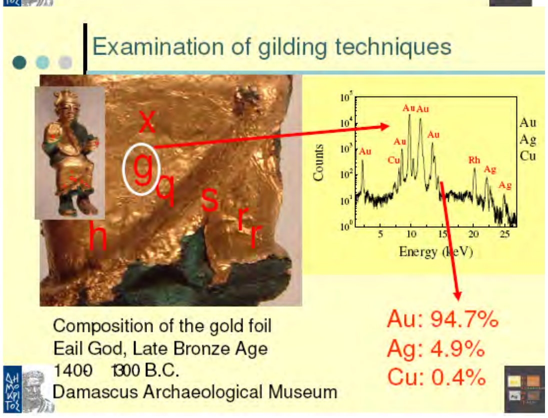
Results of the micro-XRF area mapping on an area of Armour-6, Armoury Palace Museum, Malta The intensity variation of Au- Lα and Hg- Lα characteristic X-rays is identical, whereas the Cu-Kα one shows some relative intensity variations, although it resembled the general trend followed by Au and Hg lines. Operating conditions: 50 kV, 600 μA, "unfiltered excitation", 20s/step, 0.1mm/ step. The results show that the gilding technique applied on the armour surface is fire-gilding, amalgamation.



Mean values of the ratio of Au and Hg X-ray intensities versus the Au one, from area mappings on three different armours (#6, 7 and #14) The mean values where deduced among a subgroup of the area map spots, where the Au intensity varies between 0-10%, 10-20%, 30-40% etc with respect to its maximum value. The results show that even in the areas where the thickness of the gilded area is very thin (the gilding has been degraded), the bonding of gold and mercury remains strong.



Micro-XRF analysis of a green corrosion product (left) on the surface of a copper-base rounded section bracelet (#216) belonging to the Umm Qais archaeological museum. The analysis was performed at the Numismatic Museum of Yarmouk, University, Irbid, Jordan At the right, the micro-XRF spectra (50kV, 600μA, 30sec) from the green and the bare surface of the alloy are compared. The coexistence of Cu and Cl suggests the presence of atacamite-paratacamite.



Results of the XRF quantification analysis developed at Demokritos in the case of gold and gold-gilded copper artifacts examined at the National Museum of Damascus. The possibility to analyze different locations on the same artifact may reveal information regarding the quality control of the manufacture process, i.e. the composition and thickness of the gold used at different areas or parts of the artifact.

b) LIBS spectroscopy

The LIBS technique, also referred to as laser-induced plasma spectroscopy (LIPS), has emerged in the past twenty years as a promising tool for the spectrochemical analysis of the elemental content of materials [22-26]. The analytical information derives by time- and spectrally-resolving the optical emission of a transient micro-plasma generated by focusing a nanosecond pulse from a laser on a solid surface (laser ablation). The characteristic, sharp atomic emission peaks in the LIBS spectrum enable the identification of the elements contained in the plasma plume, reflecting the local elemental composition of the solid sample. The peak intensity or the integrated emission of individual spectral lines can be associated with the concentration of the elements in the sample, leading to quantitative analysis based on calibration curves (obtained by analyzing appropriate reference samples) or on calibration-free methods [27].

Starting in 1997, with an original paper by the **IESL-FORTH** group [28], LIBS was shown as a potentially useful tool for analysis of works of art and archaeological findings. Since then, research that demonstrates the potential of LIBS in the field of cultural heritage has been reported in the literature describing analytical studies of materials in a variety of objects including painted artworks, icons, polychromes, pottery, sculpture, metal, glass and stone artifacts [29-35].

Obviously in the context of dealing with art objects several of the characteristic features of LIBS are considered quite important such as for example the ability to carry out the analysis in *situ*, namely on the object itself, with no need for sampling or sample preparation. The latter, coupled to the fact that a typical measurement requires a single laser pulse and the corresponding spectrum is acquired in less than one second, offers unparalleled speed. In addition, because of the tight focusing of the laser beam the lateral spatial resolution achieved is nearly microscopic (the diameter of the area probed is on the order of 100 microns). Even though the analysis leads to material removal from the surface, the loss in a typical LIBS experiment, is minimal (in the tens or hundreds of nanograms range) and any damage to the sample surface is practically invisible to the naked eye. Thus LIBS can be considered as a nearly non-destructive technique.

Through this project FORTH’s main aim was to investigate on the possibilities of using portable LIBS techniques to analyse the materials and potentially monitor the degradation phenomena observed on Metal collections in Mediterranean. With this aim the work has been organized as follows:

- Basic research was focused on the establishment of LIBS analysis potential and limitations in the analysis of metal objects of Cultural Heritage value. Within this scope the **LIBS analysis was optimized** following studies on different laser parameters (operative wavelength, laser pulse duration), set-ups (i.e. double pulse configurations) and methodologies (i.e. investigation on quantitative results). A major part of this work was a collaborative effort of FORTH with NILES. Through this collaboration a PhD student from NILES has been visited FORTH for a period of 3 months. Tests were performed on reference samples prepared in collaboration with PROMET projects end-users (i.e. TEI, CNR-ISMN, SVUOM)
- Based on this research **an integrated transportable and user-friendly LIBS system** for metal surface analysis was designed, developed and constructed. This system succeeded to overcome many practical issues and successfully take LIBS technology outside the research laboratory into real case archaeological analysis applications. To achieve this, a series of systematic and detailed tests and evaluations have been made both on model and real samples. The 1st on site campaign on September 2006 in ancient Messene in Peloponnese, Greece, highlighted several practical issues and gave the opportunity for further development and optimization of the system (i.e. by addition of an imaging system to locate the sampling areas). During the 2nd on-site campaign to Syria and Jordan on October- November 2007 the optimized portable LIBS instrument was tested on real gold, gilded and bronze artifacts from the Archaeological Museum of Damascus in Syria and the Numismatic Museum of the

Yarmouk University in Jordan. In both campaigns **the complementarity of the LIBS technique to μ-XRF analytical system** developed by Democritos was investigated.

- In parallel FORTH research team has been investigating the possibilities of combining LIBS analysis with other alternative analytical techniques, such as laser ablation mass analysis and/or laser Raman spectroscopy. This effort resulted to a publication where the potential use of a **hybrid LIBS-Raman** system for the spectroscopic analysis of archaeological and historical objects was discussed (A. Giakoumaki et al, Appl. Phys A 2006).
- Furthermore, a series of studies have shown the potential of the **LIBS analytical methodology to measure the thickness of the various protective coatings** usually encountered on metal objects (P. Pouli et al, Spec Acta B., 60, 2005).

The increasing demand for minimal intervention in combination with restrictions in sampling and transportation of cultural heritage and archaeological objects has led to the development of portable instrumentation for their analysis and characterization. The LIBS technique has been already incorporated in transportable and portable systems mainly for geochemical and environmental applications. Based on previous experience with a transportable system for the analysis of archaeological objects FORTH has developed and constructed a new fully portable LIBS system, LMNTII. The system developed through the PROMET project enables rapid, multi-elemental, in situ analysis with minimum influence on the sample surface while in some cases there is also the possibility for quantitative analysis. Furthermore, a depth profiling analysis is possible, when multilayered samples are examined

The development of advanced portable analytical techniques for the reliable, simple and fast analysis and characterization of metallic artifacts of CH value is very important as it enables the conservators/restorers to evaluate the preservation condition of the objects in-situ in the museums and archaeological excavation sites as well as it provides valuable information for the provenance, manufacturing information and history of these objects. Towards this objective PROMET had a major impact as it made possible the development and construction of two portable/transportable instruments (LIBS and μ-XRF) which were tested successfully on real case studies both individually as well as complementary in an attempt to investigate their potential in the characterization of the different bulk materials and corrosion layers usually encountered on metal objects with CH value. Furthermore systematic studies in the laboratories enabled the investigation of the optimum parameters for reliable results establishing also the detection limits and the limitations and potential of the developed analytical methodologies while it was possible to investigate their complementarity with other alternative analytical techniques (i.e. LIBS-Raman) and their prospective to answer to critical questions of the conservators/restorers (i.e. LIBS depth-profiling).

The portable LIBS instrument developed through the PROMET project for the rapid, multi-elemental and in-situ analysis of metallic objects of CH value is shown in the following photos (Figure 1):

Demonstration of the portable LIBS unit (left) and the case with all the equipment (right)

Figure 1

The system was tested and evaluated in various reference and real samples and it was shown to be able to discriminate between different corrosion layers on metal objects with archaeological value. A typical case on a decorative foil exhibited in the Museum of ancient Messene in Peloponnese, Greece is shown in figure 2:

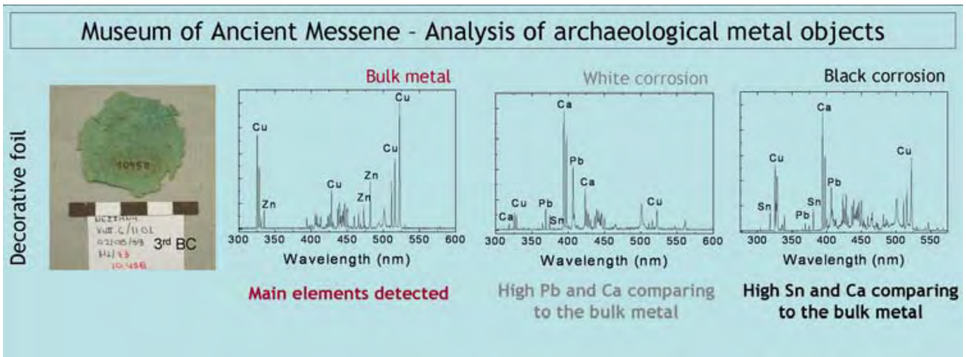


Figure 2

Furthermore the FORTH research team has been investigating on the potential use of LIBS analysis with other alternative analytical techniques. A Schematic drawing of the hybrid LIBS-Raman system proposed for the spectroscopic analysis of archaeological and historical objects is shown in Figure 3:

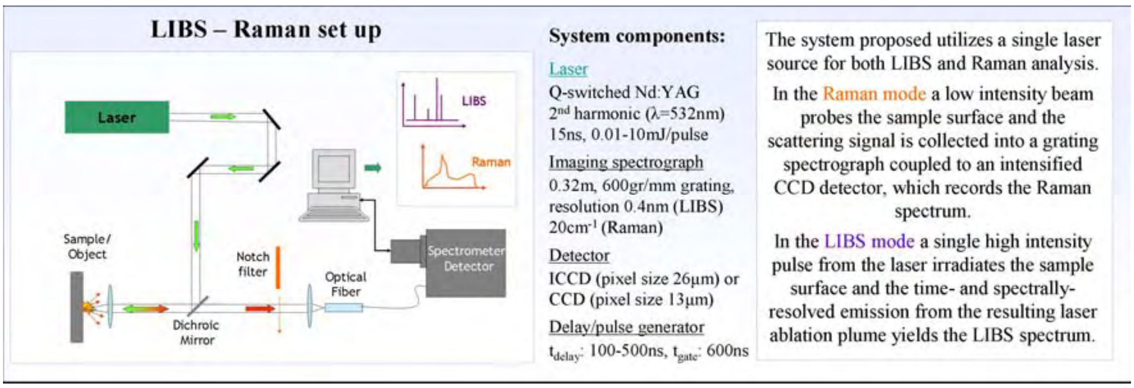


Figure 3

From the two detection systems used (an ICCD and a CCD) it was shown that with the CCD detection it was possible to collect clean and reliable single-shot LIBS spectra. Spectral lines appear somewhat broader compared to the ones in the gated spectra obtained using the ICCD. Raman spectra obtained with the CCD show superior S/N ratio because of more efficient cooling of the sensor. Also the smaller pixel size of the CCD gives rise to slightly better spectral resolution (Figure 4).

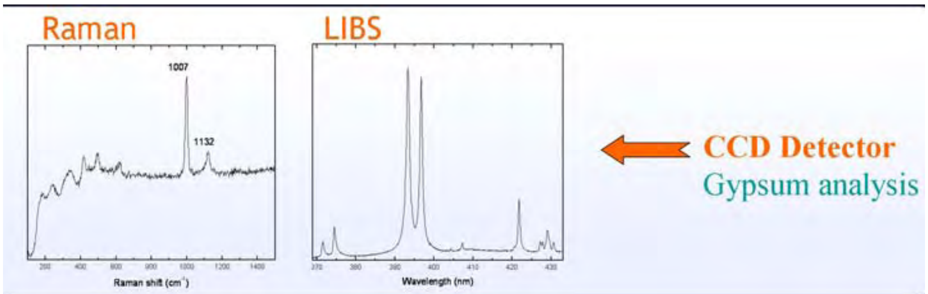


Figure 4

In parallel a series of studies were performed aimed to investigate the potential use of LIBS as a probe for estimating the thickness of different types of organic coating materials, applied to metals, following a stratigraphic analysis approach. LIBS was used to obtain stratigraphic profiles in a wide variety of materials including objects of art. This is done by monitoring specific spectral features in the LIBS spectra produced from successive laser pulses on the surface. In the case of coating thickness measurement through LIBS the characteristic emission from the metal substrate will signal the end point of the measurements while the knowledge of the ablation etch-depth per pulse for the coating material is required in order to provide a good estimate of the film thickness (Figure 5).

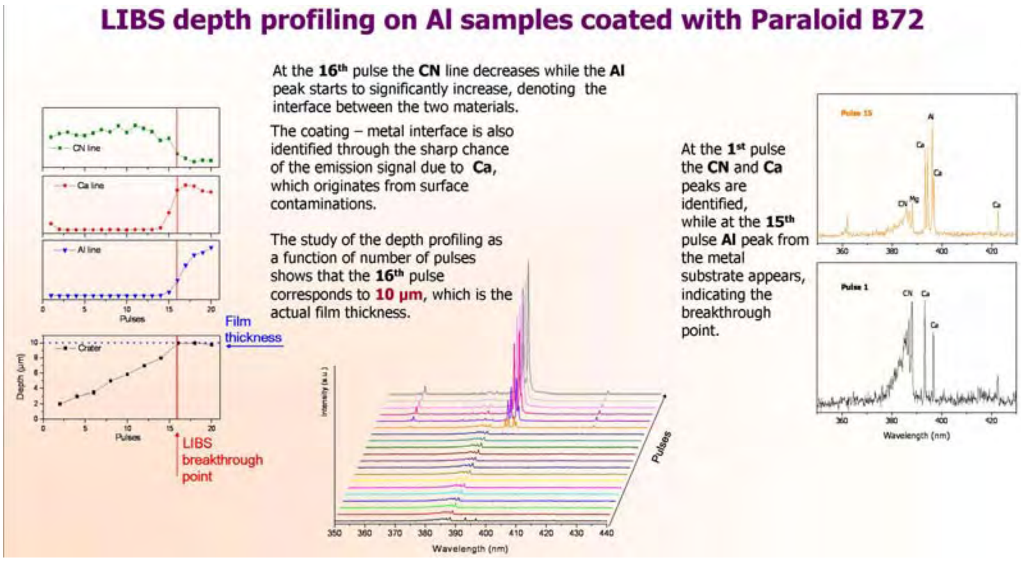


Figure 5

A novel analytical approach that combines LIBS and XRF, has been also applied for the characterization of archaeological copper alloys at the museum of Ancient Messene in Greece. Two versatile, portable units were incorporated in one set-up, in which both the laser and the X-ray beam were aligned enabling analysis to be performed at the same spot on the surface of the object under analysis. This was demonstrated successfully by analyzing a series of bronze objects (mainly copper alloys containing tin, zinc and lead) from a wide chronological period (4th century B.C. – 6th century A.D). Moreover, the stratigraphic analysis obtained with the LIBS technique, is very useful for the in-depth characterization of an object and the discrimination between corrosion layers and bulk material type. Therefore by collecting XRF data following single-pulse LIBS measurements it was possible to gather complementary and enhanced information about the elemental stratigraphy of the analyzed corrosion layer. This was a collaborative effort between FORTH and Demokritos. The combined µ-XRF /LIBS setup and a typical example of the results is shown in Figure 6:

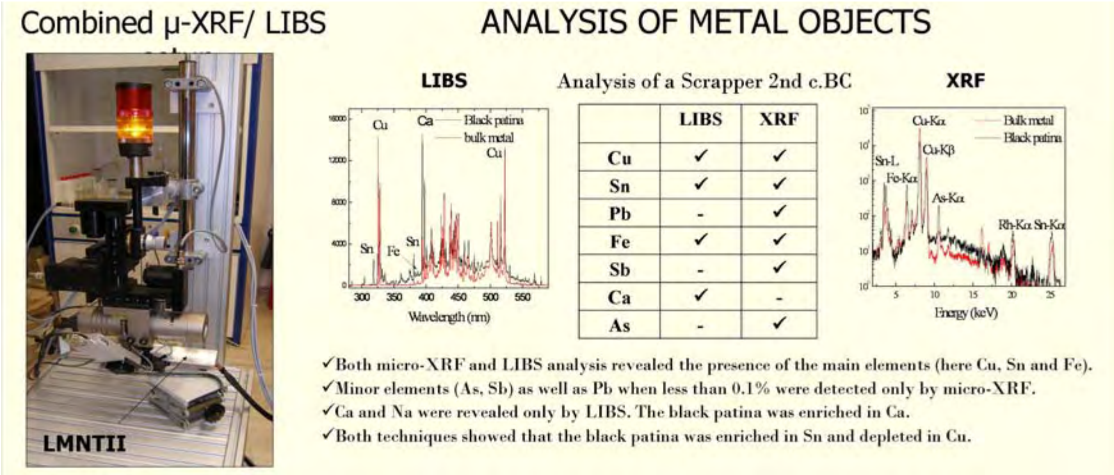


Figure 6

1.4 Survey and Damage Assessment of the Museum Collections (Workpackage 2)

One major aspect of the PROMET project is the development of new strategies to assess the collections under study by designing technology and condition survey approaches. Surveys of metals collections housed in 11 museums throughout the Mediterranean have been carried out using a systematic survey approach, which involves using either a statistical methodology in assessing the technology and condition of a large sample of the objects and a data-mining technique to survey a random sample from the collection, or, in the case of precious metal objects, an in-depth diagnostic investigation of the chemical and mineralogical properties of a representative number of artifacts.

For the PROMET project, the 11 collections studied had different questions for their assessment and thus different approaches were developed to conduct their respective survey.

For collections stemming from museums located at archaeological sites, such as the case of Ancient Messene in Greece or Umm Qais in Jordan, where objects have been excavated and have yet to be treated, the main questions for the survey of such large collections of copper and/or iron alloy artifacts are as follows:

- What objects from the museum collection are in urgent need of treatment?
- What objects would benefit from treatment?
- What objects do not require treatment?

After treatment of such archaeological collection and prior to display in a museum, a conservation laboratory may decide to identify the most effective treatment, as was the goal of the iron collections excavated from *El Saucedo* and *Calatrava la Vieja* and temporarily stored at the Department of Prehistory and Archaeology of the Autonomous University of Madrid. Here, professional C-Rs decided to randomly select a representative sample of the collection using visual inspection, as its main criteria for the assessment, and to design a database to insert and assess the collected data.

For historical collections that have undergone different treatments or protection systems throughout the centuries, such as the Palace Armoury collection in Malta, the main question is to understand the factors (ie, display conditions, protective system applied etc.) that affect the condition and may have changed the value of those objects.

For historical collections housed in University Museums, such as Yarmouk University in Jordan or the National Technical University of Athens in Greece that houses a small silver collection, the main question is how the display cases and the surrounding environment of the museum affect the tarnishing of these objects.

For archaeological museums with large collections of precious metals, such as the Egyptian Museum in Cairo and the Museum of Sant'Antioco in Sardinia, a representative sample needed to be selected to survey the collection based on its archaeological value. Since the objects come from excavations or tombs, a technological investigation of the composition of the bulk material, as well as of the morphology and composition of the corrosion layers is essential to best determine the optimum ways to preserve these types of objects.

Some PROMET partners decided to focus on a particular technological question for their archaeological collections, concerning a specific period or type of object, while also observing the condition of the objects. For example, at Van Archaeological Museum in the city of Van of Eastern Anatolia in Turkey, there are over 65,000 artifacts in the collection. However, the archaeologist responsible selected only 10 artifacts for the survey, so as to provide data about the Urartian metallurgy such as casting information. The study of these artifacts allows us to obtain important information about the metal workers during the first millennium BC.

In the case of the Rabat Archaeological Museum in Morocco again the curators decided to choose to survey only a selected group of objects representing archaeological bronzes from dates from the Roman Era, first and third century AD from the sites of Banasa and Thamusida.

In the case of the National Archaeological Museum of Damascus, Syria the curators selected 50 of the most important copper alloy coins that needed to be catalogued for their survey.

Partner TEI - *Case Study: The Archaeological Museum of Ancient Messene*

The collection of excavated artifacts is housed in the Archaeological Museum of Ancient Messene, which is situated at the top of the archaeological site of the ancient city of Messene. The museum was established between the years 1968-1972 under state governance. The museum houses a typical archaeological collection with a great variety of artifacts: sculptures, building elements, pottery, metals, inscriptions, skeletal material. After every year's systematic excavation period in August an increasing number of new material finds are excavated and placed in the storage facilities of the museum.

The first level of the building (at street level) houses the exhibition halls of the museum, where some important artifacts are on display, like marble sculptures and vessels. The lower level has offices, washroom facilities, and two storage rooms with partly controlled conditions, where the personnel work and many of the finds under study and/or in need of conservation treatment are stored. In one of the study rooms there is a small conservation laboratory, where a large collection of coins can be found in a coinage safety case. In another part of the building there are storage rooms (for ceramics) with uncontrolled humid conditions.

The conservation laboratory has one professional C-R, four conservation technicians (full time), and two part time C-Rs. Many other professionals work at the museum, as archaeologists studying the collection or architects and engineers involved in the restoration of the archaeological site.

The Metals Collection of Ancient Messene

In the storage rooms of the Museum of Ancient Messene is housed a rich collection of copper and iron alloys articles, increasing in number after the systematic annual excavation periods during summer time. The objects are significant for the study of ancient metallurgy (study of alloys and compositions, study of manufacturing techniques, decoration and plating techniques). They provide information for the city's everyday public life, funeral practices, and equipment used as tools. Thus the artifacts exhibit archaeological value as most of them can be dated, historical value, technological value concerning materials and techniques, functional value, social value as records of the city's public life and religious value. They cover an extended period of time, since the city was inhabited from 369 BC, when it was established, to fifteenth century AD.

Material finds were first collected during the systematic excavation periods 1909-1925 (by archaeologist G. Oikonomou), 1957-1974 (by archaeologist A. Orlandos) and 1987 until the present day (by archaeologist P. Themelis). Some artifacts have been gathered from nearby estates by villagers.

The following tables present the characteristic types of the examined collection.

TOOLS-INSTRUMENTS	*Scrapers, spatulas, chisels, medical tools, spades, needles, tongs, a quill, an ax, and a hook*
ACCESSORIES OF DOORS & FURNITURE	*Simple nails, decorative nails, cringles, parts of locks, keys*
DECORATIVE ARTIFACTS	*Mirrors, buckles, rings, pins, bracelets, earrings, and a necklace*
VESSELS	*Small vessels, rims, handles, bases, covers, decorative elements*
FIGURINES-STATUETTES	*Animal & human*
WEAPONS	*Spear & arrow shafts, savrotiras, shields*

Table 1 A description of the types of copper alloy artifacts found in the museum of Ancient Messene

WEAPONS	*Shaft & arrow peaks, savrotiras, daggers, butcher knives*
TOOLS-INSTRUMENTS	*Scrapers, scissors, spatulas, spades, cradles, chisels, knife and carving blades, hooks, needles, tongs*
ACCESSORIES OF DOORS & FURNITURE	*Simple & decorative nails, cringles, parts of locks, keys, sheathing foils*

Table 2 A description of the types of wrought iron artifacts found in the museum of Ancient Messene.

The entire collection is kept in one of the museum's storage rooms. The present condition of the metals collection is the result of the interaction of three factors: burial environment, handling after excavation and before treatment and storage environment. The museum building was constructed to serve the purposes of a small regional museum with exhibition rooms, storage facilities and amenities for the people working inside. Unfortunately, during the construction, there was no provision for the climatic conditions of Ancient Messene or the environmental factors affecting the interior museum environment. There is no monitoring of the environmental conditions and relative humidity rates can be high during the winter months. The central heating system does not operate properly due to bad installation, especially during winter and spring months where temperatures are low.

During excavation, the iron and copper alloy finds from wet soil were usually left to dry out and were usually stored in wooden boxes in contact with organic materials and other metals, like lead alloys. This was the situation until 2004. Then the copper and iron alloys objects were separated and placed in polyethylene bags and kept in the storage rooms. In the past, few metal finds (apart from the coins) received treatment due to limited funds.

Technological and Condition Survey

The approach described above for a technological and condition survey was carried out using visual examination of a representative sample of 873 objects -324 copper alloys objects and 549 iron alloys objects respectively from a preselected sample. Selecting the sample was based on the following criteria:

a. Objects that could be dated with certainty, following the excavation stratigraphy and the archaeological typology. Dating could refer to a specific period (for example, Hellenistic period) or more strictly to specific years.
b. Objects that preserved their shape and the relevant technological information (dimensions, shape, form etc.). Unidentifiable fragments were not included.
c. Objects that could not be dated, but preserved their shape and technological information, and their authenticity was not doubted when they were compared to objects of the same type that could be dated.
d. Objects excavated from all complexes of the site were selected in order for us to have a representative sample of the whole collection.

The greatest part of the selected metal finds is dated from the fifth century BC until the late fifth – beginning of sixth century AD. The main body is dated from the fourth century BC to the second century AD.

Results of the Technological and Condition Survey

The sample was classified according to technological characteristics and the frequency of distribution of all types in the total sample was determined. An example of the results of this survey is given below for copper alloy nails:

			SIMPLE COPPER ALLOY NAILS					
			Body Shank		**Head's shape**			
					Circular			
			Circular	***Rectangular***	Flat	Convex	***Mushroom***	***Rectangular***
Body shank	***Circular***		21	0	14	7	0	1
	Rectangular		/	48	34	11	3	0
Head's shape	***Circular***	**Flat**	/	/	48	0	0	0
		Convex	/	/	/	18	0	0
	Mushroom		/	/	/	/	3	0
	Rectangular		/	/	/	/	/	1

Table 3 Burt Frequency Table presenting the technological characteristics of simple nails

The Burt Frequency Table given above allows for the classification tree for the nail types to be determined. A similar approach was carried out for all the types of metal artifacts under study.

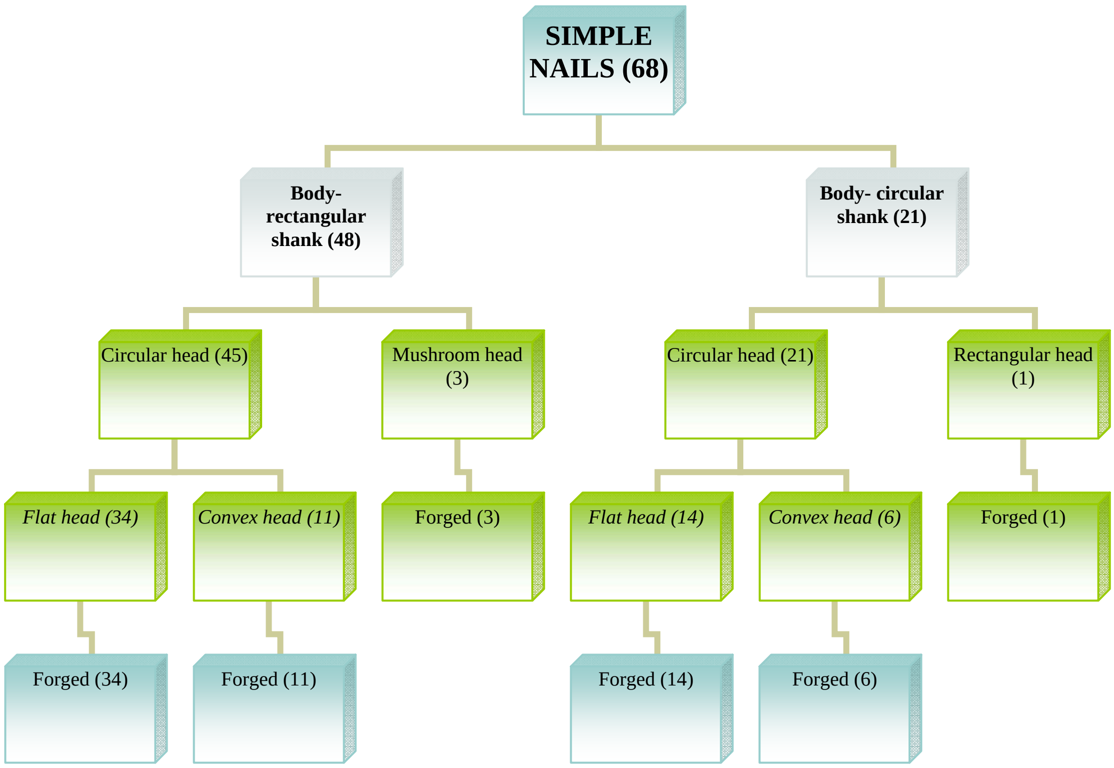


Figure 1 Classification tree presenting the technological characteristics of simple nails

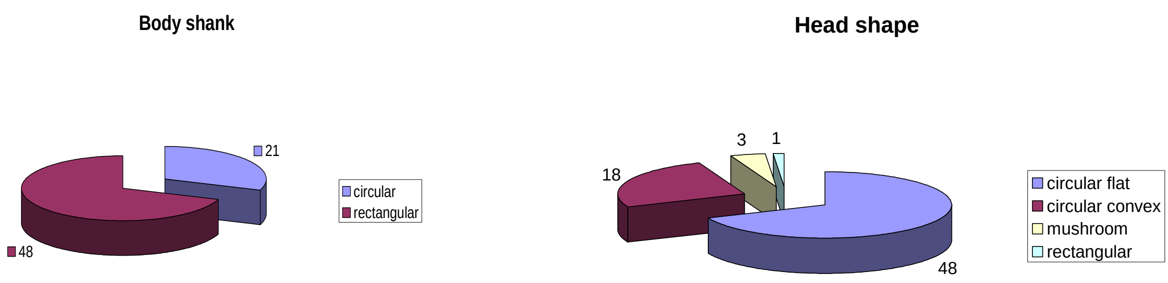


Figure 2 Pie charts presenting the technological characteristics of simple nails

From the Burt frequency table, the classification tree and the above pie charts the following observations could be made:

1. All copper alloy nails were made with the hammering technique.
2. Seventy per cent of the nails have a rectangular body shank, while thirty per cent have a circular body shank.
3. Sixty-nine per cent of the nails have flat circular heads, twenty-six per cent have convex circular heads and only four per cent and one per cent have mushroom and rectangular heads respectively.
4. From 21 nails with circular body shank, 66,6per cent have flat circular heads, 33,3per cent have convex circular heads and 0,1per cent has a rectangular head.
5. From 48 nails with rectangular body shank, 70,8per cent have flat circular heads, 22,9per cent have convex heads and 6,3per cent have mushroom heads.

The results of the condition survey for the 873 copper and iron alloy finds are given in the following frequency tables (Tables 4 and 5) and pie charts (Figures 3 and 4).

COPPER		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	NO	45	13,9	13,9	13,9
	COULD BENEFIT	150	46,3	46,3	60,2
	YES	129	39,8	39,8	100,0
	Total	324	100,0	100,0	

Table 4 Frequency table presenting the treatment priorities for copper artifacts

Copper alloys artifacts conservation levels

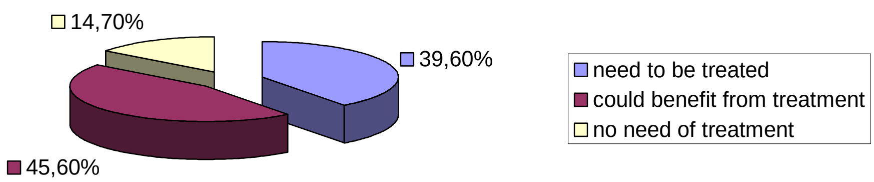


Figure 3 Pie chart presenting the treatment priorities for copper artifacts

IRON		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	NO	10	1,8	1,8	1,8
	COULD BENEFIT	176	32,1	32,1	33,9
	YES	363	66,1	66,1	100,0
	Total	549	100,0	100,0	

Table 5 Frequency table presenting the treatment priorities for iron artifacts

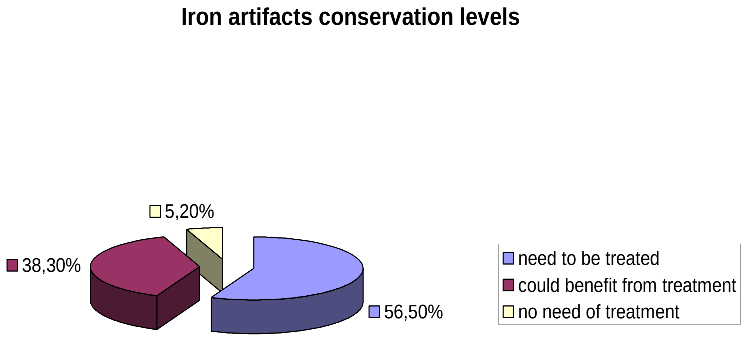


Figure 4 Pie chart presenting the treatment priorities for iron artifacts

Based on our visual inspection, it was determined that 129 copper alloys and 363 iron alloys artifacts are in urgent need of treatment. The copper alloys exhibit uneven surface deposits with localised intensive corrosion products, loss of material during handling and fragility. The iron alloys exhibit clear signs of active corrosion, through characteristic spalling and akaganeite formation. These objects are classified as first treatment priority.

Another category comprises 129 copper alloys and 176 iron alloys artifacts which could benefit from treatment. These objects cannot be dated with certainty, but present intensive corrosion problems or they can be dated, but present smooth and even patinas and are visually characterised as stable. In the first case, it is not urgent to treat an artifact that may not be authentic and in the latter case it is not urgent to treat an artifact that is stable.

The rest of the artifacts cannot be dated with certainty and are stable, so there is no need to treat them, but just store them in controlled conditions.

A limitation of this approach is that assessment is based on visual inspection. If the person carrying out the survey is not adequately trained, for example, to identify active as opposed to stable corrosion products then this assessment will be flawed. However, it may be also the case that it is difficult to determine active corrosion if the objects were not allowed to dry out and were stored in a microclimate similar to the burial environment. Similarly, it is sometimes difficult to spot bronze disease on copper alloy finds that are heavily corroded. Here diagnostic testing of such material becomes important in order to verify the presence/absence of such active corrosion.

Our survey concluded that it is very important that excavated metal finds from Ancient Messene are kept in similar conditions to the burial environment prior to conservation treatment. This holds true especially for iron alloys artifacts, which a radiographic examination found to retain a substantial amount of metal, but with clear signs of active corrosion (Giannoulaki *et al.* 2007). The conservation priority is to set up a mass stabilisation treatment for these finds. Our visual inspection of the copper alloys finds found them to be metastable after 10 years from excavation and only objects which present bulky corrosion products, uneven surfaces and fragility during handling should be an urgent treatment priority. However, upon further diagnostic testing of the mineralogical corrosion layers of a representative sample of 34 objects, we found that only one object contained chloride which, in turn, contained a corrosion product, paratacamite. As a result, it is quite possible that those objects that were visually identified as having active corrosion are in fact stable corrosion products.

Nevertheless, this conclusion does not affect the overall results. In order to deal with this problem, we chose other independent variables to predict the variable (answer): (i) urgent to be treated, (ii) could benefit from treatment and (iii) no need to be treated? The results presented only one per cent difference and this demonstrated the appropriateness of the statistical technique applied to predict the answer and determine treatment priority levels.

Partner RSS - *Umm Qais Archaeological Museum, Jordan*

The modern town of Umm Qais is the site of the ancient Greco-Roman town of Gadara, one of the cities of the Decapolis and, according to the Bible, the place where Jesus cast out the devil from two men into a herd of pigs (Matthew 8: 28-34). Rising 346 meters above sea level with views of Lake Tiberias and the Golan Heights, Umm Qais is the best vantage point in northern Jordan. The Umm Qais archaeological site overall area is ≈487000m^2 of which ≈8000m^2 are actually under excavation. The Umm Qais archaeological museum houses only 397 archaeological finds, since the site is still under excavation. From this collection, 52 are metal and the rest are pottery and marble finds. Most metallic finds are made of copper alloys.

The Umm Qais museum with a total of 2012m^2 housing is divided as follows: display galleries of 200m^2; storage spaces of 145m^2; administration offices of 100m^2; and the rest are open areas. Concerning staff, the archaeological site has an archaeologist, a C-R, an engineer drafter, six technicians, and a curator with 20 guards. The total number of staff increases up to 70 during the systematic excavation period from April to December every year. The artifacts are carefully handled and stored after excavation and before cleaning. Despite the fact that the main conservation laboratory is situated in Amman, first-aid conservation activities and documentation are carried out under the supervision of a specialised foreign mission in collaboration with the Umm Qais museum staff. Materials for conservation are provided by foreign missions. Concerning pottery, all conservation and repair procedures are carried on-site.

A technological survey showed that most of the metal artifacts were copper based material, and of decorative class. As shown in the photos and classification tree of the bracelets, the technological typology established demonstrates the archaeological and technological characteristics of these objects.

A condition survey showed that 28.8 per cent of the artifacts excavated from wet soil, and 62.8 per cent of the copper alloy collection show signs of active corrosion due to the corrosive environment of high relative humidity, which highlights the importance of monitoring and controlling environmental conditions in the display and storage areas of the museum.

In terms of technology, 37.2 per cent of the finds are joined mechanically/ metallurgically, 38.3 per cent were manufactured by forging, 18.1 per cent by casting, 40 per cent by both forging and casting, 4.3 per cent by blowing, and 30.9 per cent by rolling.

Our assessment determined the different ‘values’ for these metal finds that were 68.1 per cent of aesthetic, 26.6 per cent of technological, 7.4 per cent of political, 4.3 per cent of economic, 2.1 per cent of admiration and 14.9 per cent of religion value. Again the survey results indicate that for many of the artifacts more than one value is considered important.

Thus, using the above approach for the copper alloy finds surveyed and analysed in this study, our assessment showed that 62.8 per cent of the artifacts are in urgent need of treatment, while 31.9 per cent could benefit from treatment. It should be noted that 31.9 per cent have no metal core, 35.1per cent are of little metal core and the rest are of recognised metal core.

Partner HM - *Case Study: The Palace Armoury Collection of Malta*

A statistical approach was applied by the partner Heritage Malta (HM) in order for them to focus more on classifying the comprehensive record of their past interventions (cleaning, protective coating applied), type and extent of corrosion, and method of display, which are interrelated factors and cannot be studied independently. For HM, the aim of the survey was to find the correlation between different factors allowing for an evaluation of the protective systems used for the collection of the Palace Armoury in Malta.

The Palace Armoury is run by Heritage Malta, the national agency in charge of sites and museums. It is one of the world’s greatest arms and armour collections and is maintained in its original setting since inception. The Armoury ranks as one of the most valuable historic monuments of European culture. The museum collection includes arms, armours, guns, cannon and rifles amongst others, once the property of the Knights of the Order of St. John during their reside in Malta (1530-1799). It is therefore a military collection. The arms and armour collection is exhibited in two large halls. Most of the armour elements are exhibited in the right hall, while the arms collection is exhibited in the left hall. Display galleries occupy around 563m^2, storage spaces 24m^2, administration offices 31m^2, conservation laboratories 31m^2 and public amenities 10m^2. Libraries are inside the administration offices.

Today the collection is managed by a senior curator, Emmanuel Magro Conti, and a curator, Michael Stroud. There are a few “guardians” who look after the admission. Although the collection does not have an in-house conservator, a HM conservator from the Conservation Division dedicates some of his time to the Palace Armoury.

The Palace Armoury is one of the most popular museums in Malta (more than 100,000 visitors per year). Excluding several armour pieces (full suits of armour) belonging to Grand Masters like Jean Parisot de la Vallette and Alof de Wignacourt, the majority of the exhibits are field armour belonging to infantry. The collection surveyed and studied for the purpose of PROMET consists of iron-based armour items dating from 16-17th century, which are exhibited in the right hall. The collection is exhibited in showcases, but also attached to the walls, and a large number of items are stored within the premises of the museum (reserve collection). Table 1 shows the number of artifacts exhibited in the right hall. The armour items hanging on the walls of the left hall were not surveyed.

Location	**Number of artifacts**
Showcases	201
Walls	119
Reserve collection	1025
Total	**1345**

Table 1 Number of artifacts exhibited in the right hall

In 1975, the armoury was transferred from the first floor of the Palace (a site it had occupied since inception) to the ground floor level (originally the Palace stables). This transfer has most possibly accelerated the degradation processes of the artifacts since the walls of the “new” exhibit halls suffer from a rising damp phenomenon as the environmental conditions inside the museum are not controlled. The collection suffers from traffic pollution entering from the main door as well as the chloride-laden Mediterranean atmosphere that is characterised by elevated and often fluctuating relative humidity with relatively small temperature changes. The artifacts in the reserve collection and those attached to the walls appear to be considerably more corroded than those displayed in display cases that appear to be in a better state of conservation. One of the common forms of corrosion observed on varnished armour pieces is filiform corrosion, whilst generalised corrosion appears on many objects, especially those displayed on the walls.

In 2005 and 2007, important refurbishment work was carried out at the Palace Armoury. On that occasion some artifacts exposed on the walls were integrated in the showcases. New showcases were built and the old showcases were cleaned and refurbished. Artifacts were moved and exhibited in chronological order and / or type of artifact.

The aim of the survey was to understand and record how different factors affect the collection’s state of conservation. The objectives of the survey were to understand the collection, the type of objects found and their manufacturing techniques, how the display methods used affected their preservation, the corrosion forms and corrosion products found on these objects, how the conservation treatments (with particular emphasis on cleaning methods and protective system applied) that had been used over the years had affected their condition and whether past treatments had changed/altered the values of the objects. Another objective of the survey was to provide the museum, for the first time, with a comprehensive record of the collection. Finally, of particular importance was the evaluation of the protective coatings used for these objects by analysing the survey results and by studying the coatings used.

Surveys are time consuming and expensive and, in order to be most effective, they have to be designed based on the collection and on each individual aim and objective. Certain given parameters related to the collection, the function of the museum and of the building that housed the collection, helped us define the best method to follow in the survey.

It should be noted that handling the objects was not possible, therefore closer inspection was not carried out. Additionally, due to the large number of visitors the museum receives daily, the display cabinets were not opened and as a result, all observations were made visually from the outside using torches. The objects displayed on the walls were also examined in a similar manner. The lack of proper examination was one of the biggest problems of the survey, because none of the objects were examined close, or under a stereomicroscope and a lot of the observations were assumptions based on both the information provided by the curator and the experience of the C-Rs conducting the survey. Therefore, the information gathered concerns the exterior of the armours that were visually accessible.

Additionally, the survey was conducted within strict timeframes. In order to have meaningful results, the survey had to be carried out before the reorganisation of the new exhibition so that conclusions about the display method, the protective coatings and the protection they provide in relation to the environment they were exposed to for the past years could be drawn. The reorganisation of the collection involved movement of the objects in different showcases, partial cleaning (even if it was only dusting) and occasional restoration of some pieces.

In addition to time restrictions due to the reorganisation of the collection, there was another problem related to the hours the survey could take place daily. The collection is housed in the Grand Master's Palace which also houses the Parliament of Malta thus, for security reasons no one was allowed to stay after the closing time of the museum. Subsequently, the survey could only be undertaken during opening hours of the museum (8:00-17:00).

Another limitation was the lack of documentation regarding past treatments carried out on the objects. It is evident by visual observation that the objects have been treated by different professionals that have used different methods and materials. Still, there was no documentation of the treatments and any information available came from the curator of the museum and a few general documents proposing methods and materials. In the latter, it is not always clear whether these methods were followed at some point in time or not.

Taking into account all the aforementioned limitations and the fact that the survey was going to be undertaken by different C-Rs and conservation students, it is obvious that there was a need to develop a method that would allow the collection of data in the most objective way. Also, since one of the objectives of the survey was to evaluate the coatings used in the collection, it was considered necessary that the method used would allow their evaluation. In a nutshell, the aim was to "objectify" the data recording and to standardise the information collected.

Forms/databases, criteria for field definitions, and data analysis

The survey sheet contained the following information: display number, Palace Armoury and Heritage Malta Conservation Division object numbers, object type (e.g. helmet), material type (e.g. iron, copper, leather) and distribution, surface features (e.g. engraving) and distribution, assumed coating (e.g. oil, varnish) and distribution, indications of corrosion removal (e.g. abrasion marks) and distribution, surface deposits (e.g. dust) and distribution, mechanical deterioration (e.g. losses, deformation) and distribution, corrosion presence, type, activity (e.g. active, dormant, unsure), position of corrosion products relative to coatings (e.g. above, in, below, unsure) and distribution on object. Additional space was given for further comments outside the survey form's fields.

Collected data were imported into a MS Access database prepared especially. MS Access was chosen as a readily available program which could later be transferred in a MySQL database that would allow statistical analysis of the data. The aim of this analysis was to identify patterns between different fields of the database such as the object, the environment objects are exposed to, the corrosion forms they present and the protective system applied on them. This also permitted a better evaluation of the protective systems applied in the past and a better understanding of the reasons why these systems failed to protect objects in the collection's environment.

The surveyed objects were representative of the whole collection since most of them were considered. The following table refers to the whole collection and presents the type of objects, the position of the armour elements and their number in the three exhibition conditions: showcases, walls and shelves in the reserve collection.

Types	**Showcases** (right hall)	**Walls** (in the two halls)	**Reserve Collection**	**Total**
Breastplates	40	21	132	193
Backplates	28	22	131	181
Full arms	11	14	90	115
Pauldrons	27	16	182	225
Couters	1	25	65	91
Helmets	47	165	102	314
Tassets	24	50	155	229
½ full armours	18	0	8	26
Vambraces	0	5	157	162
Gorgets	5	0	3	8

Table 2 The position of the armour elements

For artifacts on the walls, only artifacts of the right hall were surveyed (119 out of 318). The number of objects fully surveyed was 388. The artifacts surveyed and their general characteristics are presented in Table 3 below.

PALACE ARMOURY COLLECTION			
Number of objects surveyed	388	Corrosion Activity	
Number of objects with corrosion	368	Active	100*
General corrosion	173	Dormant	72*
Localised	203		
Filiform	221	Unsure	260*
Coating Type			
Varnish	278	Varnish (single protection system)	80
Wax	63	Wax (single protection system)	28
Oil	236	Oil (single protection system)	62
Multiple coatings			
Varnish + Wax	28		
Varnish + Oil	165		
Wax + Oil	2		
Varnish + Wax + Oil	3		

Table 3 List of artifacts surveyed and general characteristics observed

* Objects often presented more than one type of corrosion which could in turn be active, dormant or unsure. The corrosion activity was marked "unsure" when it was not possible to distinguish whether the corrosion was active or dormant. Although a large number of objects were marked unsure, from these results it is obvious that a large percentage of objects present signs of active corrosion.

The objects in the display cabinets appear to be in better condition than those on the walls. However, although the objects in the display cabinets were expected to be in better condition as they are less exposed to environmental changes, they are also the objects that attract more attention and are therefore cleaned more frequently than those on the walls where access is generally more restricted. From the objects on the wall it is a general observation that oblique surfaces, where dust is more easily deposited, present more corrosion. It should be noted that the objects that do not present any corrosion at all had been recently cleaned and all corrosion had been removed. The figure below is a good example of localised corrosion on an artifact exposed on the wall, which developed further into general corrosion.

Figure 1 Localised corrosion on an artifact exposed on the wall.

From the data collected the majority of the objects present one or more types of corrosion as can be seen in the following pie chart.

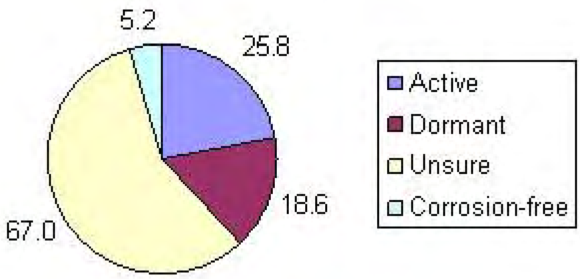


Figure 2 Corrosivity of surveyed objects at the Palace Armoury

As regards protection systems, we observed different types (varnishes, wax and oil) but as shown on the following figure most of the artifacts were covered with varnish or oil. A number of different varnishes have been used and without analysis it is difficult to determine which of the varnishes used over the past 30 years is more effective. Nevertheless, a large number of objects coated with varnish present filiform corrosion (221 out of 278).

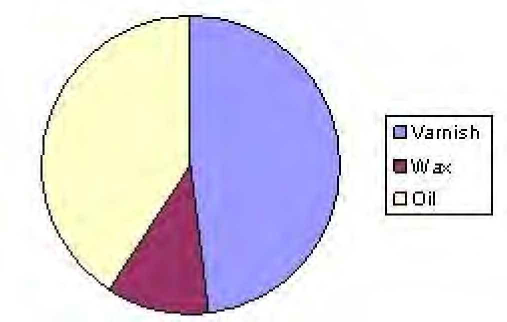


Figure 3 Protection systems used in the Palace Armoury collection

It should be noted, however, that most of the objects are covered with multiple layers of different protection systems. From the figure below it is evident that less than one fourth of the total number of objects treated with varnishes are covered with varnish only.

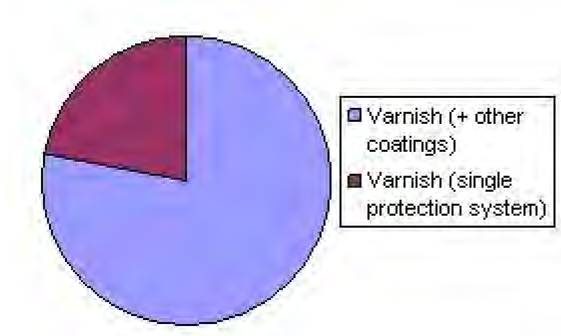


Figure 4 Ratio of artifacts covered with varnish alone or in combination with other protection systems

Often protection systems have been combined: for example, varnish with oil (165) or wax (28). Here varnish is applied first and a second protection system at a later stage, probably because the first protection system has failed.

As said before, the aim of this analysis was to identify patterns between different fields of the database. To illustrate the use of the database, we worked on 40 artifacts for preliminary compilation of results. Figure 5 below summarises the results obtained.

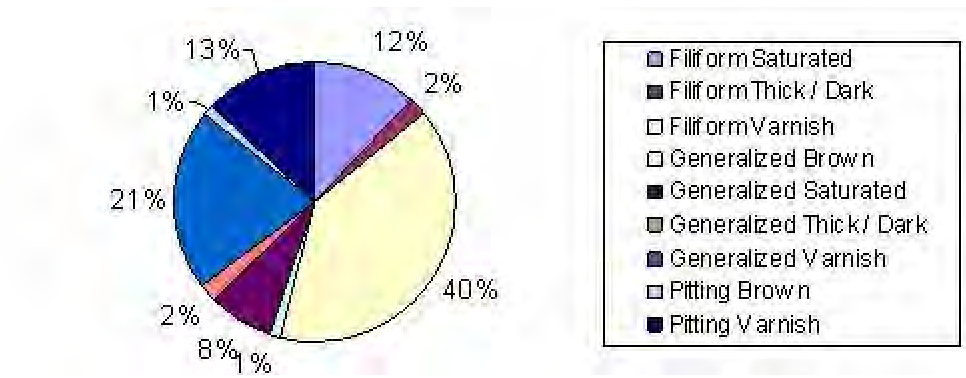


Figure 5 Summary of the results collected from the survey

We can clearly see that, when filiform corrosion is observed, it is in most cases when varnish has been applied on the metal surface but the presence of varnish also leads to the formation of generalised corrosion. The different forms of corrosion were studied in relation to the environment the objects were exposed to and the protection system used. Often treatments failed to protect a metal not only because they were unsuitable or inadequate for its protection, but also because of lack of maintenance.

Partner CSIC-CENIM - *Case Study: Iron Artifacts from El Saucedo and Calatrava la Vieja Excavations, Spain*

A group of archaeological objects that are currently stored at the conservation-restoration laboratory of the Department of Prehistory and Archaeology of the Autonomous University of Madrid were surveyed after treatment. This collection is therefore a subgroup of all the objects that have been excavated by archaeologists of the Department and have undergone subsequent conservation. After conservation treatment and study, some of them will go on display in the archaeological museums of Toledo (those from *El Saucedo*) and Ciudad Real (those from *Calatrava la Vieja)*. According to a current law in Spain, the direct control of, and responsibility for, the Cultural Heritage lies with Autonomous Communities (Regional Governments). In our case, the objects are owned by the Autonomous Community of *Castilla-La Mancha*.

The collection is not currently on display, and the areas dedicated to the collection comprise 400 m^2 of storage spaces, 80 m^2 of conservation laboratories and 30 m^2 for administrative and research activities. Objects are not stored in a controlled environment. Most of the work on the collection is carried out in the conservation lab, including most of the documentation work.

The personnel that works exclusively with the collection consists of 1 archaeologist and 3 C-Rs/restorers. Additionally, 24 conservation students are working in the collection as these lines are written.

The site of *Calatrava la Vieja* was founded by the Omeya dynasty in the eighth century, to protect the road from Toledo to Cordoba. It was conquered by Alfonso VII in 1147, who gave it to the Catholic Church. Finally, it ended under the control of the Order of Calatrava that established its headquarters there, also known as 'see', until 1217, when the see of the order was moved to the nearby place of *Calatrava la Nueva* ("the new"). *Calatrava la Vieja* ("the old") was finally abandoned and depopulated during the sixteenth century.

The site of *El Saucedo* is a roman villa, occupied from the first to the eighth century AD. It is located near Caesarobriga (*Talavera de la Reina, Toledo*).

The iron objects from *El Saucedo* are from a blacksmith workshop, and therefore represent a good sample of techniques and uses of iron. The iron objects from *Calatrava la Vieja* are an assortment of various objects and tools used in the city. The objects were excavated from a wet environment (the Guadiana river is very close to the Calatrava site, and El Saucedo is in an irrigated land in a valley) but, unfortunately, no measures were taken by the archaeologists in charge of the excavation to prevent the objects from drying after the excavation.

The value of the collection is mainly the historical and technological information it provides about the cities and the societies where the objects come from. But in addition to their historical value, these objects also have an educational purpose, since they are used for training conservation students of the University. The following table summarises the composition of the collection.

	Type of object	*Number of Iron objects*		*Dates (origin)*
		Total	*Conserved*	
Calatrava	Various	~150	40	9th to 14th cent. AD
El Saucedo	Blacksmith workshop	~125	44	3rd to 4th cent. AD

Table 1 The collection from El Saucedo and Calatrava la Vieja

The collection is not displayed and, before and after conservation treatments, the objects are kept in polyethylene bags deposited in plastic containers. These containers are kept in the conservation laboratory, with no climate or pollution control systems. Nevertheless, the climatic conditions (temperature and relative humidity) are not particularly aggressive.

The general treatment after excavation involves removal of sand and particles bonded to the surface, mechanical cleaning and removal of corrosion layers up to the “original surface”, and application of a protective acrylic layer: 5-8per cent Paraloid B-72 + 2per cent microcrystalline wax in a xylene-acetone mix (1:1) . These treatments are performed by conservation students, under the guidance of professors and conservation professionals.

The dechlorination treatment considered to have the best results for this collection involved the use of cold hydrogen plasma. However, as this technique is not available in the laboratory of the University, the objects were not dechlorinated.. Other traditional dechlorination treatments were also considered but rejected because they were not effective at preserving the original surface of the iron objects. Curatorial criteria imposed by the directors of the excavations gave priority to the original aspect of the objects as opposed to chemical stability, so that the stability of those objects was controlled by preventive conservation measures and/or the use or corrosion inhibitors. Additionally, the long time required for those traditional treatments was considered to be unacceptable due to the huge amount of objects to be restored by the laboratory.

The main objective of the survey was to study the conservation condition of the objects after the application of restoration treatments on them, identifying any possible influence of parameters such as the origin of the object, the type of object, the type of treatment that had been applied, or the presence/absence of metallic core. In order to achieve this objective, a representative sample of the collection, randomly selected, was examined by visual inspection by a C-R. In order to avoid different interpretations, all objects were examined by the same person.

The data was entered in a MS Access database. This database is intended to serve as a follow-up tool of the conservation condition of the objects in the future, providing a convenient tool for assessing the evolution of the conservation of individual objects, the whole collection or a part of it.

A representative sample of 61 objects (25 from *Calatrava* and 36 from *El Saucedo*) was revised by visual inspection. It was decided to limit the survey only to already conserved objects, since the ones that have not been cleaned are very difficult to analyze or to estimate their condition.

The following histogram (Figure 1) shows the distribution of the dates of excavation and conservation of the objects.

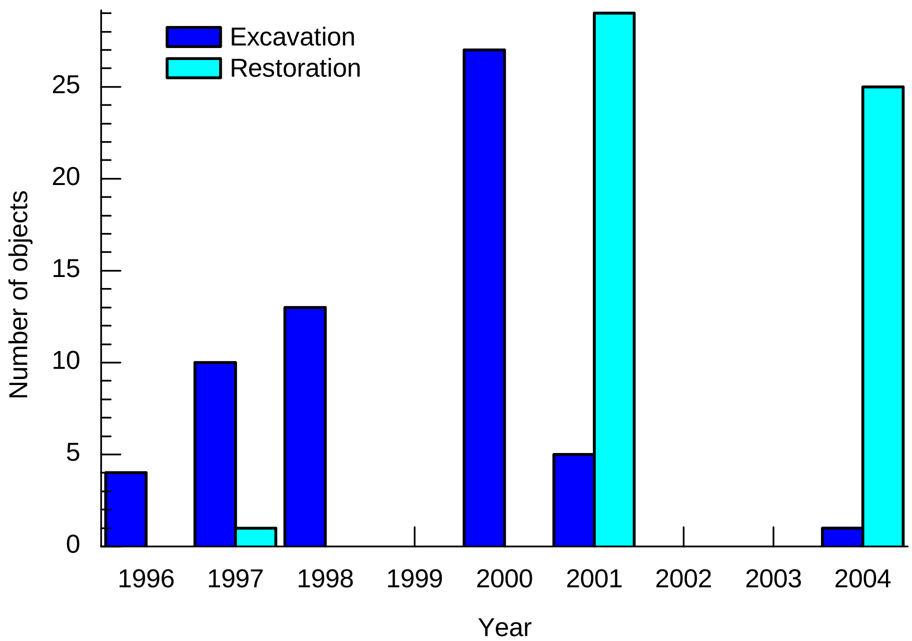


Figure 1 Dates of excavation and conservation-restoration of the objects

The following figure summarises the type of objects. Apart from the unidentified objects, the most important groups are nails, rings, horseshoes, plates, hooks and knives.

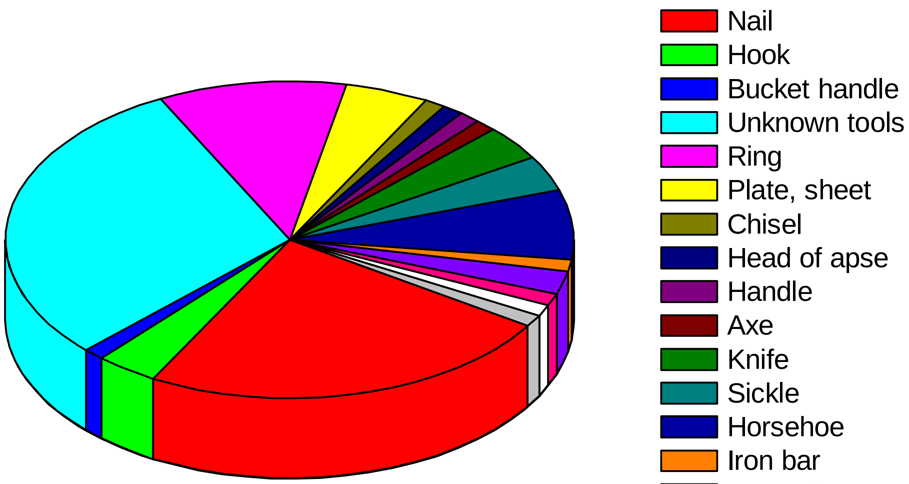


Figure 2 Types of excavated objects

All objects are made of iron or low carbon steel, and have been shaped using a forging process. The most outstanding feature (from a technological point of view, and also due to the implications that it has for the conservation of the objects) is that 4 objects (6.6 per cent) are iron objects covered by a layer of copper. These objects are cowbells or sheepbells that were covered by a layer or copper to improve the sound. The technology for the fabrication of these objects has remained the same in some areas of Spain today, and involves the addition of copper filings to the surface of a layer of iron, and the subsequent formation of a uniform layer by heating and hammering.

The next figure shows the integrity of the objects studied. In general, objects coming from *El Saucedo* have a better integrity, which can be mostly attributed to the fact that many of them are small and simple objects, like nails.

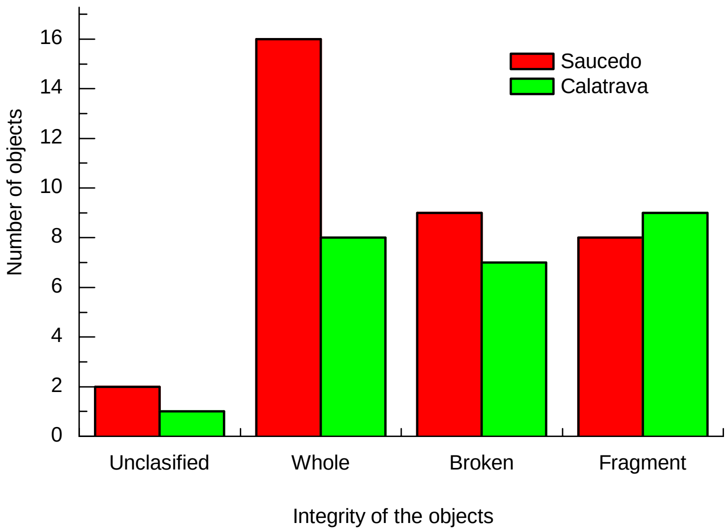


Figure 3 Integrity of the objects

There are important differences in the presence of a metallic core between the two origins, as is shown in the next graph. While about half of the objects coming from *El Saucedo* have a metallic core, more than three quarters of the objects coming from *Calatrava* are completely mineralised.

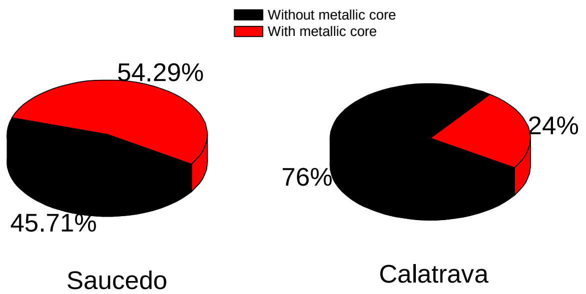


Figure 4 Metallic cores in the objects from *Calatrava* and *El Saucedo*

All objects were mechanically cleaned and protected by a first layer of 5-8per cent Paraloid B-72 and a top layer of 2per cent microcrystalline wax in a xylene-acetone mix (1:1). After that, all objects were stored in polyethylene bags in the uncontrolled atmosphere of the restoration laboratory.

Commercial inhibitors based on organotitanates were applied to objects from *Calatrava*. According to the previous experience of the C-Rs involved (experiments had been carried out in similar iron objects for 5 years), this treatment improved the conservation of these objects.

The following figure shows the presence of active corrosion in the objects, separated by their origin. It can be seen that there are important differences in the presence of active corrosion, in that it is scarce in objects from *Calatrava* but appears in about half of the objects from *El Saucedo*.

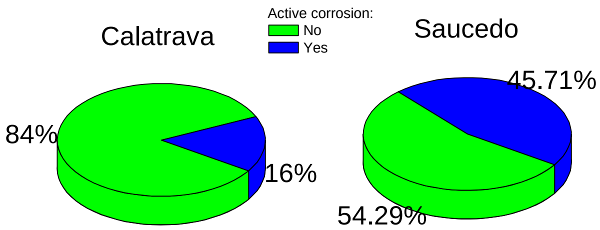


Figure 5 Active corrosion in the objects from *Calatrava* and *El Saucedo*

If we consider only objects with metallic core (see Figure 6), the percentage of objects with active corrosion increases in both cases, but again objects from El Saucedo present more conservation problems. Strictly speaking, corrosion is only possible in those objects with metallic core. However, the term “active corrosion” is commonly applied not only to the reaction of the metal with the environment, but also to the transformation of the already present corrosion products, including the degradation of products like akaganeite. Those transformations produce a deterioration of the object, causing, in some cases, the loss of some parts and changes in the volume and/or shape of the remaining object.

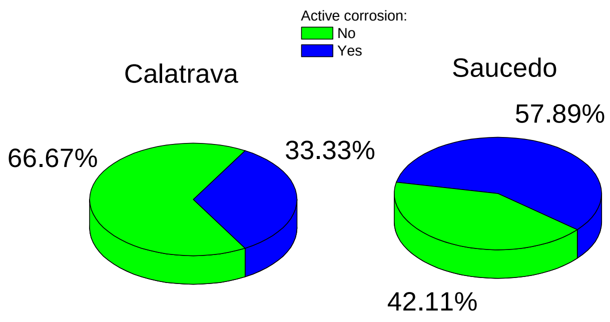


Figure 6 Active corrosion in objects with metallic core

With only the data obtained in this survey it is not possible to establish whether the differences between the two origins can be attributed to the treatment with inhibitors or to the origin of the objects. However, according to the C-Rs' previous experience, the Calatrava objects presented fewer problems of active corrosion even without organotitanates treatment.

The survey found differences in the state of conservation of the objects according to their origin, with those from *El Saucedo* being in a worse state than those from *Calatrava.* The higher percentage of objects with active corrosion from *El* Saucedo suggests that those objects will benefit from storage in a better controlled environment. It is known that chloride containing objects cannot be considered stable even in RH as low as 15per cent, but it is unquestionable that a low RH and the use of other measures (like treatments with corrosion inhibitors or protection with coatings) will greatly reduce their degradation rate. The database created for this survey was a useful tool for conducting the survey and for analysing the data. More importantly, this database will serve in follow-up surveys of the objects in the future.

Partner YU-FAA - *The Museum of Jordanian Heritage, Yarmouk University*

The Museum of Jordanian Heritage is part of the Faculty of Archaeology and Anthropology at Yarmouk University. The museum recounts the story of mankind from its earliest stages until today. It was established in 1984 in cooperation with the German Government and was officially opened in 1988. The museum reflects the research and field projects conducted by the institute faculty, researchers, and technicians whether independently or in cooperation with other local and foreign institutes.

The museum consists of three main exhibits; the main gallery, the numismatics hall and the temporary hall. The main gallery consists of four halls. The first one deals with Jordan's prehistory, features exhibits on Hunters and Gatherers and food production. Hall two presents the development of City-States and Territorial States. The third hall presents Jordan during the Classical Periods: Nabateans, Roman and Byzantine cultural materials excavated from different sites in Jordan are exhibited in this hall. The fourth hall highlights Jordan during the Islamic Period. Carefully selected cultural materials that belong to Umayyad, Abbasid, Ayyubid/Mamluk and Ottoman periods are exhibited in this hall. The exhibit in this hall extends to cover part of Jordan's recent cultural heritage. This includes a traditional "druggist shop", a "blacksmith shop, a "potters workshop" and "carpentry and weaving shops".

The fourth hall leads the visitor to the museum courtyard which has been specially designed to present examples of Jordan's traditions in architecture and other arts. The fully reconstructed rural house-complex from northern Jordan displays basic local architectural elements, such as cross-vaulted rooms, transversal arches and arched facades. The visitor enters completely furnished living and guest rooms, a stable and bread oven room.

The museum has a second floor which contains exhibits that present and explain various topics related to ancient technology. Ancient techniques of stone implements making, rock art, pottery and glass making, ancient metallurgy, basketry and textiles techniques are shown on this floor. In addition, there is a display of some ancient inscriptions, seals and amulets.

The temporary exhibit hall is dedicated to the purpose of organising special exhibits for a limited period of time. The exhibits in this hall are carefully designed to underline specific issues that serve the museum aims, especially those related to public awareness. This has been done through the exhibition of recent archaeological discoveries and some special and private heritage collections.

The Museum of Jordanian heritage houses archaeological materials and ethnographic materials from all over Jordan. A large proportion of the collection has come from the field projects conducted by the Faculty of Archaeology and Anthropology. The following are areas of the main exhibition halls and the conservation and storage facilities: display galleries ($1200m^2$), storage spaces ($2000m^2$), administration offices ($80m^2$), libraries, conservation laboratories ($500m^2$), and public amenities ($9m^2$). The museum is run by the following administrative and technical staff: 1 full-time curator, 2 full-time archaeologists, 3 museum technicians, and 3 C-Rs. The museum is supported by the analytical and photography lab of the Faculty of Archaeology.

The examined samples are part of a large collection of coins exhibited at the Numismatics Hall of the Museum. The exhibition consists of eleven showcases, which contain the coins with explanatory historical texts and maps in Arabic and English. Exhibited coins date from the emergence of coinage during the Lydian period through Hellenistic, Nabatean, Roman, Byzantine, Islamic and British mandate periods. There are 1,200 exhibited coins, from which 150 are made of gold based alloys, 420 made of silver based alloys, and 630 made of copper based alloys.

Ten silver based coins were selected from the Islamic collection for the purpose of the damage assessment study. All the selected coins were minted at one of the most important minting centres during the Umayyad period at the city of Wāsit in Iraq. The selected coins were minted in a short time span (34 years) in the period A.H. 90 (AD 708) to A.H. 124 (AD 741).

This type of silver coins has a very high historical and scientific significance. The coins were issued during a rich historical period of the Umayyad rule (AH. 90-124/AD 708-741). The selected coins were minted during the reigns of three prominent Umayyad caliphs; al-Walid Ibn Abd al-Malik (A.H. 86-96/AD 705-714), Sulaimān Ibn Abd al-Malik (A.H. 96-99/AD 714-717) and Hishām Ibn Abd al-Malik (A.H. 105-125/AD 723-742). Due to its political, economical and administrative importance, Wāsit had almost the exclusive rights of minting dirhems since the year A.H. 106 until the end of the Umayyad rule in AH.132. A sample of the study collection is shown in Figure 1.

Figure 1 Sample of the coins used in the damage assessment study

The coins are displayed in specially designed airtight museum showcases. However, there is neither general environmental control at the numismatic hall nor a microclimate control of the showcases. The numismatic hall is an all-day "open door" museum. The consequence of this high level of dust and pollution combined with high temperatures and relative humidity variations is rapid tarnishing, which leads to frequent cleaning and results in accelerated wear.

Condition Assessment

The condition assessment study was done over a period of 12 months to investigate seasonal trends. The selected coins were periodically checked for any sign of corrosion or tarnish, which was recorded. Visual and microscopic investigation was used for that purpose. The quality of the surrounding environment including evaluation of humidity and temperature fluctuations and levels of sulphur and chlorides was monitored. H_2S, NO_2, O_3, OCS and chloride concentrations in and outside the display hall were monitored. Diffusion tubes were placed inside the exhibition hall at two locations near the entrance and close to the display cases where the silver coins are displayed. Diffusion tubes were also placed at two locations outside the exhibition hall.

The aim of the study was to correlate pollutant levels with tarnishing rates so as to be able to predict further damage to silver artifacts. Attention was focused on the levels of H_2S; the way silver acts as an H_2S sink and the concentration inside a closed display case as a function of leakage rate and amount of silver present.

XRF, XRD and Energy dispersive X-ray microanalysis with a scanning electron microscope (SEM-EDX) were used to identify the nature of the corrosion products formed on the surface of the coins. This enabled determining the extent of damage of the artifact and understanding the corrosion causes and mechanisms. In addition, the presence of chloride or sulfide ions gives an indication about the presence of corrosion, its type and extent within the surface of the metal artifact. SEM-EDX was used to assess the extent and nature of the corrosion of the coins. The first EDX-SEM analysis was done in four different but neighbouring points on coin 3 as shown in Figure 2. The results of the analysis are presented in Table 1. Further analysis was carried out on a corrosion area for coin 3 and the results are given in Table 2**.**

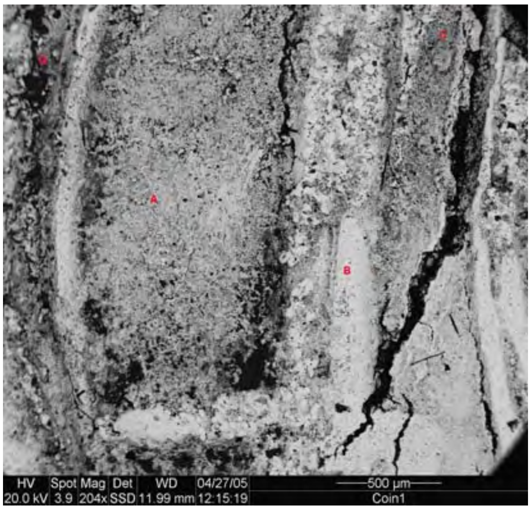


Figure 2 SEM microphotograph showing the extent of corrosion of a silver coin

	wt.% in area A	wt.% in area B	wt.% in area C	wt.% in area D	Average wt. %	standard deviation
O	15.7	5.4	27.7	30.3	19.8	11.5
Zn	0.1	0.6	0.8	0.4	0.5	0.3
Na	0.8	0.9	0.9	0.6	0.8	0.1
Mg	1.1	1.5	1.2	0.9	1.2	0.2
Al	1.0	1.1	2.0	2.7	1.7	0.8
Si	2.2	1.2	6.5	8.8	4.7	3.6
P	0.5	0.7	0.5	0.4	0.5	0.1
Au	2.0	2.3	1.4	1.2	1.7	0.5
Hg	0.9	2.4	0.8	0.5	1.2	0.9
S	0.5	0.7	0.5	0.7	0.6	0.1
Cl	1.3	1.2	1.0	0.8	1.1	0.2
Ag	73.6	81.7	56.2	52.4	66.0	14.0
K	0.2	0.3	0.4	0.5	0.4	0.1
Total≅	100	100	100	100	100	

Table 1 Chemical composition of points on coin 3 using SEM-EDX analysis (percent error = 0.01%).

Element	wt%
O	29.9
Zn	0.6
Na	0.3
Mg	0.8
Al	4.4
Si	24.2
P	0.4
Au	0.9
Hg	0.6
S	0.5
Cl	8.0
Ag	27.4
K	4.1
Total≅	100

Table 2 Chemical composition of a corrosion area on coin 3 using SEM-EDX analysis (percent error = 0.01per cent).

The coins used in the study are representative of the Islamic silver coins displayed in the museum. Islamic silver coins make around 80per cent of the overall silver coins displayed. The selected coins are highly significant as they represent the Islamic tradition of silver coinage during the Abbasid Period (750-1099 AD).

Concerning the identification of the nature of corrosion on the examined collection, the results of the visual and microscopic investigations presented in Table 3 show that all coins have a thin general corrosion layer formed. Some of the coins suffer from localised corrosion and some others have slight embrittlement problems.

Coin number	State of preservation	Corrosion Forms	Analysis
1	good	Uniform general tarnish layer mainly composed of silver sulfide with some localised silver chloride patches. Hair Cracks can be seen under the microscope.	SEM/EDX and XRF The main element is Ag +minor elements : Cu, Pb. (Cl + S) were detected as part of the corrosion layer.
2	very good	Good conservation state, small cracks scattered in the surface of the coin can be seen under the microscope.	SEM/EDX and XRF The main element is Ag +minor element : Cu. (Cl + S) were detected as part of the corrosion layer.
3	badly corroded	General and uniform corrosion in addition to the presence of cracks and lost parts.	As above.
4	very good	Slightly surface corrosion.	SEM/EDX and XRF The main element is Ag +minor elements : Cu, Pb. (Cl + S) were detected as part of the corrosion layer.
5	fair	Active localised surface corrosion. A discontinuous grey to black corrosion layer is present on the surface of the coin.	As above.
6	fair	Active localised surface corrosion. A discontinuous grey to black corrosion layer is present on the surface of the coin. Hair cracks especially at the edges.	As above.
7	good	Surface mild corrosion. Uniform general tarnish layer mainly composed of silver sulfide with some localised silver chloride patches in addition to hair cracks	As above.
8	Very good	Slightly surface corrosion with some localised silver chloride patches.	As above.
9	Badly corroded	Silver sulfide patches appear on the edges as evidence of localised corrosion. In addition, hair cracks are scattered on the surface of the coin. Embrittlement is a predominate feature.	As above.
10	fair	Active localised surface corrosion. A discontinuous grey to black corrosion layer is present on the surface of the coin.	As above.

Table 3 Corrosion forms using different techniques of coin analysis

Acanthite (Ag_2S) and chlorargyrite (AgCl) have been detected by XRD on all of the selected coins. In addition small amounts of talc and quartz were detected due to professional handling. It is possible that these particles could attract water and create differential aeration cells responsible for dramatic localised corrosion. The formation of silver sulphide is mostly due to the reduced sulphur in the indoor atmosphere. At neutral pH, the HS^- ion is the main reduced sulphur constituent from either H_2S or carbonyl sulphide (COS). This ion can either react directly with silver ions or sorb onto the surface. HS^- could be produced outdoors by the catalytic exhausts of the cars.

Two mechanisms may possibly generate silver chloride: chloride ions enter the aqueous layer at the surface of silver either through the incorporation of gaseous HCl or through the deposition of chlorine-containing airborne particles and a solid product may form by precipitation of the aqueous ionic salt AgCl (this process is the most likely to happen); the chloride ion may also be sorbed onto the surface and form silver chloride when the aqueous layer evaporates.

The results of the XRF analysis for the ten silver coins analysed show that all the coins have a high silver content, and indicates the high quality control of the manufacturing process of these Islamic coins (Al Saad and Bani Hani 2007). All of the coins contain copper, and most of them have appreciable amounts of lead which indicates the deliberate additions of these two metals in the alloy used for the manufacturing of the coins. Copper could have been deliberately added to debase the silver coins and save the more expensive silver. In addition, there is a technical reason for the addition of copper to silver. Pure silver is normally considered too soft to be used for coinage and could relatively easily be worn in circulation. The addition of copper increased considerably the strength, hardness and wear-resistance of silver without leaving a deleterious effect on its ductility and formability. The chemical analysis results show an appreciable amount of lead present in the coins. This indicates that the silver used in the coins was produced by the cupelation process. The complete removal of lead in this process seems never to have been achieved. Silver coins can be embrittled in the course of time due to the remains of lead left from cupelation. It has been found that this is particularly bad in the presence of copper. Condition assessment of the coins shows clear correlation between lead content and degree of embrittlement of these coins. The analysis of the corrosion products reveals a relatively high chloride content in some of the coins with very low content of sulfide. This indicates that silver chloride rather than silver sulfide is the major corrosion product of these coins. It can be concluded that the coins were excavated from a chloride rich burial environment.

An examination using SEM revealed corrosion and the phenomenon of embrittlement, both of which are present in most of the studied coins. The SEM investigation shows localised corrosion that penetrates the silver and results in embrittlement due to cracking along the corrosion paths. In addition, visually undetected scratches probably caused by mishandling or improper cleaning were seen on the surface of many coins. Using SEM, we were able to relate uncorroded regions with the non-inscribed regions, whereas it appears that corrosion and embrittlement are concentrated in the inscribed regions where the corrosive agents are trapped. In addition, the coins greatly suffer from the rims with some parts totally lost. This may be a result of the synergistic action of plane of weakness that occurs because of the continuous downfall on the rim and corrosion that increase the weakness of this part of the coin.

Correlation between the museum environment and corrosion

The results of the environmental monitoring of the museum show that pollutants rather than humidity and temperature fluctuations are the major cause of silver corrosion. There has been no considerable seasonal variation in the humidity and temperature levels inside and outside the show cases. The average humidity level is around 55 per cent with a seasonal change of around 15 per cent.

The Museum of Jordanian Heritage is located at about 300m from the main road that has heavy traffic around the clock. The average monitored external nitrogen dioxide concentration was 17ppb. This only decreased slightly inside the building to an average value of 13ppb, representing 76 per cent of the external concentration. External sulphur dioxide has an average level of 7.5ppb which decreases to around 3ppb inside.

H_2S levels are around 350ppt average value inside and outside the exhibition hall. The first thing that needs to be said here is that there is statistically no significant difference between the indoor and outdoor situations; it does seem in general that the outdoor concentrations are less than, or similar to those from the indoor sites. Interestingly, the temporal variation in these outdoor concentrations seems to be generally lower than those from the indoor sites. This is not necessarily surprising as one might expect enhanced variability in an actively used building.

Location	H_2S (average) (ppt)
Exhibition hall entrance	339
Exhibition hall	345
Inside show case	339
Outside museum	365
Outside museum	349

Table 4 H_2S concentrations at different locations

It is concluded that H_2S concentrations alone are insufficient to explain observed tarnishing rates. Other atmospheric chemical components working either separately (e.g. OCS) or synergistically with H_2S (e.g. HCl, OA) combine to produce observed tarnish. The origin of chloride ions in the museum may be surface cleaning agents. The OCS concentrations found in three locations are all higher than the H_2S concentrations determined simultaneously. Generally the outside values range from 550 to 750 ppt.

The history of the artifact itself is also important as this will determine the number of reactive centres on the silver surface, and hence the tarnish rate.

Silver is rapidly tarnished by sulfides in the museum environment. This was traditionally assumed to be the result of traces of hydrogen sulfide, but it is now known that silver is susceptible to attack by a wider range of sulfides, the most notable being carbonyl sulfide. Carbonyl sulfide is the most concentrated naturally occurring sulfide in the atmosphere. Indoors it can be generated from the ageing of materials such as wool. The rate of tarnishing of silver by sulfides is much affected by the presence of other pollutants such as chlorides.

The conservation requirements of the selected coins vary to a large degree, as they depend on the nature and state of corrosion and on the nature of the contaminants. Some of the coins need cleaning to remove the localised disfiguring corrosion at the rims. Some of them need only cosmetic cleaning to remove some of the copper corrosion that obstructs some of the details and for aesthetic reasons. Chlorides need to be removed to stabilize the coins and to reduce their damaging effect on the copper component of base silver alloys.

The crucial factor guiding decisions about cleaning and/or consolidation of an object is its stability. Priority should be given to stabilisation and only later can questions about appearance and legibility, which are generally more subjective, be addressed. In some cases, the preservation of details such as evidence of manufacturing techniques may guide the selection of methods of treatment.

It can be concluded that the best strategy to ensure future protection of silver objects in display and to minimize the need to implement costly interventive conservation is to monitor and control the surrounding environment and to keep sulphides and chlorides levels at the lowest possible.

There are two types of possible methods:

– High tech methods, such as air conditioning with filtration and absorption.
– Low-tech methods, such as sealing, absorption, and removal. They are more accessible, cheap, simple, compatible and aesthetic, but less effective and efficient.

The latter type is more appropriate in the case of the Museum of Jordanian Heritage.

Partner NTUA - *Museum of Technology, National Technological University of Athens*

The Museum of Technology of Athens, where the silver articles are stored is located in the centre of Athens. The collection of silver articles consists of silver jewelry, different silver icons and coins. Most of these objects are benefactors' gifts to the NTUA. The area is mainly polluted by traffic with increased percentages of sulphur dioxide and particulate matter originating from vehicles and the dust of the city.

The museum collection mainly consists of old scientific instruments and donations from people. Approximately $500m^2$ have been devoted to instruments and artifacts, including the research laboratories as well as the library. No permanent professional staff is dedicated to this museum. The historians and architects involved are members of the University staff. The artifacts are displayed in wooden and glass display cases and they are not covered by any protective system. There are also many artifacts in storage.

The silver artifacts have been offered by a benefactor and have been kept in storage. Some of them come from the 19^{th} century, but there are modern objects, too. The silver artifacts affected by the environment were considered for the survey. The artifacts were examined in-*situ* by visual inspection, manual handling and optical microscopy. Also, small enough objects were examined by XRD and SEM – EDS. No invasive methods were used and no sampling was performed. All articles were examined under a stereoscope with a CCD camera in order to detect minute areas affected by localised corrosion, especially near the welds and the valleys of the engraved surface.

Nine articles were at our disposal from the Technology Museum of Athens. Four of them were small enough to be handled for microscope examination and with a patina on their surface. Unfortunately, not many historical or archaeological aspects were available for these objects. The only information for one of them, a religious silver icon representing Saint Gerasimos, is that it originated from the island of Kefalonia, in the Ionian Sea in western Greece and was transported to Athens where it was left exposed to urban environment. The icon has a thick layer of silver sulphides and from a macroscopic point of view it seems to be in a quite bad corrosion state. Furthermore, a mark on the tarnished surface of one coin indicates 1810 as the year of circulation and by the inscriptions on it, seems to be of Spanish origin. The three other objects were silver medals with sulphide corrosion developed on their surface. There are also some bracelets from the 19th century, which were produced by a combination of different manufacturing techniques such as soldering, chain, filigree or stamping. There are no rare artifacts, but some of them are possibly of historic value.

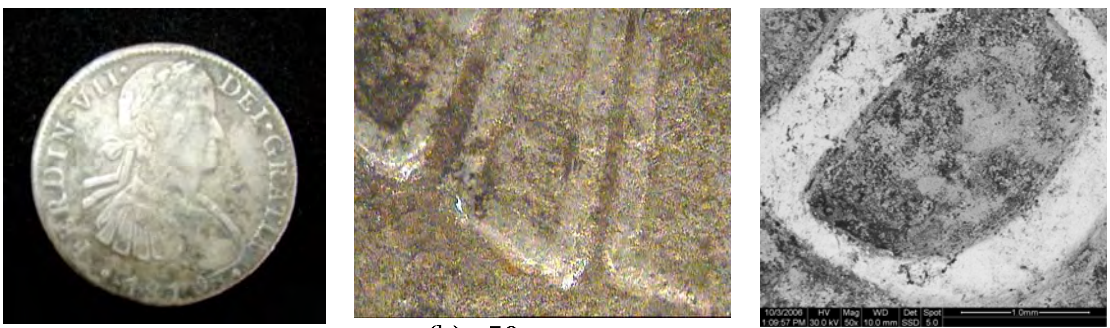
The objects were tarnished at more or less degree with the indication of a local corrosion process taken place especially at the joints. The attack is usually higher on the flat low areas of the high relief; while higher areas of the objects are not as attacked and in most cases are shiny. Commonly observed corrosion forms are general and localised corrosion.

The techniques involved for the examination of the articles are characterised as non-destructive. It should be noted that the objects were analysed by the available means only when their geometry permitted it. In more specific terms:

- The objects were analysed by XRD using an automatic diffractometer Siemens D5000 (Cu Kα X-ray source) in order to identify the crystalline phases of the oxide layer on the surface.
- The surfaces of the objects were also observed under the optical microscope (Leitz Aristomet), incorporated with a digital Sony CCD-Hi Resolution video camera and the accompanying image analysis software.
- The nature of the adhering to the surface layer was determined by SEM with EDS microanalysis.

The XRD spectra reveals the presence of acanthite, Ag_2S and chloroargyrite, AgCl as main corrosion products observed on the silver articles surface.

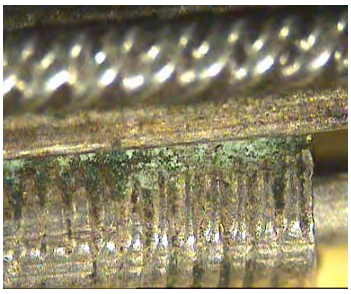
The evaluation of the results obtained by the SEM-EDS examination of the selected objects indicates that the metal base material should be silver-copper alloy with 1.5 to 7 wt% Cu. On the surface of the examined objects, apart from sulphur or chlorine, traces of other elements, such as Al, Fe, Ca, Si or Mg were also detected at the niches of the engraved areas, probably due to the accumulation of particulates and humidity. Two samples from the collection are presented in Figures 1 and 2 that follow.



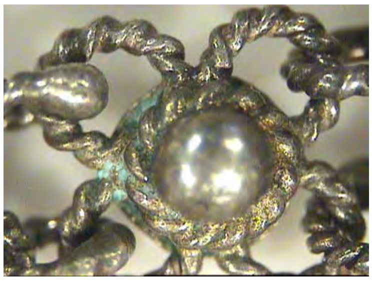
(a) (b) x50 (c)

Figure 1 Spanish coin (1810)

Figure 2 presents (a) a representative OM (b) an SEM (c) and a micro photograph of the coin; the lighter colour area is cleaner than the surrounding more affected area with accumulations of corrosion products and particulates at the niches.



x25



x25

Figure 2 Silver bracelet left, optical microscope photographs, corrosion of the weld

Environmental conditions in the museum

From the experience over the years and from the investigation of the conditions of storage and display in museum contexts, it is clear that air pollutants are of primary concern. The silver items were kept in oak lacquered cabinets. Table 1 provides the results of the analysis of the air within the museum performed by Quadrupole Mass Spectrometry (QMS). The analysis showed concentration of some ions of interest in the air sample.

C^+: 600 ppb,	$C_3H_6^+$: non detectable
Ar^{++}: 1000 ppb	$C_3H_7^+$: 20 ppb
CO_2^{++} 20 ppb	$C_2H_5^+$: 10 ppb
$C_2H_2^+$: 30 ppb	SO^+ : 40 ppb
NO^+ 100 ppb	SO_2^+ : 80 ppb
$C_3H_3^+$: non detectable	$C_6H_6^+$: non detectable
$C_3H_5^+$: non detectable	

Table 1 Results from the Quadrupole Mass Spectroscopy of air samples from the museum environment (total pressure 10^{-6} mbar).

Reduced sulfur species in addition to nitrogen dioxide may dramatically increase the rate of silver tarnishing. Nitrogen dioxide and oxygen act as the oxidising agents that are available to form a redox couple with silver to produce silver ions Ag^+, hence the formation of Ag_2S processes by the occurrence of sulfide ions in the environment. Silver chloride may possibly be generated by two mechanisms: chloride ions enters the aqueous layer at the surface of silver either through the incorporation of gaseous HCl or through the deposition of chlorine-containing airborne particles and a solid product may form by precipitation of the aqueous ionic salt AgCl (this process is the most likely to happen); the chloride ion may also be sorbed onto the surface and form silver chloride when the aqueous layer evaporates. Indoor, the origin of chloride ions may be surface cleaning agents or, as in the case of many Greek museums, proximity to the sea.

Commonly observed corrosion forms on the silver artifacts are general and localised corrosion. The degradation process is mainly due to the presence of galvanic corrosion phenomena combined with the action of chloride and sulphide ions coming from the environment. Acanthite, Ag_2S and chloroargyrite, AgCl are the main corrosion products.

The preventive conservation procedure in these cases could be the removal of chlorides and the utilisation of inhibiting and protective coatings to ensure long-term chemical-physical stability of the artifacts and to stop the degradation of the copper islands present in the silver-based alloys. The protective system based on barrier properties offered by nano-alumina pigmented Paraloid coatings seems to be quite sufficient to protect metal surface against aggressive agents, without compromising the aesthetic aspect of the metal/coating system (Vasiliou *et al.* 2007) and looks promising for the protection of silver-based alloys artifacts against tarnishing.

Partners EMMC and NRC-EC - *The Egyptian Museum*

The Egyptian Museum was built in 1902 with the aim not only to display artifacts but also to protect them from looting and the trade of Egyptian antiquities. Earlier attempts had been made to create a museum but then it was decided to build a new museum to accommodate the growing number of artifacts from the various excavations taking place at the time throughout Egypt. A French architect, Dourgnon, won a competition for the design of the museum and created the museum in its neo-classical style as it remains in Tahrir Square in Cairo. The museum is a public organisation that has been owned and maintained, since its foundation, by the Egyptian government under the Ministry of Culture.

The Egyptian Museum consists of one main building that stretches over an expanse of 15,000m^2 of land and houses over 132,000 objects, 1,416 of which are silver, excluding the silver coin collection. The range and variety of objects in this enormous collection varies widely and constitutes a detailed and extensive look into the history and culture of ancient Egypt. The artifacts of the museum are displayed on two floors of the building. However, a third floor and a basement as large as the entire museum serve as storage facilities. Nearly 300 employees work to maintain and upkeep the Egyptian Museum which is open seven days a week.

Other facilities also available at the museum are a library, the most advanced papyrus laboratory in the Middle East, a conservation laboratory and a school for adults and a school for the blind, which are part of a successful educational program. New additions have also been mrecently to the museum with a soon opening Children's Museum as well as a temporary exhibition room that regularly hosts different exhibitions related to ancient Egypt.

The Museum is not air conditioned, nor is temperature or relative humidity controlled due to the high ceiling of the building. For ventilation, the museum depends on its big windows, which are open all day during visiting hours, thus the air inside the museum and also in the show cases is affected to some extent by the air surrounding the Museum and its pollutants. More than 1.5 million tourists visit the museum annually, in addition to half a million Egyptians. Moreover, the environmental conditions vary remarkably depending on the time of the day and of the season and this variation could play a critical role for the life of the artifacts.

The types of silver objects that make up the collection are religious items (e.g. head of bird, amulet, naos), household items (e.g. spoon, cups), jewellery (e.g. anklets, earrings), cosmetic (e.g. statuettes, bracelets), and other items (e.g. mirrors).

The collection covers a range of periods from Roman period (3rd – to 6th Century AD), Ptolemaic Period (305 - 30 BC), Pharaonic Period from 21st – 31st Dynasty (1075 - 332 BC), Pharaonic Period from 7th -20th Dynasty (2150 - 1075 BC) and Old Kingdom from 3rd - 6th Dynasty (2575 - 2920 BC). The materials used are silver and electrum. The size of objects varies from very small (e.g. statuette measuring 2.8 cm) to very big (e.g. sarcophagus of Sheshonq II). Sixty-one objects originating from excavations were examined for this survey.

The Egyptian Museum has one largest collections of metal artifacts world-wide (more than 16,281 objects), covering a complete representation of its history, and the a great variety of metal artifacts, such as bronze and copper, gold, electrum, silver, iron, lead, tin and antimony. The Egyptian Museum is also the largest museum in the world for ancient Egyptian artifacts and therefore the most significant in Egypt and worldwide. The strategy used for the selection of objects was based on the following criteria:

- Objects covering all periods, starting from 3rd –6th Century A.D. through to Ptolemaic Period, late Period, New Kingdom, Intermediate Period, Old Kingdom and Predynasty Period
- Archaeological value.
- Great importance from a religious viewpoint.
- Different uses or applications.
- Providing information about historical context, technology, use and environment.

The examined collection represents 4.3 per cent of the total number of silver objects in the Egyptian Museum, excluding coins. The examined collection is also 0.05per cent of the entire collection of objects in the Egyptian Museum, metal or otherwise.

Materials	**Number of objects**
Silver	52
Electrum	9

Table 1 Materials and number of objects

Period	**number of objects**
Roman (3rd – to 6th Century AD)	9
Ptolemaic (305 – 30 BC)	7
Period from 21st – 31st Dynasty (1075 – 332 BC)	11
Period from 7th – 20th Dynasty (2150 – 1075 BC)	31
Old Kingdom 3rd – 6th Dynasty (2575 – 2920 BC)	3

Table 2 Periods and number of objects

No.	Object types	Number of objects	**No.**	Object types	Number of objects
1	Vessel	1	**17**	Naos	1
2	Horse shoe	1	**18**	Earring	2
3	Horse saddle	1	**19**	Heart	1
4	Spear hand	1	**20**	Shell	1
5	Sarcophagus	1	**21**	Griffon	1
6	Coffin	4	**22**	Crown	1
7	Bracelet	6	**23**	Anklet	1
8	Jug	2	**24**	Spoon	2
9	Amulet	1	**25**	Cup	3
10	Head of bird	1	**26**	Dish	2
11	Plate	3	**27**	Mirror	3
12	Ingot	3	**28**	Statuette	3
13	Coil of wire	6	**29**	Winged Scarab	1
14	Foundation deposit	3	**30**	Kohl sticks	1
15	Holly eyes	1	**31**	Needles	1

16	Falcon	1	**32**	Coin	1

Table 3 Object types and number of objects

The general condition of the silver alloy objects in the collection varies with tarnish in black, red, grey, white, and dull colour cracks, soil remains and corrosion can be observed on the surface of some objects.

The XRDF-system (X-ray diffractometer equipped with X-ray fluorescence spectrometer) and portable XRF were applied non–destructively in order to perform elemental analysis and determine the mineralogical composition of the silver based artifacts by the Egyptian Museum and NRC teams respectively. The portable XRF is NITON/XLt with software version 4.1.

The XRDF results (see Table 4) indicate that the corrosion products contain silver chloride (AgCl), silver bromide (AgBr) and cuprite (Cu_2O). It is interesting to note that silver sulphide was not detected by XRDF, possibly due to the thinness of the tarnished layer or that its composition is amorphous.

The XRF results indicate (see Table 5) that the content of Ag ranges from 88.3-96.4 wt. per cent, Au ranges from 0.2-2.5 wt. per cent, Cu ranges from 0.5 to 9.6 wt. per cent, and Pb ranges from 0.2 to 1.1 wt. per cent during the Roman period.

In the Ptolemaic period, the Ag content ranges from 83.9-99.4 wt. per cent, Au ranges from 0.9 to 1.5 wt. per cent, Cu ranges from 4.2-12.8 wt. per cent, and Pb ranges from 0.18-9.3 wt. per cent. During the period from 21st – 31st dynasty, the Ag content ranges from 90.7-98.4 wt. per cent, Au ranges from 0.5 to 4.6 wt. per cent, Cu ranges from 0.89-3.9 wt. per cent, and Pb ranges from 0.2 to 0.9 wt. per cent.

In the period from the 7th – 20th dynasty the Ag content ranges from 68.2-97.6 wt. per cent Au ranges from 0.2 to 24.9 wt. per cent, Cu ranges from 0.3 to 11.3 wt. per cent, and Pb ranges from 0.1 to 0.73 wt. per cent.

In the Old Kingdom, 3rd – 6th dynasty, the Ag content ranges from 85.4-96.8 wt. per cent, Au ranges from 2.0 to 2.1 wt. per cent, and Cu ranges from 0.5 to 3.9 wt. per cent.

It was found that in the examined collection, the Pb element is absent from the pieces dating to the Old Kingdom period and from the electrum objects (see Table 5).

Object no.	Chemical analysis	Mineralogical composition	Analysis tool
J.e:70766	Ag,Au,Cu,Si,Fe,Al,Mg,Ca,P,Fe, Ti,Cl,Br	Silver(Ag), chloroargyrite (AgCl) & quartz(SiO2)	XRD & (E-SEM-EDX)
Sr:3881	Ag,Au,Cu,Pb,Cl,Br,Ca,P,Fe,Ti, S	Silver(Ag), chloroargyrite (AgCl)	XRDF-system
J.e:70776	Ag,Au,Cu,Pb,Cl,Br,Ca,Mg,Fe	Silver(Ag), chloroargyrite (AgCl) & silver bromide(AgBr)	XRDF-system
J.e:70771	Ag,Cu,Au,Pb,Fe,Ca,Br	Silver(Ag), chloroargyrite (AgCl) & cuprite(Cu2O)	XRDF-system

Table 4 Results of the analysis of objects

Period	Elements / Values	**Ag**	**Au**	**Cu**	**Pb**	Fe	Sn	Zn	Other elements
Roman period from 3rd – to 6th Century AD	Max. value	**97.4**	**2.5**	**9.6**	**1.1**	1.7	1.8	-	Br,S,Cl,Ca,P, Ti, Si ,Al & Mg in some objects
	Min. value	**88.3**	**0.2**	**0.5**	**0.2**	0.2		-	
Ptolemaic Period, Reign of Ptolemy XI (305 - 30 BC)	Max. value	**99.5**	**1.5**	**12.8**	**9.3**	6.6	2.8	-	
	Min. value	**83.9**	**0.9**	**4.2**	**0.2**	4.6	0.6	-	
Period from 21st – 31st Dynasty (1075 - 332 BC)	Max. value	**98.4**	**4.6**	**3.9**	**0.9**	0.7	1.3	1.6	
	Min. value	**90.7**	**0.5**	**0.9**	**0.2**	0.4	0.7	0.7	
Period from 7th - 20th Dynasty (2150 - 1075 BC)	Max. value	**97.6**	**0.2**	**11.3**	**0.7**	7.7	1.4	0.9	
	Min. value	**68.2**	**24.9**	**0.3**	**0.1**	0.2	0.3	0.1	
Old Kingdom from 3rd - 6th Dynasty (2575 - 2920 BC)	Max. value	**96.8**	**2.1**	**3.9**	**-**	5.7	2.5	-	**Bi** 2.6
	Min. value	**85.4**	**2.0**	**0.5**	**-**	0.6	1.1	-	**Bi** 1.9
Electrum collections (different period)	Max. value	**64.7**	**52.6**	**5.1**	**-**	1.1	2.6		**Sb** 0.3
	Min. value	**40.8**	**27.9**	**0.5**	**-**	0.3	1.3		

Table 5 Results of the analysis of objects with a 0.5%error

Generally, it can be concluded that the ancient silver Egyptian artifacts are essentially composed of Ag with minor elements of Au, Cu, and Sn, Pb and Fe. While Electrum is composed mainly of Ag, Au and other minor elements.

Partners POLITO and CNR-ISMN - *Museo Archeologico Comunale "Ferruccio Barreca" of Sant'Antioco, Sardinia, Italy*

The Municipal Archaeological Museum of Sant'Antioco, opened in 2005, is located in Sant'Antioco, Sardinia (Italy), near the tofet and hosts the most important exhibition of the Phoenician-Punic culture in the Mediterranean Basin, comprising archaeological artifacts from the inhabited centre of Sant'Antioco and from other areas of Sulcis.

The collections, enriched by the archaeological excavations carried out in the last centuries and by occasional findings, include 15.000 archaeological artifacts: jewels, coins, weapons, amulets, gems, mosaics, glasses, common use objects, large bronze and marble statues, reconstructions of tombs of the 5th century BC. Of particular interest are the big statues of two lions in tufaceous materials (see Figure 4.39), positioned at the sides of the door of the ancient Sant'Antioco, named Sulky, and dated back to the 5th and 4th century BC.


Figure 1 (left) Lion statues originally located at the sides of the door of the ancient Sant'Antioco,,and now exposed in the Museo Archeologico Municipale "Ferruccio Barreca" of Sant'Antioco (right)

The collection of metallic artifacts consists of more than 1,000 gold, silver and copper based artifacts. Some representative jewels, cups and coins have been selected for the study after examining several silver or gold-based archaeological artifacts of Phoenician-Punic and Roman periods and/or fragments of them.

The artifacts, selected for their technological and artistic relevance are representative of the whole collection, and are important from a historical point of view because they are objects made of precious metals and constitute witnesses of the ancient economy and art.

The conservation state and general exposure conditions of the items are in some cases very good; only few coins and artifacts are characterised by heavy degradation phenomena induced by soil constituents attack and chloride and sulphide corrosion. The more precious items are stored in showcases where the environmental parameters are continuously controlled. The other artifacts are stored in polyethylene containers avoiding any contamination and pollution as well as post-burial degradation.

Only archaeological artifacts that have never been restored or subjected to any conservation treatment have been considered in order to better identify degradation phenomena. The only treatment needed was cleaning, in order to remove raw encrustations and soil relics.

The survey aims to identify the chemical composition of the bulk material and to ascertain the morphology and the chemical composition of the corrosion layers present on the artifacts.

Different analytical techniques were used: in-*situ* Optical Microscopy (OM), SEM and XRD. The experimental apparatus that have been employed are: portable Leica microscopes equipped with digital cameras, FEG-SEM-EDS Leo 1530, SEM-EDS Cambridge 360, XRD diffractometer Seifert D3000. The conditions of the analysis were non-invasive or in some cases micro-destructive.

As a matter of fact, non-destructive techniques are important tools for C-Rs to obtain information about the condition of the artifacts; moreover, the possibility of performing the characterisation in-*situ*, without transferring the artifacts from the museum to the laboratory can prevent further damages. In this survey, a successful application of a portable OM for the in-*situ* characterisation of precious ancient artifacts in the museum was performed.

Approximately five per cent of the collection was examined in the survey with particular attention to gold and gold-plated artifacts and to silver and silver-plated artifacts.

Gold and gold-plated artifacts

All the gold artifacts have been found in good condition. Figure 2 shows a gold earring produced by means of different manufacturing techniques, including casting, joining, twisting and heat hammering.

A softened (by heat) wire has been partially beaten to a thin sheet and shaped to the required dimensions. The conservation state of the earring is good notwithstanding the cracks in the thinner areas of the central part. Probably the metal had been overheated, which induced brittleness and increased the possibility of cracking with age. Because of the absence of surface corrosion phenomena, no chemical treatment was applied, only washing with water and gentle cleaning from the soil components.

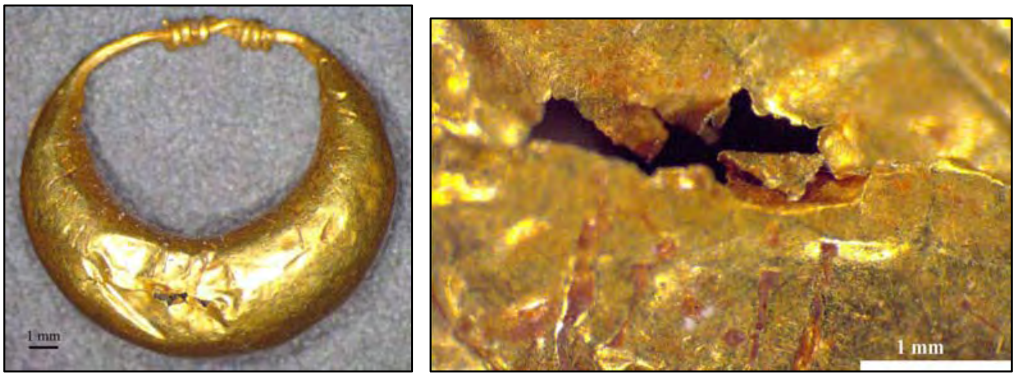


Figure 2 (left) Optical micrograph of a gold earring with enlargement of the cracked area (right)

On the other gold artefacts, no surface degradation phenomena have been evidenced, while the observed susceptibility to cracks with ageing has been related to metal overheating that induces brittleness. The gold artifacts are not corroded but only brittle, so they do not need any protection: the only recommendation is to avoid incorrect manipulations that can cause mechanical stresses.

On the contrary, the gold-plated artifacts show severe corrosion problems, as in the gold-plated silver earring in Figure 2 and the gold-plated brooches for braid of hair shown in Figure 3.

Figure 3 (left) Optical micrograph of gold-plated brooches for braid of hair with the enlargement of a cracked area of the brooch on the left (right)

The gold-plated brooches in Figure 3 show noticeable degradation that took place from the interior which was made of copper; as a matter of fact, they are cracked in some areas with the exposed copper substrate covered by corrosion products. In particular, on these artifacts the presence of noticeable amounts of paratacamite was detected by XRD. Galvanic corrosion phenomena, with copper acting as anode of the couple, associated with the ubiquitous presence of chlorides lead to the precipitation of these corrosion products.

Silver and silver-plated artifacts

Some of the silver artifacts were found fragmented already during the archaeological excavations; these artifacts are in an extremely brittle condition and tend to break easily with a little stress and a small deformation. Even though the artifacts show signs of external corrosion, this is not the only cause of brittleness that can also be attributed to ageing phenomena. It is worth noting that silver must have been quite ductile when the artifacts were produced and with time, the metallurgical properties were modified, thus inducing brittleness. This is the case of the silver bracelets shown in Figure 4 below.

Figure 4 Carthaginian silver bracelets (left), optical images of the cross-section of a fragment (right)

The optical images of the cross-section of a fragment clearly show the inter-granular nature of the fractured surface of the silver bracelet and the presence of small cuprite inclusions dispersed in the silver matrix.

The micro-chemical and micro-morphological analysis of the external corrosion products of the bracelets show mainly chloroargyrite (AgCl) and digenite (Cu_9S_5) as can be seen in the XRD diffractograms.

Silver-plated artifacts are characterised by complex degradation phenomena**.** The ring shown in Figure 5 consists of a copper substrate plated by a layer of silver. The chemical composition of the alloy used for plating the copper substrate is Ag 91.3, Cu 7.3, Pb 0.70 (wt per cent). The artifact is fractured in the welded regions and bronze disease is found in the copper enriched areas.

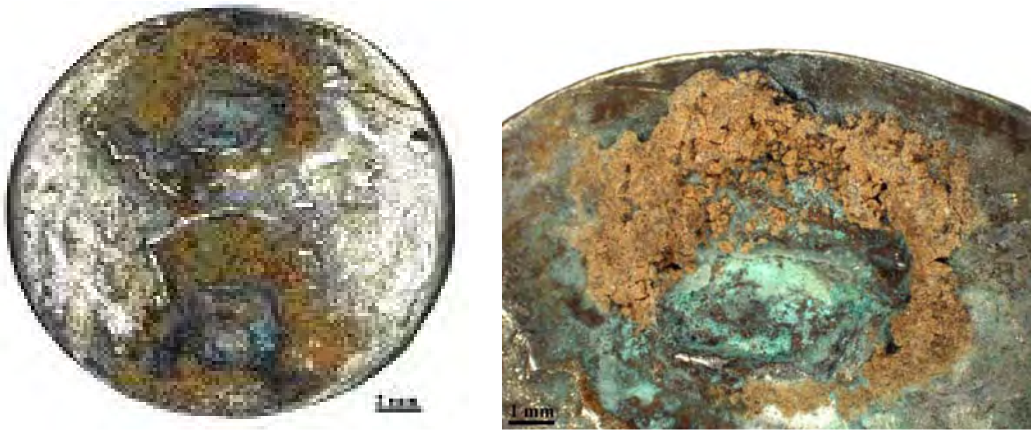


Figure 5 Silver-plated ring produced by soldering a ring (left), enlargement of the corroded area (right)

The in-*situ* OM observations of the gold artifacts exhibited in the Archaeological Museum of Sant'Antioco confirm their good conservation state. At present, no protection treatment is required. However, a preventive conservation procedure in showcases may be useful in order to control the environment by using exhibition showcases with inert gases inside, as well as activated charcoal filters and silica gel.

On the contrary, the survey conducted by OM and other analytical techniques indicated that the degradation of gold-plated, silver and silver-plated artifacts is mainly due to the presence of galvanic corrosion phenomena combined with the action of chloride ions coming from the environment. The appropriate preventive conservation procedure, in these cases, could be the removal of chlorides and the utilisation of inhibiting and protective coatings to ensure long-term chemical-physical stability to the artifacts and to stop the degradation of the copper islands present in the silver-based alloys. Interesting results were obtained with PECVD SiO_x-like coatings that show excellent barrier properties against aggressive agents and look really promising for the protection of silver-based alloys artifacts against tarnishing (Angelini *et al.* 2004; Grassini *et al.* 2007).

The adopted multidisciplinary approach to the survey of the collection of the Archaeological Museum of Sant'Antioco, performed in cooperation with the Director of the Museum, an archaeologist, and C-Rs, may help them to find the history and the evolution through ages of the archaeological remains and, when feasible, to preserve, restore and protect them without causing further damages.

Furthermore, the possibility of employing portable instruments is very promising in helping to answer specific questions concerning conservation aspects and for investigating degradation phenomena of precious ancient artifacts. Once this investigation is completed, it is possible to choose the most suitable environmental conditions for the storage and exhibition of these artifacts.

Partners IBN-DC and EGE-PNEA - *The Archaeological Museums of Rabat, Morocco and Van, Turkey*

The Rabat Archaeological Museum and the Van Archaeological Museum in the city of Van of Eastern Anatolia represent two important museums in their respective countries of Morocco and Turkey. These museums house tens of thousands of artifacts, and some of the most important archaeological copper alloy collections excavated from the region.

At the Archaeological Museum of Rabat, a large collection of archaeological bronzes have been collected since the nineteenth century from excavations in Morocco, the most famous ones being between the seventh and the sixth century BC, and at the end of the third century AD. Around 360 bronze objects are on display, but the exact number in the museum's reserve is unknown since the collection has yet to be inventoried. The bronze collection is exhibited in an oval room with surface area of 162m^2. Up to 2003, this room had 24 windows which were usually kept closed to keep out the natural light. However, the museum is located around 200m from a main avenue, which is heavily polluted due to car traffic, and is situated near the Atlantic Ocean so that the presence of salt aerosols is almost certain. Traces of salt efflorescence were found on the roof of this exhibition room, indicating that water infiltrated into the room. Furthermore, the walls were covered by wooden panels, which absorbed humidity in the winter but released it in the summer.

During the summer 2003, the museum was completely renovated. The large exhibition case in the oval room was replaced by several mobile display cases with filtered lighting. The new display cases helped to decrease the penetration of insects, dust, and airborne pollutants. The lighting of the room was improved by installing a new electrical network and by closing permanently the 24 windows to avoid any natural light.

Two luxmeters were placed in the display cases to monitor the lighting. One of them is located near the door, and the other inside the room. On average 250 luxes were recorded during the year with a peak of 900 luxes in July and August between 6 and 8 a.m. in the morning coinciding with sunshine. The meter placed near the door recorded an average of around 350 luxes with a peak in October equivalent to 500 luxes between 8 and 10 a.m. in the morning.

Climate sensors were placed at various locations in the room to monitor the thermo-hygrometric variations. Initial results show that the RH recorded during three days in November fluctuated between 73 per cent to 92 per cent, and the temperature between 18 and 21°C. However, even during the summer months, the average RH is observed to be higher than 60 per cent.

In terms of conservation treatment, there is little record of which bronzes have undergone treatment. The museum's archives mention that some bronzes were mechanically cleaned up to the 1960s. Furthermore, seven bronze objects from the Volubilis collection were treated in France in 1986 at the Laboratory of Archaeology of Metals in Nancy/Jarville, where it was necessary to dechlorinate and stabilise the objects.

Between 2000 and 2001, the International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM) organised a course of conservation-restoration of the cultural heritage called "Rabat Course" with the aim to strengthen the experience of scholars from the Maghreb countries. Thus, the metal collection of the museum (bronze and iron) benefited from several studies related to the conditions of their exhibition and storage rooms.

The archaeological bronze objects selected for the PROMET project were discovered at the site of Banasa and Thamusida. They represent the Roman era (first and third centuries AD) and are divided into two groups: Roman Gods such as Bacchus, Jupiter and Snake; and decorative objects, such as a female chest, wall lamps, oil lamp, as well as a phalere. The main corrosion problem, which is present on many of these objects, is active corrosion or bronze disease.

The copper alloy and iron objects studied for the PROMET project from the Van Archaeological Museum were made by the Urartian people that lived in East Anatolia between 830-600 BC. The objects were found in a fortress that lasted only 30 years between 673-645 BC. This limited time span can give us very valuable information about the metallurgy of the kingdom in a specific period. All objects came from a controlled excavation providing historical and archaeological data. All artifacts were manufactured by the Urartians in the seventh century BC providing information on technological features of their metallurgy. They were all made by a workshop owned by the kingdom using certain metallurgical standards.

The objects found in both museums were in good condition upon excavation, but now in the museum they are actively corroding. The main problem is that there are no C-Rs that work permanently for the museum and can care for the collection.

Partner MC-DAM - *The National Museum of Damascus, Syria*

The National Museum of Damascus was built in 1936 during the French Mandatory and under the auspices of the Ministry of Education. During the second half of the twentieth century, many blocks were added to its nucleus structure to host the endless significant and magnificent excavated finds. Moreover, the museum collection is represented and classified according to the objects' chronology and the origin of their finds, material, and subject. These objects are very important and represent the Syrian treasures. The metal alloy artifacts of the museum collection are a mixture of many different types from different eras, sites, and regions. The metal collection surveyed for PROMET represents prehistoric, Assyrian, Roman, Byzantine and Islamic objects, and comprises archaeological, ritual, domestic, artistic, warlike historical and economic artifacts with various alloys and technologies. The museum houses 7,467 metal artifacts from different regions in its exhibition area, whereas the size of the collection in the storage rooms was not available for the survey. The metal collection is distributed in the museum according to Table 1. Moreover, the percentage of treated artifacts is 27.2 per cent, but only 13.9 per cent of the total number of metal artifacts shows signs of recurring active corrosion.

Damascus national museum metals artifacts on display	**Bronze**	**Gilded bronze or, bronze with gold/ silver**	**Silver**	**Gold**	**Iron**	**Lead**	**Total**
Pre- historical department	142	3	560	31	1	-	**737**
Classical department	209	2	8	2	14	3	**238**
Islamic department	6126	-	174	165	27	-	**6492**
Total							**7467**

Table 1. The number of metal artifacts on display at the National Museum of Damascus according to the Departments of the Museum.

The excavated metal artifacts in the National Museum come from varied environmental conditions. Syria has varied climates from dry, semi – dry, moderate to wet. Moreover, the archaeological sites are spread all around the Syrian landscape and buried in different kinds of soil environment. The artifacts that come from the same geographical area or environmental conditions usually have the same deterioration appearance even if they have a varying alloy composition and/or represent different eras. For example, copper alloys that come from the north and the east of Syria near the Euphrates River suffer greatly from bronze disease upon excavation, and sometimes a copper alloy artifact may be found completely mineralised. The copper alloy artifacts that come from the desert or a dry climate like the one at the ancient site of Palmyra have an active white - green corrosion layer with blisters. While the copper alloy artifacts that come from middle Syria like Aleppo, Hama, and Homs, or from the south of Syria have green active corrosion layers. The copper alloy artifacts that come from the coast or from the sites close to the sea have an active green corrosion layer with lots of hard blisters, and/or bronze disease, and when trying to remove the blisters, the artifact loses its patina and shows the bare metal surface. Finally, the copper alloy artifacts that come from tombs often have a calcium carbonate layer or a bulky appearance with many blisters.

The iron alloy artifacts from most sites usually have blisters and flaking appearance and have a red hard crust and salts. The iron artifacts from Palmyra and Homs have soft yellowish corrosion spots, while the iron artifacts that come from sites very close to the sea, and from tombs, have a bulky shape or active corrosion.

The silver alloy artifacts have a lilac to black or green corrosion layer depending on the alloy composition; the artifacts from the coast that do not contain copper have a lilac corrosion layer, and some are very fragile and completely mineralised. While all silver alloys that contain copper have green corrosion layers regardless of the site from which they were excavated.

The museum building is old and located near the city centre in a highly polluted area; moreover most of the showcases and the materials used are very old and not of appropriate museum standards. Many artifacts are displayed without any conservation treatment including the necessary stabilisation treatment, while those treated may be suffering from the inappropriate conservation methods and materials. Furthermore, the metal artifacts are often displayed in cases next to other types of artifacts such as organic materials.

Unfortunately, the museum has no climate control, but is expected to have central heating - cooling and ventilation system within two years time. Since 2005, the temperature and relative humidity have been monitored. The ventilation of the museum is dependant on the large windows, which are kept closed as much as possible, since the museum in located on one of the busiest streets in central Damascus. The environmental conditions vary due to the location of the hall and/or the location near the heating system in winter; however, the RH and T fluctuations during the day and night are small except in winter due to the heating system which works only during the day time. However, the maximum values that have been registered for T and RH from the internal halls are 34°C and 49 per cent respectively. The following T and RH were recorded during the four seasons:

Autumn 16.5°C and 43.6 per cent;

Winter 12.6°C and 45.62 per cent;

Spring 19.4°C and 36.4 per cent;

Summer 29.4°C and 45.4 per cent.

Thus, stable metal artifacts can easily be maintained at this level of RH.

The collection of 50 copper alloy artifacts surveyed for the PROMET project is a very small portion of the Syrian treasures housed in the museum. Nonetheless, they were chosen so as to have varying technology and chemical composition. Also, from a conservation point of view, they were chosen for the following reasons:

1. The artifacts are very important and need to be catalogued, and to be preserved properly using the proper conservation method based on their damage assessment.
2. Some artifacts came from the same archaeological site, but represented different eras.
3. The artifacts were found in differing environmental conditions, and stored and/or preserved with inappropriate materials.
4. In general, the corrosion for these artifacts from the same geographical area is similar.

Non-destructive portable XRF was used for the analysis. Semi-quantitative results could only be obtained with this system. The results showed the following:

- Bronze coins that came from the Roman period at Kan Al –Alatna near Damascus (Roman Army camp), were in fact silver, containing a high concentration of Cu. The coins had a thick layer of copper corrosion products over the silvered surface, which was still preserved.
- The analyses show that artifacts that come from the Roman period in general have high content of Pb, especially those that come from the Palmyra site. As a result, the white corrosion layer most probably corresponds to lead corrosion products.
- The Byzantine coins from Sargela show a high content of Cu (90 per cent at least) and the lowest level among all coins for Pb (it does not exceed 1.5 per cent).
- The copper alloy coins from Hussan Suliman site from different eras have the same types of corrosion.
- The Phoenician coins had a low content of Pb.

The chemical analysis of the 50 copper alloy artifacts provided important information about the objects, on the basis of which the most appropriate conservation methods could be applied.

1.5 New Materials Developed and/or Tested for the Protection of Metals (Workpackage 3)

It is well established within the conservation field that the best way of assuring the long term preservation of stable metal objects is by setting up preventive conservation strategies. Unfortunately such a policy is not always easy to apply in the Mediterranean region where metal collections are stored and exhibited in inappropriate conditions (historic buildings without any air monitoring system), exposed to aggressive environmental conditions and affected by lack of funds and trained museum staff. Therefore, the use of protection systems is imperative to minimise further corrosion of the objects during storage or exhibition.

The problem we are facing is whether current protection systems are suitable for the long-term protection of objects in the Mediterranean region.

Within PROMET, we developed a strategy that meets the needs of the Mediterranean region. The aim was to determine**,** by means of a systematic scientific approach**,** the most compatible, reversible and environmentally-friendly corrosion inhibitors and/or coatings to protect monuments and objects made of copper, iron, and silver alloys within the Mediterranean region. The 'environmentally-friendly' feature was essential considering that usually there is no proper way to dispose of toxic chemicals and/or standard conservation laboratory may be nonexistent.

For metal objects from indoor collections many types of protection systems have been used or are still in use such as organic and inorganic coatings, conversion coatings (obtained from existing unstable corrosion products transformed with appropriate chemicals into stable and protective corrosion layers) and corrosion inhibitors. Of all the protection systems that were originally developed for industrial purposes, only those that meet the standards of the cultural heritage domain (reversibility, transparency and/or limited surface change, long-term efficiency) have remained in use.

Within PROMET, we were interested in testing and developing temporary and permanent systems for cultural heritage objects stored or exhibited in uncontrolled conditions. Corrosion inhibitors (CIs) usually respond to the need of short-term protection, whilst coatings (synthetic microcrystalline waxes or varnishes) are believed to be more appropriate for long-term protection (5-10 years). The factors that affect the efficiency of the protection systems are the following:

- the type of metal substrate (corroded surface, bare metal, patinated during fabrication, or worked surface such as sand-blasted);
- the presence of soluble and insoluble salts;
- the corrosion processes (influenced by corrosion inducers such as fluctuation of relative humidity (RH) and temperature, or by protective corrosion products such as sulphate and oxide on Cu alloys);
- the mode of action.

Furthermore, when a coating is not uniformly applied on the metal substrate or does not have the necessary thickness, and if there are surface defects such as bubble holes and cracks, air and moisture could penetrate, resulting in pitting or filiform corrosion. For good coating durability after application, the applied coating must have the following properties:

- good UV resistance;
- sufficient flexibility to withstand thermal stresses;
- chemical compatibility with the metal surface in order to achieve good adhesion;
- good resistance to the environment;
- relatively low oxygen, gaseous pollutants and water permeability.

Thus, the C-R must have appropriate knowledge to select a CI / coating that is suitable for the object according to the type of surface, exposure environment, frequency of maintenance, as well as other CI / coating properties that take into consideration the final appearance of the object, and finally the ability to remove it after application, if so required.

The existing ISO or ASTM standards for testing protection systems were modified to fit the pre-corroded metal surfaces exposed in an indoor museum environment. A standard methodology had to be set up and used by all the partners to test the new protection systems considered in the project. As illustrated on Figure 1, PROMET tested the protective efficiency of traditional and innovative systems on metal coupons simulating real objects by performing accelerated climatic and/or corrosion tests and by exposing the coupons to real indoor museum and/or depositary atmospheres.

Accelerated corrosion tests were used to compare traditional and innovative protective materials and methods to find the most effective one concerning a typical indoor museum environment of the Mediterranean region. Since accelerated tests are comparable, it was expected that the real durability of protective systems could be determined. Assumptions would then be made concerning their applicability in real conditions.

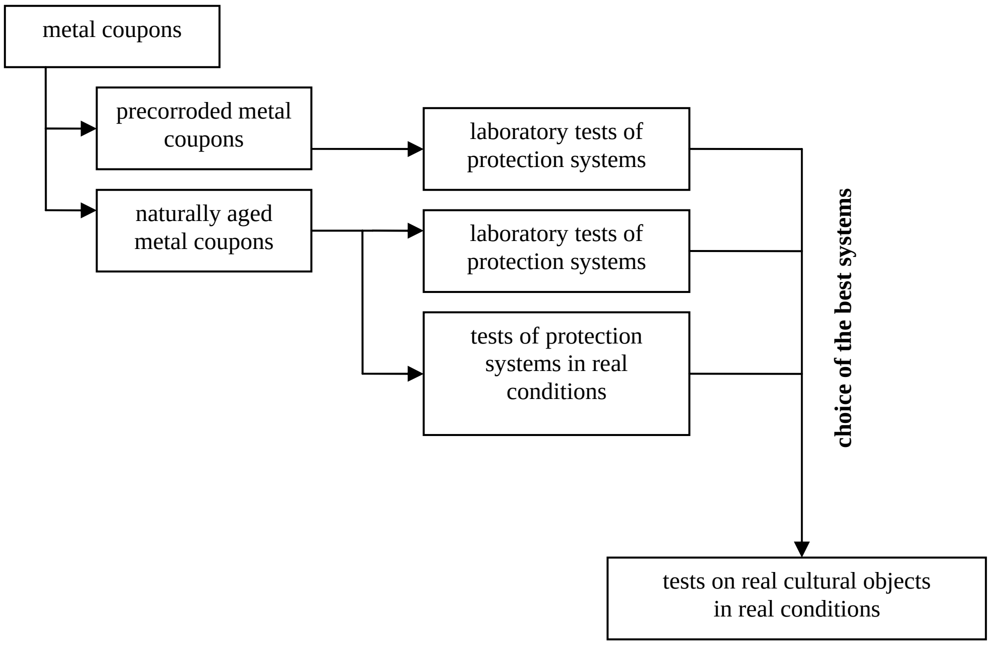


Figure 1 Methodology followed by PROMET partners for testing traditional and innovative protection systems

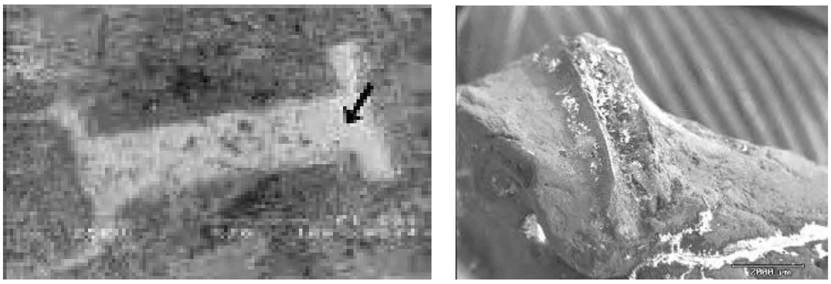
To avoid initial testing of the different protection systems on real objects, it was necessary to manufacture pre-corroded metal coupons simulating real objects, which could be used all along our experimental work. Furthermore, duplicate metal coupons could be tested to ensure the reproducibility of the results.

Each partner was required to select a few objects representative of the collection under study (see chapters one and three) for thorough examination. Figure 2 presents an overview of the objects examined.

Figure 2 Overview of some of the objects considered for examination to determine the composition and corrosion state of the metal coupons used to test the protection systems considered within PROMET.

Both non invasive, non-destructive and destructive investigations were carried out on the objects in order to determine the nature of the bulk materials and their corrosion layers. Sometimes this investigation was performed in-*situ* with portable instruments where partners DEMO or/and IESL-FORTH travelled to ancient Messene (Greece), Valletta (Malta), Damascus (Syria) and Irbid (Jordan) to carry out non-invasive to micro-destructive analytical studies of the local collections.

XRF fluorescence was used by many partners (TEI, EMMC, SVUOM, YU-FAA and NRC-EC) both on copper and silver-based objects of the collections under study, since it is a non-invasive tool for elemental analysis (Al-Saad *et al.* 2007). For small objects or small fragments that could be detached from the metal surface, the combination SEM-EDS allowed partners (CNR-ISMN, CSIC, NTUA, YU-FAA and RSS) to observe small surface details and carry out elemental analysis in a non invasive manner (Figure 3) (Al-Saad *et al.* 2007). The drawback of non invasive techniques is that it is hardly possible to determine precisely the composition of the core material on heavily corroded objects. Only destructive analysis from cross-sections of fragments taken from objects should be considered here.



a/ b/

Figure 3 Surface detail of a tarnished silver/copper coin from the Technology museum examined under SEM-EDS. Microanalysis revealed the presence of both Cl and S. XRD confirmed the formation of AgCl and of a small quantity of Ag_2S (a); (b) SEM picture showing a fragment from an iron sheep bell from Villa de *El Saucedo*, Toledo.

Some partners were allowed to take a sample of specific objects for more in-depth study, such as in the case of a backplate from the Palace Armoury collection, Valletta. After embedding, polishing and etching it, the sample was observed under a metallographic microscope. The SEM-EDS examination confirmed that the corrosion layer is constituted of loosely bound corrosion products and dust particles that were deposited on the metal surface. The surface still presents some traces of ancient corrosion products that were not removed during past cleaning interventions. These corrosion products were analysed on cross-sections using µRaman spectroscopy, which indicated the presence of ferrihydrite (an amorphous hydrated iron oxyhydroxide) mixed with goethite. Such corrosion products are typical of those analysed on historic iron objects (Monnier *et al.* 2007). IBN-DC also carried out a destructive investigation of metal samples on artifacts from the archaeology museum in Rabbat (Hajjaji *et al.* 2007).

XRD was used by most partners to determine the mineralogical composition of the corrosion products formed on the metal surfaces (Giannoulaki *et al.* 2007).

<u>Iron alloy coupons</u>

Since it was very difficult to reproduce thick corrosion layers like the ones found on archaeological iron-based objects in a short time, the iron-based coupons were produced to simulate steel historic objects. Modern low carbon steel (0.14 wt % C) was considered appropriate for the iron-based coupons. It was heat treated (4.5h at 950°C, cooled rapidly, milled and grinded) to produce the typical Widmanstätten microstructure observed on many objects.

<u>Copper alloy coupons</u>

The copper-based coupons were manufactured from a quaternary bronze alloy (85%Cu, 5%Sn, 5%Zn and 5%Pb) commonly found in Mediterranean cast archaeological collections. These coupons were grinded and polished on one side only.

<u>Silver alloy coupons</u>

The silver-based coupons were of the following four types to cover the different compositions and microstructures encountered on objects of the Mediterranean basin:

- CNR-91: Ag 97.0, Pb 1.5, Cu 1.5
- CNR-92: Ag 92.0, Pb 1.5, Cu 6.5
- CNR-141: Ag 92.5, Cu 7.5
- CNR-152: Ag 96.5, Cu 3.5

with all of them in cast condition and after heat treatment at 300°C and mechanical working. Figure 4 shows these coupons and the raw materials from which they were produced.

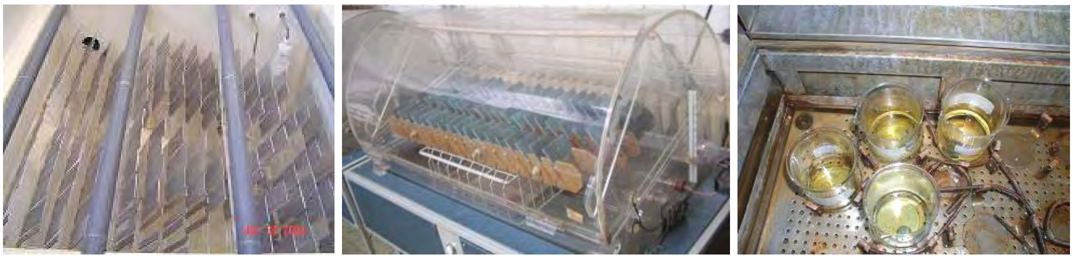
a/ b/ c/

Figure 4 Raw material to produce steel coupons (from left to right: cast, sand blasted, milled and grinded) (a); (b) Quaternary bronze, grinded and polished; and (c) silver coupons (cast material and coupons after mechanical and heat treatment).

The steel (50x75x2.5mm), bronze (50x75x5-6mm) and silver-based (Ø 15 to 19mm) coupons were manufactured by HM, SVUOM and CNR-ISMN respectively that provided reproducible materials (coupon quality controls were carried out on a few coupons chosen randomly in order to verify that all produced coupons were similar). Once manufactured the steel and bronze coupons were numbered (stamped with punches) and the partners who dealt with them carried out artificial ageing on some of these coupons.

1.5.1 Artificial ageing

The artificial ageing of the metal analogues aimed at reproducing the corrosion layers found on historic objects (for steel, bronze and silver-based alloys) and archaeological objects (for silver objects). For steel and bronze coupons, the protocols involved exposure in a humid chamber with or without pre-chemical treatment and were carried out by HM / DMME and SVUOM respectively (Figures Xa and Xb). For silver-based coupons the protocols depended on the partners and involved exposure in a humid chamber in presence of SO_2 or immersion in chemicals ($CuCl_2$, BaS, K_2S, $CuSO_4$, $5H_2O$ + $ZnCl_2$, $(NH_4)S$ (Figure Xc), or with alternate steps of drying in diluted Na_2S solution (Hughes and Row 1991)) followed in the case of the simulation of archaeological objects by an exposure on site (Tharros, Sardinia).



a/ b/ c/

Figure 5 Reproducible artificial ageing of steel ((a) by HM / DMME) and bronze ((b) by SVUOM) coupons in humid chambers with or without pre-chemical treatment and of silver-based coupons in chemicals ((c) by YU-FAA).

Figure 6 shows some of the coupons after the artificial ageing process. Steel coupons, prepared by HM/DMME, were exposed to a humid chamber (24h at 30°C/100%RH + 24h at 25°C/50-60%RH + 24h at 30°C/100%RH) (Fig. 6a). Bronze coupons, prepared by SVUOM, were brushed twice per day for three days and then immersed twice per day for two days with/in the following solution: $Cu(NO_3)_2$/ NH_4OH. They were then exposed to a humid chamber (8h at 40°C/100%RH + SO_2 + 16h at 20°C/50%RH) (Fig. 6 b). Finallly, disk-shaped silver-based coupons (Fig. 6 c), prepared by ISMN-CNR, were tarnished (by POLITO) by alternate immersion in 0.1M Na_2S aerated solution (24h in solution, followed by 24h of air exposure, 48h in solution followed by 24h of air exposure, 72h in solution followed by 24h air exposure).

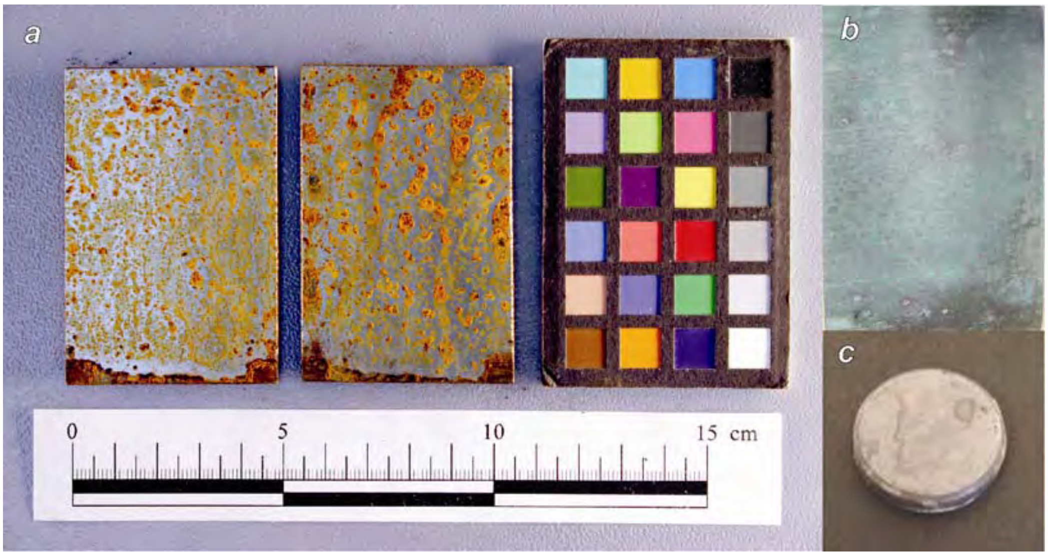
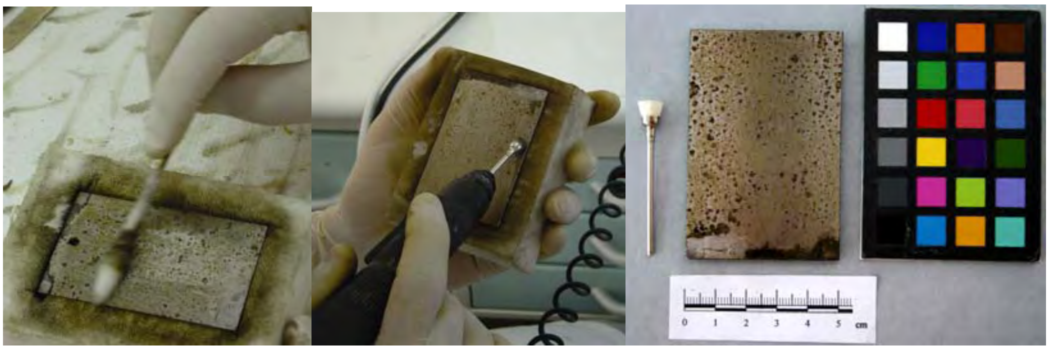


Figure 6 a) Steel coupons, prepared by HM/DMME b) Bronze coupons, prepared by SVUOM c) silver coupons.

The artificially aged coupons were further cleaned mechanically (iron, copper-based coupons and silver coupons exposed at Tharros site) or chemically / electrochemically (with alkaline dithionite (MacLeod 1979) or by galvanic coupling with aluminium in carbonate / bicarbonate solution for tarnished silver coupons) so as to reproduce fully the surface of real objects ready for application of protection systems. The cleaning and application of protection systems were carried out by the same professional C-R for each set of coupons (steel, bronze and silver-based alloys) so as to respect the original surface of the coupons. Figure 7 shows the protocol followed on steel coupons covered with local orange powdery blisters as well as the appearance of the coupons at the end of the mechanical cleaning. Bronze coupons did not require final mechanical cleaning since the corrosion layer formed was quite adherent.



a/ b/ c/

Figure 7 Final preparation of the steel coupons: (a) cotton swab moistened with ethanol rolled lightly over the surface to collect the powdery and non adherent orange corrosion products; (b) use of a rotating drill to remove any remaining powdery compounds; no pressure; use of fibre brush (pig hair) slightly inclined; (c) the coupon after mechanical cleaning (to compare to Figure 6a).

Analysis of the corrosion layers (remaining on the metal surfaces) using X-ray diffraction and µRaman spectroscopy revealed the presence of ferrihydrite/magnetite on steel coupons and brochantite/antlerite/$Cu_2(OH)_3NO_3$ on bronze coupons. AgCl, Ag_2S and CuCl formed on silver-based coupons tarnished artificially in chemicals were reduced to metallic silver and copper during the cleaning process. AgCl and $Cu_2(OH)_3Cl$ on coupons exposed on the Tharros site were maintained after the ultrasound cleaning process in iso-propilic alcohol. At the end of the cleaning process, the metal surfaces were similar to those expected to be found on historic and archaeological objects prepared for being protected.

1.5.2 Natural ageing

Another group of metal coupons (50 per partner for steel and bronze, only a few for silver-based materials) were naturally aged on site during a period of one year to simulate natural corrosion forms as for real objects. The exposure rack design reflected the collections' conditions of exposure (objects in showcases: a vertical rack; objects freestanding in exhibition halls and suffering from dust deposition: a rack with a slope of 30°). Figure 8 shows the distribution of the 50 coupons (steel or bronze) on the racks (references in yellow, coupons exposed three months in blue, coupons exposed six months in pink and coupons exposed 12 months in green).

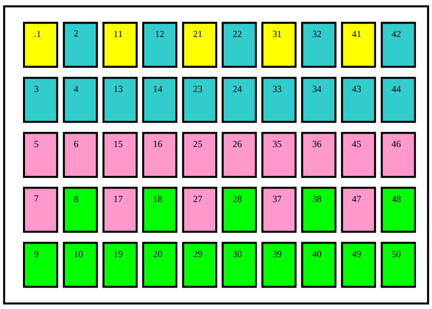


Figure 8 Distribution of the coupons on the rack.

Table 1 presents the site of exposure chosen by each partner and Figure 9 an overview of the conditions of exposure. None of these sites presented a controlled environment and were thus characteristic of the conditions of exhibition or storage of metal collections in the Mediterranean region.

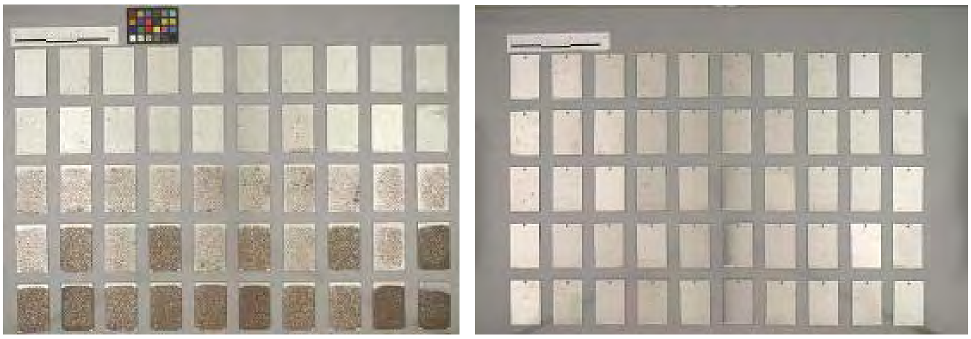
Partner / Country	**Metal(s) tested**	**Rack design**	**Site of exposure**
TEI / GR	steel / bronze	vertical	Benaki museum, Athens (storage area)
HM / MT	steel	oblique	Palace Armoury, Valletta (exhibition hall)
IBN-DC / MO	steel / bronze	oblique	Archaeology museum, Rabat (bronze room and storage area)
ALP-ME / SY	steel / bronze	vertical	Aleppo museum, Aleppo (Prehistory section)
EMMC / EG	Bronze	horizontal	Egyptian museum, Cairo (showcase of room 37)
SVUOM / CZ	Bronze	vertical	National museum, Prague (depositary 103)
RSS / JO	Bronze	oblique	Umm Qais museum, Umm Qais (exhibition room)
YU-FAA / JO	Silver	oblique	Museum of Jordanian Heritage, Irbid (cabinet of the exhibition hall)
NTUA / GR	Silver	oblique	Technology museum, Athens (showcase)
POLITO / I	Silver	horizontal	National Roman museum of Rome, Rome (exhibition room)

Table 1 Site of exposure of the metal coupons for natural ageing chosen by each partner.

Figure 9 Overview of some of the conditions of exposure of the coupons (steel, bronze and silver-based) proposed by the partners.

The corrosion progress was followed along the exposure period, but more specifically after three, six and 12 months, when observation by binocular, colour change measurements, SEM-EDS investigations were carried out on the series of removed coupons (five coupons initially (references), 15 coupons after three months, 15 coupons after six months and 15 after 12 months). HM developed a remote monitoring photographic capture (RMPC) system designed to take pictures on a daily basis (Crawford *et al.* 2007). It was particularly adapted to follow the corrosion progress before the coupons became fully covered with localised forms of corrosion. Also, RH and T were recorded all along the exposure period using different recording devices. Some partners also monitored the level of pollutants (NO_x) and corrosivity was determined by iron, copper and silver corrosion resistance sensors (SVUOM according to ISO 11844 for the National museum in Prague, Knotkova *et al.* 2007).

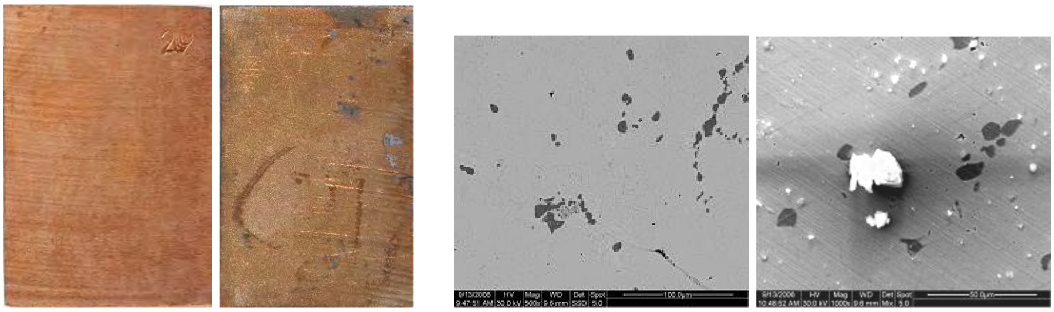
The HM and IBN-DC results found that dust particles (containing Ca, Si, Al) and salts (NaCl) favoured the development of localised corrosion as shown in Figure 10. Steel coupons exposed at the Palace Armoury, Valletta and the Archaeology museum, Rabat (rack with a slope) appeared covered with general corrosion after one year of exposure. The same coupons exposed at Benaki Museum in Greece and Aleppo Museum in Syria, but in vertical position, were still in good condition after the same period of exposure.



a/ b/

Figure 10 General appearance of the whole series of steel coupons after different periods of exposure at the Palace Armoury (a) and the Aleppo museum (b) at the end of the ageing process.

The corrosion developed on bronze coupons was minimal, therefore, difficult to monitor. Only local spots of corrosion appeared at casting pores originally present on the metal surface (they favour water condensation) as indicated on Figure 11a. As regards silver-based coupons, no alteration (National Roman museum, Rome) or slight tarnishing (Ag_2S and AgCl at the Museum of Jordanian Heritage, Irbid, Technology museum, Athens and Egyptian museum, Cairo) were observed. In the latter case, dust particles acted as nucleation sites for corrosion attack as shown in Figure Xb.



a/

b/

Figure 11 (a) Appearance of bronze coupons before and after exposure of 1 year in depositary n°103 of the National museum (Prague); (b) SEM pictures of coupon CNR 92 (Ag 92.0, Pb 1.5, Cu 6.5) before and after exposure of 1 year at the Technology museum of Athens.

After exposure, the steel coupons were cleaned following the same protocol as for the artificially aged coupons. The technique applied was adapted though to the level of alteration of the coupons (Figure 12a). The bronze coupons were degreased with acetone with a cotton swab, mechanically cleaned with a scalpel wherever green spots had formed (Figure 12b). The procedure was carried out under a microscope. Tarnishing on silver-based coupons was stripped off using chemicals (thiourea and formic acid) and mechanical cleaning with a soft cloth. Similarly to an earlier approach, the same professional C-R cleaned the whole series of coupons (steel, bronze and silver-based alloys).

a/ b/

Figure 12 Cleaning processes after the on-site exposure of the steel ((a) by HM) and bronze coupons ((b) by TEI).

The coupon surfaces were recorded at the end of the ageing process and after the cleaning process. Steel coupons had corrosion products that were analysed using µRaman spectroscopy: ferrihydrite, goethite and lepidocrocite were found. These compounds were closer to the composition of corrosion layers on real objects than on the artificially aged coupons.

The layer of corrosion products on bronze coupons was so thin after exposure in most tested indoor environments that its chemical composition could hardly be analysed. Bronze coupons exposed in depositary 103 of the National museum of Prague were analysed after three, six, nine and 12 months of exposure by SEM/EDAX methods. The dark spots contained a significant amount of sulphur (probably a mixture of CuO/CuO_2, sulphide and sulphate copper corrosion products). The white and/or grey spots formed on the surface defects (in pits, holes, cracks) contained both lead and zinc (probably $2PbCO_3$,$Pb(OH)_2$, mixed with ZnO, $Zn(OH)_2$, $ZnCO_3$ and $Zn_5(CO_3)_2(OH)_6$).

No corrosion product could be found on silver coupons (they had been pre-cleaned).

1.5.3 <u>Protection systems selected by PROMET partners</u>

A market survey was carried out by some PROMET participating countries (Siatou *et al.* 2007). Safe commercial products suitable for the purposes of our project were identified and constituted one group of protection systems to test. The second group comprised innovative compounds developed within the project. After some preliminary work carried out to optimise some of the partners' protection systems in order for them to meet the PROMET requirements, the following protection systems were selected for further testing.

1.5.3.1 Corrosion inhibitors

Sodium carboxylates and carboxylatation solutions were developed by LRMH for iron and copper-based alloys. These CIs are non-toxic compounds derived from fatty acids and extracted from vegetable oil (colza, sunflower and palm). A major corrosion rate decrease for iron-based alloys was observed through electrochemical experiments and climatic chamber tests for neutral (pH ranging from 7 to 9) sodium decanoate CH_3-$(CH_2)_8$-COONa noted NaC_{10} (above 0.01M) and slightly acid (pH ranging from 4 to 5) CH_3-$(CH_2)_{(n-2)}$-COOH noted HC_n (with n>9) with an oxidising agent solution without significant surface aspect modification. The second treatment had been developed for heavily corroded metal surfaces. The same decrease was observed on copper-based alloys for neutral sodium heptanoate NaC_7 and NaC_{10} solutions. Carboxylates can be applied with either brush or immersion, with the latter being more effective. Surface analysis of treated samples showed that the inhibition mechanism was correlated to the formation of a nanometric (for sodium carboxylate) or micrometric (for carboxylatation solution) layer of iron or copper carboxylates. The stability of this passive layer is controlled by the carboxylate's solubility which is strongly dependant on the carbon chain length (Hollner *et al.* 2007a; Hollner *et al.* 2007b). These CIs are reversible in ethanol.

CIs developed by IBN-DC such as BiTA (bitriazole) and FPTS for copper-based alloys or cactus seed extract (OTH) for iron-based alloys gave promising results on clean metal surfaces (Hammouch *et al.* 2005, Dermaj *et al.* 2005). The OTH inhibitor is a formulation based on seed oil of *Opuntia ficus indica*, a cactus that originates from Mexico and is quite abundant in Morocco. This environmentally-friendly CI is constituted of long chains of fatty acid, triethanolamine and potassium hydroxide. In this form, OTH presents good solubility and is easy to apply on metallic surfaces. The principle of action of this CI is based on adsorption and formation of a protective film (Hammouch *et al.* 2007a, Hammouch *et al.* 2007b). The FPTS formulation contains 3-phenyl-1,2,4-triazole-5-thione (PTS), triethanolamine and potassium hydroxide (Dermaj *et al.* 2007). These CIs are reversible in ethanol.

A selection of non-toxic CI additives produced by Dow Chemical Company, and Cortec Co., was made from the market survey. After initial testing by TEI, 12 highly rated products that met conservation standards were selected for further testing on steel and bronze coupons. Many CI additives applied in combination to either Paraloid B72® or Poligen ES 91009® (see below) were tested such as bis-oxazoline (alkaterge-T) by Dow Chemical Company; and calcium sulfonate (M109), a blend of triazoles (M435), and ammonium salt of tricarboxylic acid (M370) by Cortec Co.. Most of these CI additives are well known in the literature for protecting industrial objects, but they had never been used on museum objects (Siatou *et al.* 2007).

1.5.3.2 Coatings

Silane coatings developed by SVUOM were considered for bronze surfaces. The silane molecules (or trialkoxysilanes) have the general formula of $R'(CH_2)nSi(OR)_3$ (where R'= organic functionality; and OR = hydrolyzable alkoxy group, e.g., methoxy (OCH_3) or ethoxy (OC_2H_5)), which after hydrolysis in solution into silanol group -Si-OH can form covalent bonded layers on the metal surface. Silane molecules are adsorbed onto the metal surface through hydrogen bonds formed between SiOH groups of the silane molecules and MeOH groups of the metal hydroxides. Upon drying two condensation reactions occur: the one is the condensation between silanols (SiOH) from the silane solution and the metal hydroxyls (MeOH) from the metal surface hydroxides, forming covalent metallo-siloxane bonds (MeOSi) (Plueddemann 1991) according to:

$$\text{SiOH(solution)} + \text{MeOH(metal surface)} = \text{SiOMe(interface)} + H_2O$$

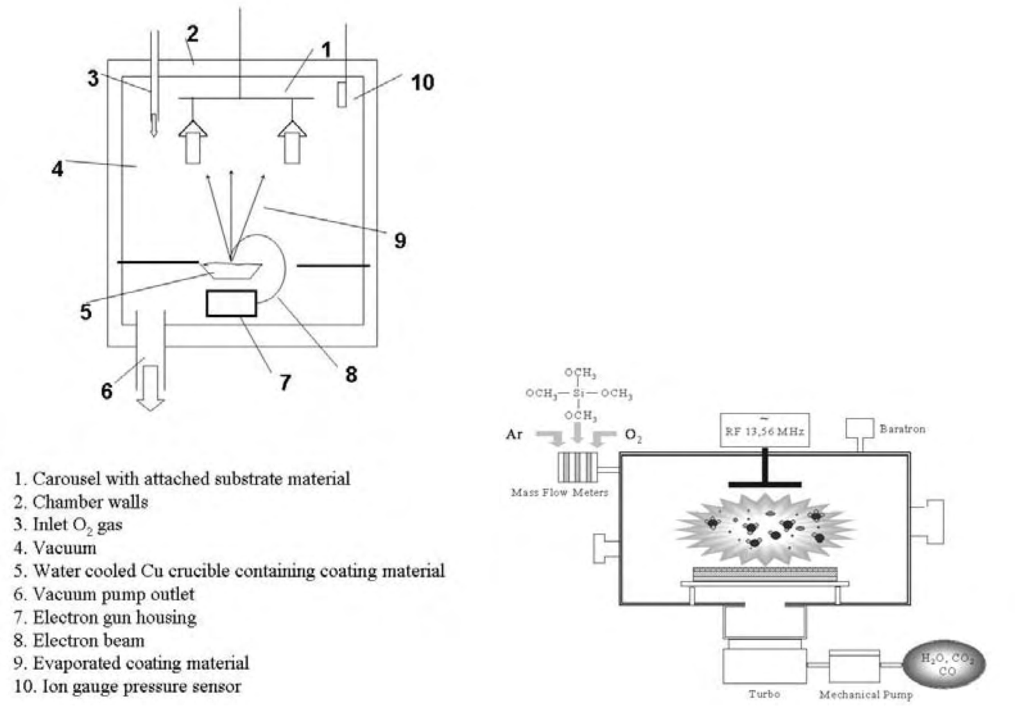
The other is the condensation among the excess SiOH groups adsorbed on the metals, forming a siloxane (SiOSi) film on the top:

$$\text{SiOH(solution)} + \text{SiOH(solution)} = \text{SiOSi(silane film)} + H_2O$$

Both -Me-O-Si- and -Si-O-Si- covalent bonds formed at the interface give an excellent adhesion to the metal substrate, as well as a hydrophobic interface. Corrosion protection of this coating is given by the barrier properties improved with crosslink density and the bis-silanes, with the general formula of $(OR)_3Si(CH_2)_nR'(CH_2)_nSi(OR)_3$, are more suitable for corrosion protection. For Cu and Cu alloys the mixtures of bis-[3-(trimethoxysilylpropyl)]amine and bis-[3-(triethoxysilyl)-propyl]-tetrasulfide (mixtures of bis-sulfur and bis-amino silanes) are recommended as corrosion protective coating (Van Ooij *et al.* 2002). Within PROMET, different combinations of suitable silanes were tested first on bare and artificially aged copper coupons (same process as for the PROMET bronze coupons) through accelerated corrosion and electrochemical tests. The combination that gave the best results is called silane A forming a copolymer at room temperature. The coating mass of silane coatings is between 3 and 6 $g.m^{-2}$ and protection is better with two layers. Reversibility of silane A is possible in 5 M NaOH.

The techniques of physical vapour deposition (PVD) and plasma enhanced chemical vapour deposition (PECVD) are well established in the industrial field to obtain void-free and well-adherent thin films (d'Agostino *et al.* 1997, Mattox 1998). The research carried out by the partners (DMME and POLITO) concentrated on defining a deposition protocol at relatively low temperatures, not comprising though the transparency and corrosion resistance of the coating. The developed coatings were deposited on steel, bronze and silver alloys. Dense SiO_2 films were deposited by DMME on polished steel coupons using the reactive low voltage ion plating (RLVIP) technique. Preliminary results with SiO_2 were promising, giving well-adherent transparent colourless coatings; however, the coating material was proved to be incompatible with the deposition chamber. As a result, titanium dioxide was evaluated as a possible substitute. TiO_2 coating was deposited by reactive evaporation (RE, Figure 13a). TiO_2 can be prepared as a thin transparent film and has the advantage of having a high linear coefficient of expansion comparable to that of steel. Furthermore titanium dioxide is a semi-conductor and can be deposited without major problems. Coating chamber parameters (such as O_2 partial pressure, temperature, coating time, or gun power) were modified to achieve the required coating properties. An unexpected problem that occurred with titanium dioxide was that it gave rise to coloured coatings as a result of the phenomenon of light interference. This could not have been anticipated nor prevented (Vella *et al.* 2007). TiO_2 coatings were tested for both short-term and long-term protection.

PECVD deposition of silicon containing organic compounds (that is organosilicons) on bronze and silver alloys coupons were studied by POLITO (Angelini *et al.* 2004 and Agostino *et al.* 2005). The system used is presented in Figure 13b. The SiO_2-like coatings are characterised by high chemical and thermal stability, good dielectric properties, and low gas permeability. With hydrogen plasma pre-treatment, the SiO_2-like film deposited is more protective. Similarly to the PVD-TiO_2 coatings, PECVD-SiO_2 coatings are coloured and their reversibility is currently under investigation. Both PVD and PECVD allow to carry out in the same reactor, before the deposition step, different substrate pre-treatments with the possibility of removing surface contaminants or performing surface modifications, like oxidation, or reduction.



a/ b/

Figure 13 Schematic of the PVD deposition of TiO_2 by DMME (a) and PECVD deposition of SiO_2-like coatings by POLITO (b).

Synthetic polyethylene wax is a ready-to-use liquid (ethylene in water) wax named Poligen ES 91009® (BASF). The coating is safe and easy to use since it is applied as a liquid (no solvent is required), and dries within 24 hours. Furthermore, this coating is reversible with the application of sodium hydroxide solutions. This new product had never been used before for conservation purposes and was tested with or without CI additives on iron and copper-based alloys.

Nano-alumina pigmented ParaloidB72® and B44® were developed by NTUA on silver-based alloys. The composite coatings gave a less shiny appearance but were expected to reduce the development of filiform corrosion by complexing the pigments into the polymer matrix. Removal of the protection is possible with toluene or acetone.

For comparison purposes, traditional coatings used in conservation were also considered: acrylic resin (Paraloid B72®), polyurethane varnish and microcrystalline wax (Renaissance® and Cosmoloid H80®), polyvinyl acetate and cellulose nitrate.

1.5.3.3. Application of the protection systems on the coupons

Innovative protection systems were applied only by the partners who developed them before sending them to the other partners for testing in their countries, so as to limit any risk of heterogeneity between the coupons tested.

For the short-term testing, the traditional protection systems were applied by the partners themselves on the artificially aged coupons sent to them by HM, SVUOM and CNR-ISMN.

For the long-term testing, the naturally aged steel and bronze coupons were first sent to HM and TEI respectively for mechanical cleaning carried out by professional C-Rs, who also applied the traditional protection system selected (Paraloid 72®) to be tested at all museum sites. Both these coupons and the others (including silver-based coupons) were mailed to the partners developing specific protection systems to be tested. The protected coupons were finally sent back to their respective countries.

1.5.4 <u>Protocols to test, examine and analyse the protection systems</u>

The consortium devised several protocols for testing, examining, and analysing the selected protection systems on pre-corroded metal coupons. Short-term testing was first considered on artificially aged coupons for a preliminary selection of protection systems. Long-term testing was carried out afterwards on naturally aged coupons to assess the effectiveness of the most promising protection systems in real conditions of exposure. The products found to be most effective were finally tested on real objects.

1.5.4.1 Short-term testing

Short-term accelerating corrosion testing is routinely used in material science to assess the behaviour of materials in specific environments. Results are needed quickly so that standard materials as well as corrosive conditions are applied. In PROMET, short-term testing was used to assess the effectiveness of innovative protection systems and compare them to traditional ones. It was carried out on artificially aged coupons using accelerated ageing in climatic chambers and electrochemical techniques.

Most protection systems except PVD, PECVD and a few others (cellulose nitrate, polyvinyl acetate, silane A and alumina nano-powder pigmented Paraloid B44® and B72®) were applied in a similar manner (by immersion) to limit any variations due to human factor:

<u>Traditional systems</u>:

- Renaissance® wax was applied by immersion (five minutes) on coupons that were preheated in an oven at 50ºC for an hour and were left to dry for 16-24h. Cosmoloid 80H® was applied dissolved in toluene (13.33g in 20 mL of toluene) by brush and was left to dry for 24h.

- Polyurethane varnish (Rylard® boat varnish) was applied by immersion (two coats). The first immersion was carried out at room temperature onto pre-heated coupons that had just been removed from the oven and were then left to dry in the lab for 16-24h. The coupons were heated at 50°C for one hour before the application of the second coat and the process was repeated.
- Paraloid B72® was applied by immersion and the number of coats varied between one and two, depending on the partner. Pre-heated coupons were immersed into 15 per cent Paraloid B72® in acetone at room temperature and left to dry in the lab for 16-24h. The second coat was applied following the same process on the coupons that were heated at 50°C.
- Cellulose nitrate (16% (w/v) in acetone) and polyvinyl acetate (14% (w/v) in acetone) were applied by brush (two coats one criss and one cross forming thus a double criss-cross film).

Innovative systems:
- Sodium carboxylates (0.1 to 0.5M NaC_{10} and NaC_7) were applied following a four-hour immersion at room temperature and carboxylatation solutions composed of carboxylic acids (HC_{10}, HC_{12} and HC_{14}) mixed with an oxidising agent (Table 7.2) were applied following a three-hour immersion. The use of long carbon chains (above 12) made it imperative to work above 30°C. Such conditions of application were considered as too harsh for real objects and solutions made of long carbon chains (above 12) were discarded beyond the short-term testing.

Solutions	**Concentration**	**Oxidising agent**
HC_{10}	30g/L	H_2O_2 (0.1M)
HC_{10}	30g/L	$NaBO_3$ (0.1M)
HC_{12}	30g/L	H_2O_2 (0.1M)
HC_{12}	30g/L	$NaBO_3$ (0.1M)
HC_{14}	30g/L	H_2O_2 (0.1M)
HC_{14}	30g/L	$NaBO_3$ (0.1M)

Table 2 Composition of the carboxylatation solutions.

- Formulation of 3-phenyl-1,2,4-triazole-5-thione (FPTS, 0.075% (w/v) in ethanol), formulation of natural *Opuntia ficus indica* (Cactus extract – OTH, 0.02% (w/v) in ethanol) and bitriazole (BiTA, 0.001M in ethanol) were applied following a three-hour immersion at room temperature or pure by brush.
- Poligen ES 91009® wax (with or without CI additives) and Paraloid B72® (with or without CI additives) were also applied following a five-minute immersion at room temperature. The selected additives are presented in Table 7.2. They were added into Poligen and Paraloid solutions and were dissolved after stirring. The coupons were left to dry in the lab for 24h.

Coating	**Solvent**	**CI additives**
15% (w/v) Paraloid B72® (pellets)	acetone	M 109 (calcium sulfonate in mineral oil carrier, liquid) 1.5% by weight (density 0.96 -1kg/L)
Poligen ES 91009® (liquid)	n/a	M 370 (water solution of ammonium salt of tricarboxylic acid, liquid) 1 part of CI to 40 parts of coating
15% (w/v) Paraloid B72® (pellets)	acetone	Alkaterge T (oxazoline type, solid) 0.1% by weight
Poligen ES 91009® (liquid)	n/a	M 235 (blend of triazoles, solid) 1% by weight
Poligen ES 91009® (liquid)	n/a	M 435 (alkaloamine salt of triazole, liquid) 1.5% by weight
15% (w/v) Paraloid B72® (pellets)	acetone	M 435 (liquid) 1.5% by weight
15% (w/v) Paraloid B72® (pellets)	acetone	M 235 (solid) 1% by weight

Table 3 Composition of Poligen ES91009® (or Paraloid B72®) + CI additives protection systems.

- Silane A constituted of 5% gamma –mercaptopropyltrimethoxysilane, 2% bis-(trimethoxysilylypropyl)amine, 1% hydrated tetraethoxysilane and 92% ethanol was mixed by hand-stirring at room temperature and it was applied on the coupons by brush. The coupons were left to dry at room temperature for one day.
- 10% (w/v) of gamma phase alumina (particle size 40 –47 nm, surface area 35-43 m^2/g, mp 2040°C (Sigma – Aldrich, product number 54, 483-3)) was added to 15% (w/v) Paraloid B72® and B44® solutions in toluene. In order to achieve better dispersion, the aluminium oxide (Al_2O_3) nanopowder was initially suspended in toluene and stirred with a magnetic stirrer for an hour. Paraloid granules were added and stirred until they were dissolved forming a milky suspension. Application by brush.
- PVD-TiO_2 coating was applied on coupons hung onto jigs (previously sandblasted) inside the chamber space (Figure 14a). The coupons were positioned at roughly the same vertical height. 3 coupons were attached per jig (three coupons x three jigs). The coupons were sputter cleaned for five minutes prior to the actual coating run. (Argon pressure: 1 $x10^{-2}$mbar; work- piece voltage bias 1000V). The coating conditions were: source material: Ti_3O_5; base pressure: 3.0 x 10^{-4} mbar; temperature: 200±20°C; O_2 partial pressure: $4x10^{-4}$mbar; total pressure: 7x 10^{-4}mbar; EB gun power: variable 200-340mA; coating time: 17 minutes. The chamber was allowed to cool down to room temperature overnight and was then pumped up to atmospheric conditions with nitrogen gas.
- PECVD-SiO_2 coating was applied on coupons positioned on the ground electrode. The coating conditions were: temperature of the plasma (T<50°C), gas and organosilicon vapour flow rates controlled by mass-flow and vapour source controllers, respectively, while a turbomolecular pump backed by a rotary pump, a throttle valve, and a pressure gauge allow to keep the pressure fixed at the selected value ($1.0 \cdot 10^{-3}$- 1.0 Torr) and gas mixture containing hexamethyldisiloxane (HMDSO) or tetraethoxysilane (TEOS) added with oxygen and argon.

The basic requirements for accelerated corrosion testing are given in ISO 7384 where the main critical factors are increased temperature, relative humidity, water condensation and corrosion stimulators (SO_2, chlorides). Simple climatic chambers or similar equipment were used. The general aspects of such testing can be found in known standards for environmental testing (i.e. EN 60 068 Environmental testing). These accelerated corrosion tests were followed by electrochemical testing, which, however was available to only some of the partners.

1.5.4.1.a. Accelerated ageing in a climatic chamber

In PROMET, the exposure conditions of the protected coupons were taken from the aforementioned standards, reflecting extreme conditions for museum objects: 16h at 90% RH and 35 °C followed by eight hours at room conditions (20 – 25 °C and RH 50 - 60%) during a minimum of 30 cycles (Figures 14a and 14b). Corrosion stimulators were used by some partners: chloride solution (3.5% w/v NaCl) applied before the protection systems on the surface of steel coupons by spraying and / or exposure to specific pollutants (8 % (v/v) SO_2 during the wet/dry cycles for bronze coupons or sulphide saturated atmosphere for tarnishing of silver – Figure 14c) to simulate aggressive conditions.

a/

b/

c/

Figure 14 Accelerating ageing for the short-term testing of the protection systems on artificially aged coupons; (a) climatic chamber (TEI testing); (b) inside of a climatic chamber with copper plates and PROMET bronze artificially aged coupons (SVUOM testing); (c) stimulation of corrosion of silver-based coupons by exposure to a sulphide saturated atmosphere (80% ammonium sulphide solution, T= room temperature during 30 days) (YU-FAA testing).

The following information was documented:

- inclination and direction of the coupons' exposure;
- the number of reference coupons and test coupons;
- dates of exposure, removal and assessment;
- qualitative description of changes in surface appearance for each evaluation, if possible with photographs of the test coupons before, during and after testing;
- quantitative and semi-quantitative results of assessment of defects of coatings and/or corrosion by application of rating systems and/or by application of other specific methods (mass gain, mass loss, changes in physical properties, density and distribution of defects or other methods of evaluation).

Monitoring of the protection systems included continuous examination of the coupons every 24h at the end of the dry testing period, taking care not to damage the surface under test. Significant changes had to be recorded and evaluated more in-depth. A final evaluation was performed at the end of the exposure period. Visual microscopical examination was used as well as weight loss/gain measurements. Some coupons were examined at the end of the exposure period by scanning electron microscopy (SEM).

This approach was followed by each partner testing the selected protection systems given in Table 4

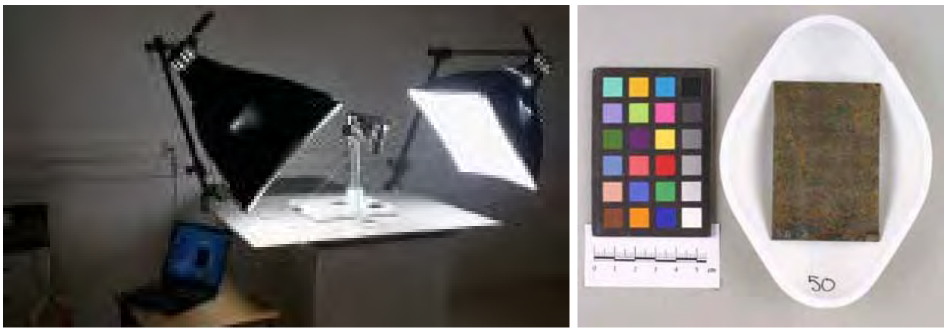
Partner	Metal alloy	Protection systems tested	Corrosion stimulators	References
HM	Steel	PVD, polyurethane varnish, Renaissance® wax and Paraloid B72®	with and without corrosion stimulator (NaCl)	Vella *et al.* 2007
TEI /	steel /	Poligen ES 91009® with or		Argyropoulos *et al.*

NILES / CSIC	bronze	without Cl additives		2007b
LRMH	steel / bronze	NaC_7, NaC_{10} and carboxylatation solutions		Hollner *et al.* 2007a, Hollner *et al.* 2007b
IBN-DC	steel / bronze	OTH, FPTS and bitriazoles	with and without corrosion stimulator (NaCl)	Hammouch *et al.* 2007a, Hammouch *et al.* 2007b, Dermaj *et al.* 2007
ALP-ME	steel / bronze	Paraloid B72® and microcrystalline Cosmoloid H80® wax		
SVUOM	steel / bronze	Silane A, NaC_7, NaC_{10} and Paraloid B72®	with and without corrosion stimulator (SO_2 + chloride salts)	
YU-FAA	silver-based alloys	Cellulose nitrate, polyvinyl acetate and Paraloid B72®	sulphide saturated atmosphere	
NTUA	silver-based alloys	Alumina nano-powder pigmented acrylic resin (Paraloid B44® and B72®)	sulphide saturated atmosphere	
NRC-EC	silver-based alloys	Alumina nano-powder pigmented acrylic resin (Paraloid B72®) and Paraloid B72®		
POLITO	Bronze and silver-based alloys	PECVD		

Table 4 Protection systems selected by PROMET partners and conditions of testing.

Visual observation (using raking light) was a simple way used to monitor the efficiency or failure of the different protection systems. However, in this way any changes at a micro level were hardly detectable. Therefore, additional examination tools were considered such as those by HM that monitored fully all metal coupons tested using visual, macro as well as microscopic observations and photography with standard reproducible studio conditions, namely same equipment, same settings and full lighting control (no variation from natural light) combined with weight measurements. Two types of photographs were taken:

- Macro-photography (Figure 15): each coupon was photographed using a Canon digital SLR camera (at recorded settings), vertical camera stand, colour calibration card, 5cm scales, two studio lamps with diffusers with bulbs of known brand and same wattage, computer laptop and coupon stands. The coupons were handled with gloves throughout the photography session.



a/ b/

Figure 15 (a) Standard photographic documentation equipment; (b) coupon photographed under standard reproducible light conditions. Coupons were placed in “weighing boats” to facilitate their handling and prevent touching them during the whole ageing process.

- Micro-photography: a specific area of the coupon was chosen and photographed through the microscope at regular inspection intervals.

Although this was a time consuming task, it allowed for a more precise observation of the way the protection system tested failed for the case of HM. Figure 16a shows the monitoring process in progress and Figures 16b and 16c the specific conditions of exposure of the coupons used by HM.

a/ b/ c/

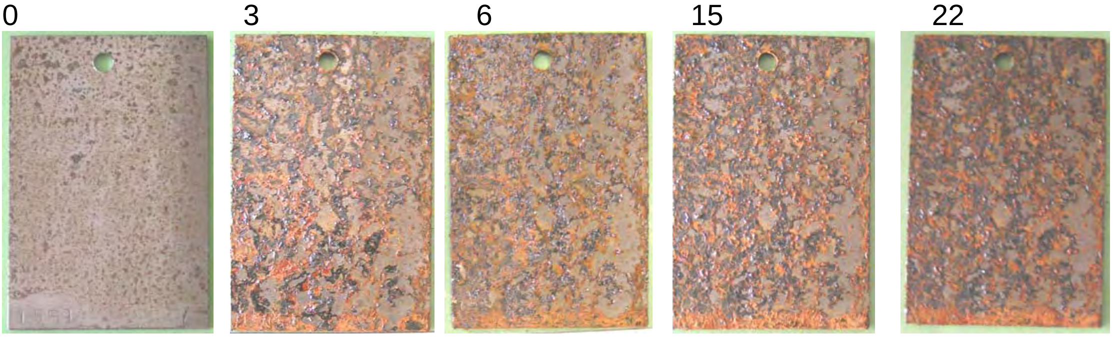
Figure 16 (a) Monitoring of the protection systems tested under binocular and photographing of zones of interest; (b) conditions of the accelerated ageing: coupons in “weighing boats” exposed horizontally on plastic mesh separating trays in a sealed box containing different salts to maintain 90% RH. RH and T were monitored with a HOBO datalogger; (c) position of the boxes in the oven to maintain 35°C.

1.5.4.1.a-1. *Steel coupons*

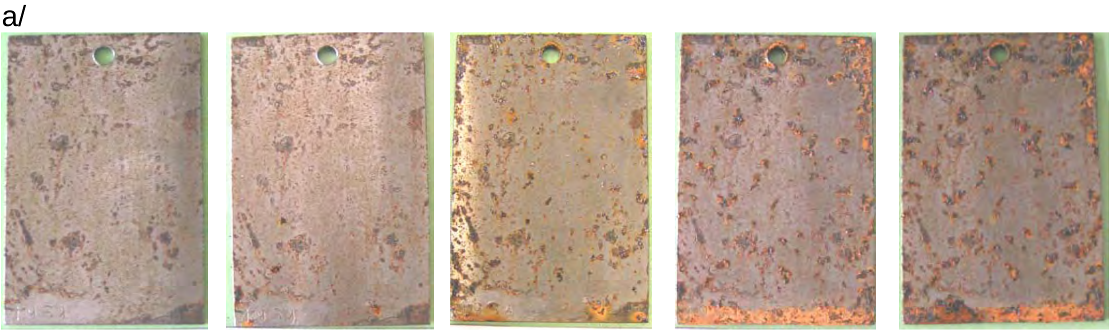
CIs tested by IBN-DC in less aggressive conditions (63-68%RH and 21-24°C) than those defined above showed that coupons protected with OTH behaved well. Results indicated that the application by brush (using pure OTH) was more effective than by immersion (Hammouch *et al.* 2007b).

On the other hand, some partners used more corrosive exposure conditions (LRMH cycle: 8h at 100% humidity, using twice-distilled water heated to 40°C and 16h under the room conditions. Duration: min. 30 cycles). As a result, the reference material corroded faster (Figure 17) and change of appearance could be easily visualised. The 0.25M (average concentration chosen for the tests) NaC_{10} CI and HC_{10} + H_2O_2 carboxylatation solution tested gave the best results (Figures 17b and 17c).

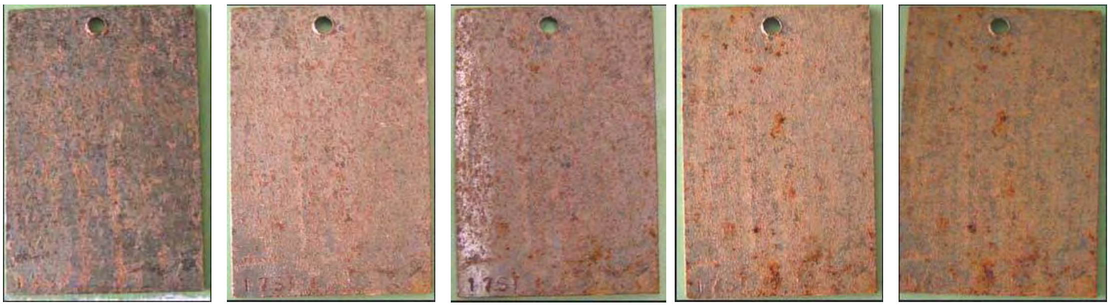
0 3 6 15 22



a/



b/

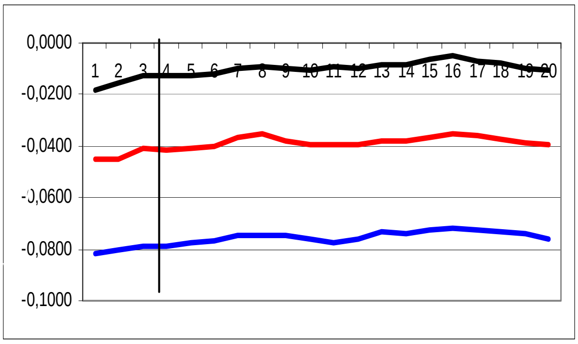
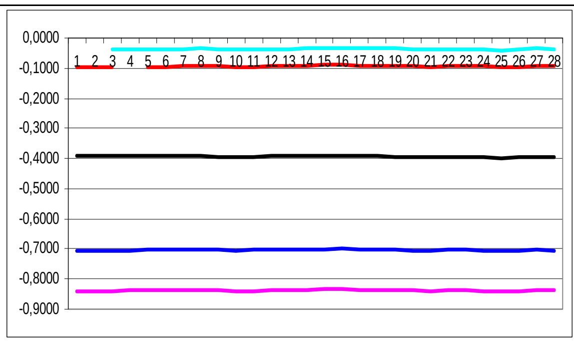


c/

Figure 17 Assessment of the efficiency of NaC_{10} (0.25M) (b) and carboxylatation solution $HC_{10} + H_2O_2$ (c) compared to non protected artificially aged steel coupons (a) when exposed to accelerated ageing cycles (LRMH protocol).

As regards the coatings tested by HM, Figure 18 shows the results obtained on the upper side of the steel coupons (due to the immersion process, the back side was not covered with a homogeneous film) at macro and micro levels without any protection and protected with traditional protection systems such as Renaissance wax® (microcrystalline) – 8µm or Paraloid B72® – 40µm and the innovative PVD coating (<1µm). Weight loss/gain versus time plots are also given. Polyurethane varnish is not considered here since it did not fail, certainly because of the thick layer (250µm) applied by immersion.

The results obtained were quite consistent for all three coupons tested per protection system: the unprotected coupons showed clear corrosion progress after only four cycles on pre-corroded areas. Weight loss/gain measurements showed a slight increase with time although the corrosion progress remained quite slow. The same occurred on coupons protected with Renaissance wax® after 14 cycles. Corrosion was localised and could not be visualised through weight loss/gain measurements. Paraloid B72® failed after six cycles on the pre-corroded zones, however, filiform corrosion appeared after 14 cycles and developed further. Weight loss/gain measurements taken in parallel showed quite a heterogeneous progression. Finally PVD coating failed almost immediately, thus showing that the coating (in the conditions tested) could not compete with traditional systems.

Macro-picture (original state)	**Micro-photograph** (during the accelerated ageing)	**Weight gain or loss** (%) versus the number of cycles
Unprotected 	 Corrosion after four cycles on pre-corroded areas	
Renaissance wax® 	 Corrosion after 14 cycles on pre-corroded areas	

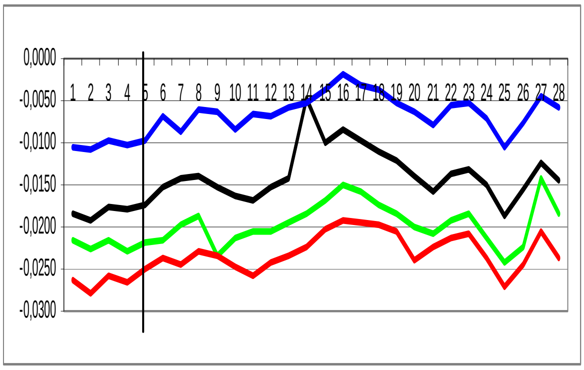
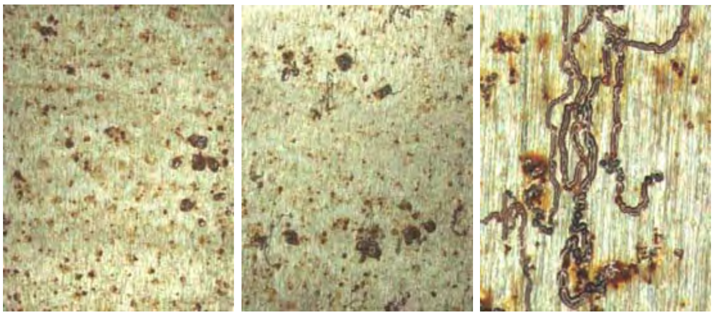
Paraloid B72® 	 After 14 cycles  After 22 cycles	
PVD coating 	 Initial condition	 After two cycles

Figure 18 Assessment of the behaviour of protection systems applied by HM on artificially aged steel coupons versus unprotected coupons. The monitoring was carried out via visual (macro) and optical (micro) observation and weight loss/gain measurements (on three to four different coupons).

The formation of filiform corrosion on steel coupons protected with Paraloid B72® was also observed by TEI while testing Poligen ES 91009® in comparison to Paraloid B72® as shown on Figure 19 (Siatou *et al.* 2007).



a/ b/ c/

Figure 19 Coating appearance at the end of the accelerated ageing process on artificially aged steel coupons. (a) Poligen ES 91009® (x0.75); (b) Paraloid B72® (x0.75); and (c) detail of (b) (x4).

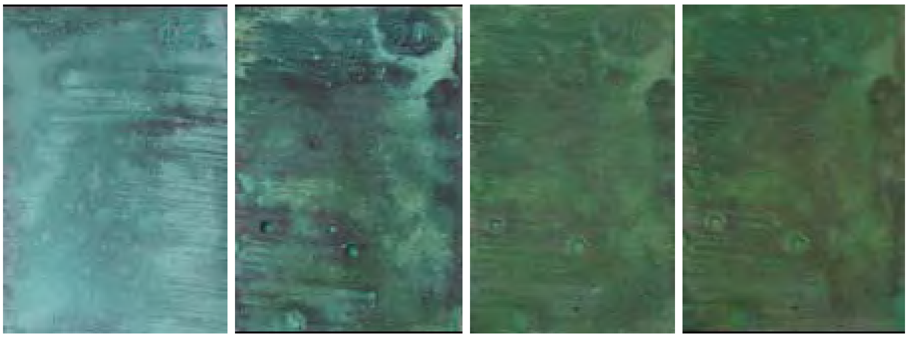
Corrosion stimulators (spraying of the coupons with NaCl before application of the protection systems) modified strongly the behaviour of the coatings tested by HM on steel coupons. Visual observation clearly showed the corrosion progress. Furthermore new forms of corrosion developed almost instantly and typical active corrosion appeared (orange droplets, weeping phenomenon). No protection system tested showed any efficiency except polyurethane varnish. The layer was so thick though that it was not representative of the behaviour in normal conditions. Weight changes were recorded for all protection systems.

1.5.4.1.a-2. *Bronze coupons*

Testing of CIs developed by LRMH (NaC_7 and NaC_{10}) showed that NaC_{10} (concentrations above 0.01M) performed the best.

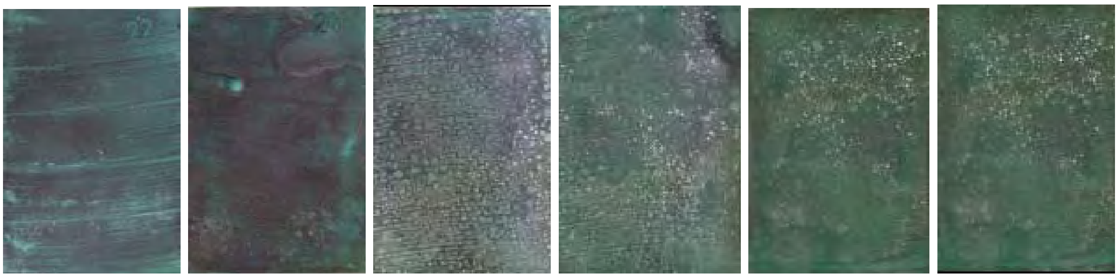
As regards coatings, Poligen ES 91009® with or without CI additives applied on thoroughly cleaned bronze coupons (to remove the loose corrosion products that would otherwise provoke cracking and exfoliation problems) showed no sign of damage. Only an increase of the luminosity of all coatings after exposure could be observed (Siatou *et al.* 2007).

The effect of aggressive pollutants such as SO_2 in combination with chloride salts during the wet/dry cycles had a strong effect on the efficiency of silane A on bronze coupons as shown on Figure 20. Without chloride contamination, silane A performed quite well after ten cycles (Figure 20a), but with chlorides the alteration of the protection system occurred after the first cycle (Figure 20b).



0 + silane A 5 10

a/



0 + silane A 1 3 5 10

b/

Figure 20 Surface appearance of artificially aged bronze coupons without (a) and with chloride contamination (b), covered with silane A and exposed during several dry/wet cycles in presence of SO_2 gas (8h at 40°C, RH 100% and 30 mL SO_2 gaseous pollution (ca 8 vol. %) followed by 16h at laboratory conditions - 60% RH and 20°C).

Additional testing was carried out by RSS following ASTM B117 (exposure during 96h to a salty (NaCl 5% w/v) atmosphere of 49% RH and 35°C) on clean bronze coupons covered with Paraloid B72®, Paraloid B72® + M109, silane A and FPTS. They showed that the best results were obtained for the coupons protected with silane A and FPTS.

1.5.4.1. a-*3. Silver-based coupons*

Only coatings were tested on silver-based alloys. When comparing the efficiency of traditional protection systems such as Paraloid B72®, polyvinyl acetate (PVA) and cellulose nitrate on silver alloy CNR-92 (Ag 92, Pb 1.5, Cu 6.5), YU-FAA discovered that the former coating performed better at accelerated tarnishing in a sulphur rich atmosphere. On pure silver coupons cellulose nitrate failed after seven cycles in the humid chamber when flaking and peeling phenomena occurred. PVA failed after 12 cycles, when blisters appeared on the metal surface. Paraloid B72® did not show visible signs of alteration during the accelerated corrosion test.

Silver coupons protected with nano-alumina pigmented Paraloid B72® and B44® coatings tested by NTUA showed that the protection systems exhibited better protective properties than their plain counterparts and B72 coatings were slightly better than the B44 ones. SEM analysis revealed that after the test exposure, 30% Ag was detected on the plain B72 coated silver coupons, while on the alumina-pigmented B72 ones half of the previous amount of Ag (15%) was obtained. Also, on the plain B44 coated silver sample, 36% Ag and 4% Cu were detected after the test exposure, while on the alumina-pigmented B44 coupons, as for the B72 ones, half of the previous amount of Ag (18 %) was detected. Colour measurements also indicated greater tarnish resistance of B72 coatings (plain and pigmented) than of the B44 ones.

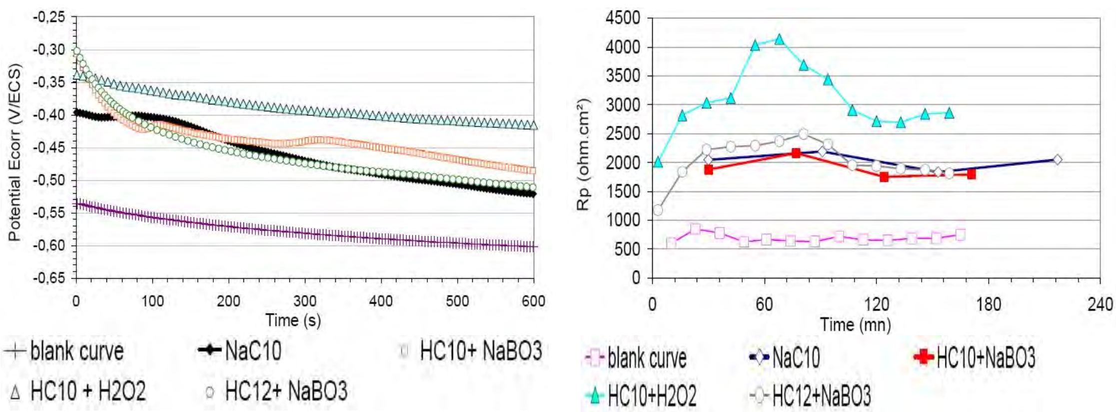
CNR152 (Ag 96.5, Cu 3.5) coupon coated with 1000nm PECVD SiO_2-like film ((HMDSO + O_2 + Ar 40 at 200W) by POLITO showed good protection after immersion in 0.1M Na_2S solution compared to uncoated coupons that tarnished completely after only ten minutes of immersion.

1.5.4.1.b. Electrochemical testing

Electrochemical measurements (Ecorr, Rp (polarisation resistance) and EIS (electrochemical impedance spectroscopy)) were standardised (Letardi 2005, Brostoff 2005 and Hallam 2004) and carried out by some of the partners under the following conditions:

- electrolyte: 0.1 M NaCl or 0.35 (%w/v) $(NH_4)_2SO_4$ + 0.05 (%w/v) NaCl;
- equilibrium time (time elapsed before the measurement start): 1 hour;
- reference electrode used: Ag/AgCl or saturated Calomel Electrode (SCE);
- counter electrode: platinum mesh or graphite rods (as large as possible);
- measurement conditions: Rp, EIS: 10 mV around Ecorr, measurements in the range of 100Khz-10mHz (or at least 40 Khz-60 mHz).

LRMH performed preliminary work on non PROMET coupons to assess the efficiency of the CIs developed (sodium carboxylates and carboxylatation solution) in comparison with traditional protection systems for iron such as tannin and phosphate solutions in an ASTM corrosion solution. This preliminary work was followed by electrochemical measurements of the new protection systems applied to the PROMET artificially aged coupons. The latter behaved the best during the accelerated ageing tests (Hollner *et al.* 2007a). Plots of Ecorr vs time are given in Figure 21a. The best results were obtained for the HC_{10} + H_2O_2 system as is shown by the Ecorr values. Rp measurements confirmed this result since they were much higher than those concerning the unprotected steel coupon and treatment with other carboxylatation solution or 0.25M NaC_{10} (Figure 21b). The Rp values decreased after 60-80 minutes because of the high corrosivity of the electrolyte used.



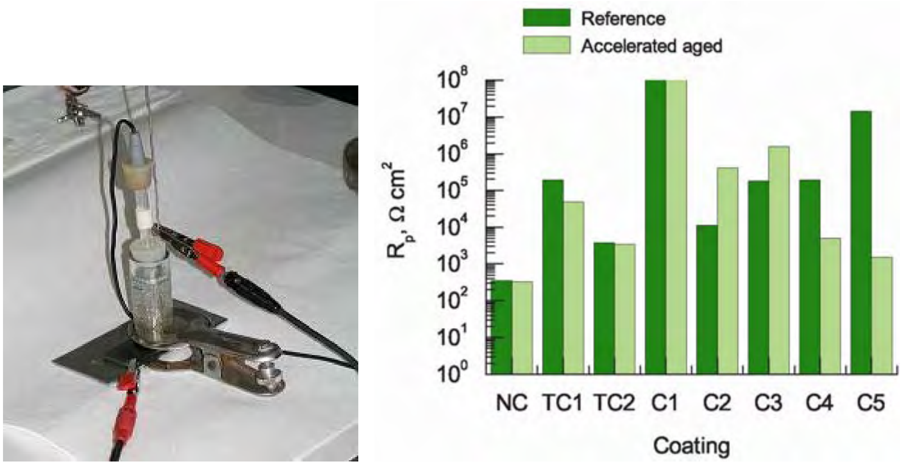
a/ b/

Figure 21 Ecorr (a) and Rp (b) vs time plots for artificially aged steel coupons treated in 0.25M NaC_{10} and carboxylatation solution in 0.1M NaCl.

IBN-DC was testing the OTH CI on artificially aged bronze coupons in 0.5M NaCl (to simulate more local conditions (exposure to marine salts) Hammouch *et al.* 2007a). The high frequencies loop increased after 72h of immersion. The capacity value associated with high frequencies loop was C=0.2uF/cm^2 (312h of immersion) and could be attributed to the establishment of a thick protective film.

POLITO carried out EIS measurements on coatings applied on clean coupons tested by HM. They confirmed the results already obtained by accelerated corrosion testing: polyurethane varnish was the most protective (due to its thickness) followed by Paraloid B72®, Renaissance wax® and PVD.

CSIC performed Rp measurements on coatings tested by TEI, both on cleaned and artificially aged iron coupons (Figure 22a, Cano *et al.* 2007, Argyropoulos *et al.* 2007a) or artificially aged bronze coupons. The results of the artificially aged iron coupons presented in Figure 22b indicate that the best protection was provided by Poligen ES 91009® without CI additives (C1). Slightly different results were obtained on cleaned iron coupons where Poligen ES 91009® coating with CI additives behaved the best (Argyropoulos *et al.* 2007a).



a/ b/

Figure 22 (a) Electrochemical device used by CSIC to measure Rp on artificially aged steel coupons unprotected (NC), protected with 15% Paraloid B72® in acetone (TC1), Renaissance wax® (TC2), Poligen ES 91009® (C1), Poligen ES 91009® with CI additives (C2 (M370) & C3 (M435)) and Paraloid B72® with CI additives (C4 (Alkaterge T) & C5 (M109); (b) results in 0.1 M NaCl (electrolyte N) for both the reference artificially aged steel coupons and the accelerated aged coupons exposed to the climatic chamber before electrochemical testing was carried out.

Electrochemical impedance spectroscopy measurements carried out on silver alloy coupons covered with nano-alumina pigmented Paraloid B72® coatings showed that they offered a better protective behaviour than nano-alumina pigmented B44 coatings. Also, both of these coatings were more effective than their plain counterparts. Tested coatings offered better protection on clean silver than on the Ag_2S and AgCl aged silver surface. It should be taken into account that, when the corrosion layers contain chlorides, the cleaning process should be carefully applied, in order to remove all chloride corrosion products. It should then be followed by a coating, which would properly isolate and seal the metal surface from any contact with air and moisture. It is assumed that the pigment enhances the protective ability of the acrylic vehicle and probably prevents the metal ions diffusion to the solid/gas interface.

1.5.4.1.c. Preliminary conclusion

Considering that the conditions of the fabrication and surface preparation of the artificially aged coupons were the same, the comparison of performance results of protection systems (innovative or/and traditional) tested on them by the different partners gave the opportunity to draw some preliminary conclusions:

- Paraloid B72® provoked filiform corrosion on artificially aged coupons.

- Microcrystalline wax failed on artificially aged steel coupons after some time of exposure.
- Corrosion stimulators (chlorides and pollutants such as SO_2) usually decreased the efficiency of protection systems and should be removed from the metal surface or the local environment.

As regards innovative protection systems, a pre-selection of compounds that behaved the best could be made so that they would afterwards be tested on coupons aged naturally, representing better the real conditions of exposure of objects (Table 5).

Metal alloy	**Protection system type**	**Protection system**	**Tested by**	**Application**
Steel	CI	NaC_{10}	ALP-ME	immersion
	CI	OTH	ALP-ME, IBN-DC	Brush
	CI	FPTS	IBN-DC	Brush
	CI	Carboxylatation solution	HM, IBN-DC, ALP-ME	immersion
	Coating	Poligen ES 91009®	TEI, HM	Brush
	Coating	Poligen ES 91009® + M370	TEI	Brush
	Coating	PVD	HM	
Bronze	CI	NaC_7	SVUOM, ALP-ME	immersion
	CI	NaC_{10}	IBN-DC, ALP-ME, SVUOM	immersion
	CI	FPTS	RSS	Brush
	CI	FPTS	IBN-DC, ALP-ME	immersion
	CI	Bitriazoles	IBN-DC	immersion
	Coating	Poligen ES 91009® + M370	TEI, NILES	Brush
	Coating	Paraloid B72® + M435	TEI, NILES	Brush
	Coating	Paraloid B72® + M109	TEI, NILES, RSS	Brush
	Coating	Silane A	SVUOM, RSS	Brush
Silver	Coating	Silane A	YU-FAA	Brush
	Coating	nano-alumina pigmented Paraloid B72® (and B44)	NTUA	Brush
	Coating	PECVD	POLITO	

Table 5 Pre-selection of protection systems that performed the best during the accelerated corrosion tests.

The conditions of application (fitting normal practice in the conservation field) of these protection systems are given in Table 6. In all cases the surface of the metal should be cleaned from dust with a soft brush and then with a cotton swab impregnated with ethanol or acetone (use talc free gloves).

Protection system	**Composition**	**Conditions of application**
Paraloid B72® or B44	15% (w/v) in acetone (or in toluene (NTUA)	1. Application by brush: from the backside first; two applications one criss and one cross are performed, forming thus a double criss-cross film Drying time: 3h of drying in between and

		24h at the end; the same on the other side.
Paraloid B72® + M435	15% (w/v) in acetone + 1.5 % wt M435. Addition of the CI, stirring until dilution	1. same as above
Paraloid B72® + M109	15% (w/v) in acetone + 1.5% wt M109. Addition of the CI, stirring until dilution. The addition of M109 to Paraloid® B72 made the coating easier to apply (maybe less viscous) and the brush strokes were not so apparent.	1. same as above
Poligen ES 91009 ®	Used as supplied (pH approx 8-9)	2. Pouring of a small quantity of Poligen ES 91009® in beaker and covering it with a glass to avoid evaporation. Leaving it for one minute so that the bubbles created from pouring the liquid in the beaker disappear. -immersion of the soft brush inside the beaker and drying off the excess liquid by pressing the edge of the brush on the beaker. Avoid any excess of Poligen ES 91009® on the brush. -application of the liquid on the coupon in a criss-cross format/ one brush immersion is enough for one side of the coupon. Setting time: the coating sets after 2-3h depending on the atmospheric conditions, during the first 20 minutes it is fluid enough to work it with a brush. Drying time: 24h of drying on each side before applying the second layer.
Poligen ES 91009 ® + M370	1 part of CI to 40 parts of coating. Addition of the CI, stirring until dilution	2. same as above
Poligen ES 91009 ® + M435	1.5% wt M435 Addition of the CI, stirring until dilution	2. same as above
Carboxylatation solution	- Decanoïc acid HC_{10} (30g/L) in distilled water 50% + ethanol 50% - Oxidising agent H_2O_2 or $NaBO_3$ (0.1M)	3. By immersion (3h), or by brush or spray (in these cases repeat the application several times). No rinsing afterwards.
NaC_7	Sodium heptanoate : 0.1M, i.e. - Heptanoïc acid (HC_7) : 13g/L in distilled water - Sodium hydroxide (NaOH): 4g/L (0.1M)	4. By immersion (3h for copper-based alloys). No rinsing afterwards.
NaC_{10}	Sodium decanoate : 0.1M, i.e. - Decanoïc acid (HC_{10}) : 17.2g/L in distilled water	5. By immersion (4h for iron-based objects and 3h for copper-based ones). No rinsing afterwards. NaC_{10} can induce

	- Sodium hydroxide (NaOH): 4g/L (0.1M)	the formation of a thin white film composed of metallic soaps. It should disappear during the ageing test.
OTH	-1g natural extract from the cactus seeds (visqueous) -1g triethanolamine (visqueous) -0.1g KOH (pellets)	6. two methods of application: - Immersion in a 0.02% (w/v) OTH/Ethanol solution for 1h - by brush: OTH (pure) directly on the metal surface (more effective method) Drying time: 48h
FPTS	-1M PTS (visqueous) -1M Triethanolamine (visqueous) -1M KOH	7. two methods of application: -immersion in a 0.075% (w/v) FPTS / absolute ethanol solution for 3h -by brush: 50% (w/v) FPTS / absolute ethanol solution Drying time: dry after immersion and 48h after application by brush
Bitriazole	Pure product manufactured in laboratory $C_4N_6H_4$, 10^{-3}M	8. Immersion of 3h in 0.001M solution BiTA + ethanol
Silane A	A mixture of 5 vol% of γ-Mercaptopropyltrimethoxysilane + 2 vol % of bis(trimethoxysilylypropyl)amine + 1 vol % of hydrated tetraethoxy silane in 92 vol% ethanol	9. Stirring the mixture for a few minutes. Application by brush (one application one criss and one cross carried out). Drying time: 24 h in laboratory conditions
Nano-alumina pigmented Paraloid B72® (and B44)	2% and 10% (w/) nanopowder aluminium oxide Al_2O_3 mixed with 15% (w/v) Paraloid B72® (or B44) solution in toluene	10. Nano-powder Al_2O_3 added and stirred until dilution in toluene. Stirring for an hour with a magnetic stirrer. Addition of Paraloid granules (milky suspension formed). Application by brush.
PVD	TiO_2	11. same as described in section 7.3.3.1 on coupons rinsed in dichloromethane solvent (for a few seconds)
PECVD	SiO_2	12. same as described in section 7.3.3.1

Table 6 Conditions of application of the best ranked protection systems to be assessed by long-term testing.

1.5.4.2 Long-term Testing

The objective of the long-term testing was to assess further the most effective coatings and CIs from the short-term testing (presented in Table 6 above) on naturally aged metal coupons exposed at museum sites chosen by the partners (the same as given in Table 1 except for TEI, where the rack with steel coupons was exposed in the exhibition room, also used as a storage area, of the museum of Criminology, and for ALP-ME, where the racks were installed in the basement of the Aleppo museum, the objective in both cases being to expose the coupons to a more aggressive environment than for the short-term testing).

Each partner testing protection systems (PS tested) on steel and bronze coupons chose three protection systems among those of Table 6 to assess along with a standard protection system (SPS) commonly used in conservation (Paraloid B72® 15% w/v in acetone) as well as unprotected coupons (UP). Paraloid B72® was applied by HM to all steel coupons and by TEI to all bronze coupons after their mechanical cleaning.

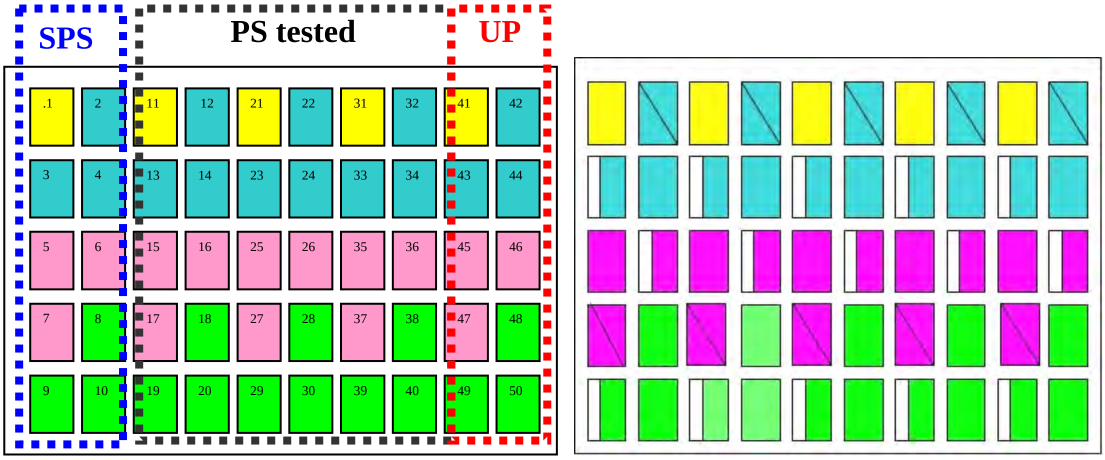
Figure 23 Application of Poligen ES 91009® on the steel coupons by brushing.

All other protection systems were applied either by professional C-Rs (Poligen ES 91009®, Figure 7.26) or the partners that developed the systems (LRMH, IBN-DC, SVUOM and DMME). At this stage, the different protection systems under testing were further examined to determine their thickness when possible (Laser Induced Breakdown Spectroscopy depth profiling (Pouli *et al.* 2005), eddy currents methods, etc.) on the reference coupons (not pre-corroded). Obviously coatings were found thicker than films formed with CIs for which thickness could not be determined.

Partners testing protection systems on silver-based coupons (NTUA, YU-FAA) also considered Paraloid B72® as a standard protection system.

1.5.4.2.a. <u>Conditions of exposure</u>

Protected steel and bronze coupons were exposed on the same rack as the one used for natural ageing of the coupons. The distribution of the protection systems on the rack is given in Figure 24. Each protection system was tested on ten coupons: one reference (in yellow on Figure 24a), three coupons pre-corroded on site for three months (in blue), three to six months (in pink) and three to 12 months (in green). Originally the coupons were planned to be documented on a regular basis (every 15 days in the best case or when they were removed in the worst) and removed following the protocol established for the preparation of the naturally aged coupons: the reference coupon would be kept stored in a silica-gel desiccated box (RH <10%) for the whole period of exposure, three coupons pre-corroded for three months and covered with PS tested (+ PST) would be removed after three months of exposure, three coupons pre-corroded for six months + PST would be removed after six months of exposure and three coupons pre-corroded for 12 months + PST would be exposed for 12 months.



a/ b/

Figure 24 (a) Distribution of the naturally aged coupons with the protection systems tested in real conditions (on-site); (b) Modified protocol of removal of the coupons used by HM.

This protocol was followed by most partners but some (HM) modified the protocol for the following reasons:

- some of the protection systems did not fail after three-month exposure. It was decided then not to remove all three coupons for each protection system. The same happened after six months. An additional nine-month observation interval was added since the last months of exposure were considered critical for corrosion development;
- it seemed important to examine whether the level of alteration of the metal surface (slightly pre-corroded, medium and heavily pre-corroded surfaces) would influence the efficiency of the protection systems;
- the role of the deposition of dust particles in protection system failure had to be clarified.

The new coupon removal protocol is illustrated in Figure 24b. One of the three coupons pre-corroded for three months was removed after three months of exposure and stored over silica-gel (RH <10%) while the other two coupons were placed back on the rack. One of the two was half cleaned[1] (the left side of each coupon) from dust deposits at three, six and nine month intervals. The other coupon was left unaltered. The same procedure was followed for coupons pre-corroded for six and 12 months. Coupons removed from the rack during the exposure period were stored in a dry environment (silica-gel containing box (RH <10%)) and photographed with all the other coupons after three, six, nine and 11 months. All coupons were finally removed after 11 months of exposure. Additional examination (SEM-EDS investigation) of all coupons was carried out by some partners at that stage.

Protected silver-based coupons were also exposed on the same rack as the one considered for natural ageing. Since only a few coupons were available, the reproducibility of the results could not be checked.

1.5.4.2.b. <u>Monitoring</u>

A thorough monitoring of the coupons was required to determine the effectiveness of the protection systems at both macroscopic and microscopic levels. Some partners (NTUA and YU-FAA) weighed the coupons before and after the testing period to determine any corrosion progress. Also, all partners recorded RH and T throughout the exposure period and some

[1] Cleaning was carried out with an oil-free air compressor. Dust particles were blown off systematically from one side of the coupon while the other side was protected. The cleaning process was carried out only on the front side of the coupons (exposed to dust deposition).

partners the level of pollutants (using passive tubes for SO_2, NO_2, O_3 and H_2S (for silver alloys) or active sampling) and particle deposits as well.

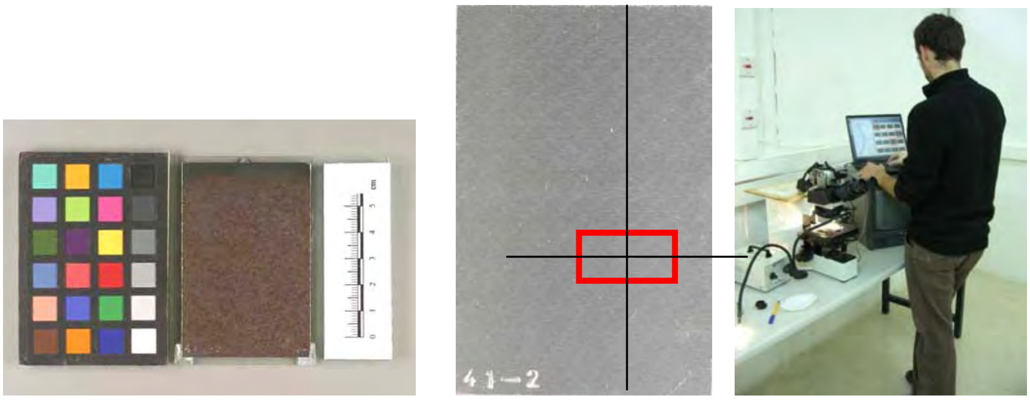
1.5.4.2.b-1. *Photographing and recording coupon changes*

The photographing of the coupons on the rack by HM is shown on Figure 25 The position of the passive tubes is also indicated.

Figure 25 Shooting of the coupons on the rack at the beginning of the exposure period, Palace Armoury, Valletta. Note the presence of the passive tubes on the right of the rack for pollutants analysis.

Monitoring of the coupons during the exposure period was carried out by HM team via standardised photography sessions of the coupons at three, six, nine and 11-month periods. Following photography and visual observation, coupons were placed back on the rack in accordance with Figure 26b. Standard reproducible studio conditions were used. Once again two categories of photographs were taken:

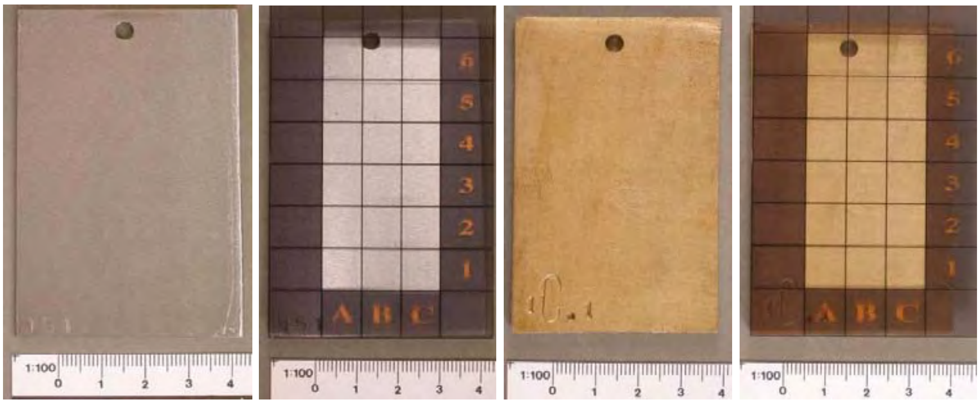
- Macro-photography (Figure 26a)
- Micro-photography (Figure 26b): micro-photographs were carried out at three, six and 11-month exposure only. A specific area of the coupon was chosen and photographed through the microscope at roughly the centre of the coupon (Figure 26b).



a/ b/

Figure 26 (a) Coupon photographed under standard reproducible light conditions; (b) Coordinate system for coupon micro-shooting (coupon was photographed at coordinates x=3 and y=2.5) and standard equipment for micro-photography.

TEI set up a different approach based on the fact that the coupons exposed in the museum of Criminology corroded at a slower rate. Observations under optical microscope and macro photographs taken at regular intervals under standard lighting conditions were used to evaluate the performance of the coatings. A mask was used during photographs to describe the areas of the coupons where failure -if any- of the coatings occurred. To avoid edge effects, the outer parts of the coupons were left out (Figure 27). Additionally, colorimetric measurements in predefined areas were carried out using a MICRO COLOR II (LMC 6) colorimeter.



a/ b/ c/ d/

Figure 27 One of the methods used by TEI for the evaluation of protective coatings was macrophotography using a grided mask placed on the steel (a) and bronze (c) coupons that allowed the exclusion of the edges and (b and d) better description of the failure areas.

1.5.4.2.b-2. *Environmental monitoring*

- <u>RH and Temperature</u>

Dataloggers were installed next to the rack and T and RH were monitored during the whole exposure period. Figure 28 presents the corresponding graph for the Palace Armoury with intervals where data are missing.

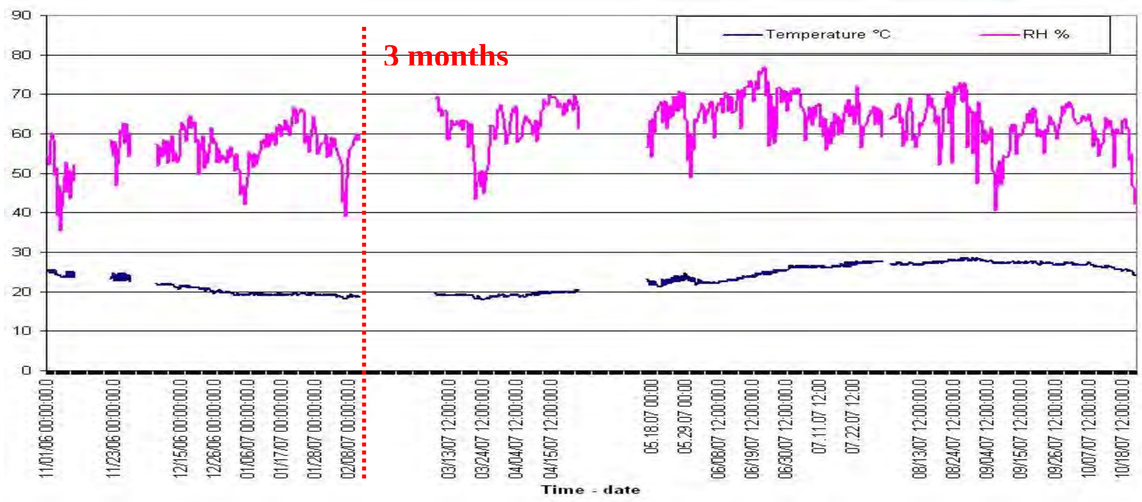
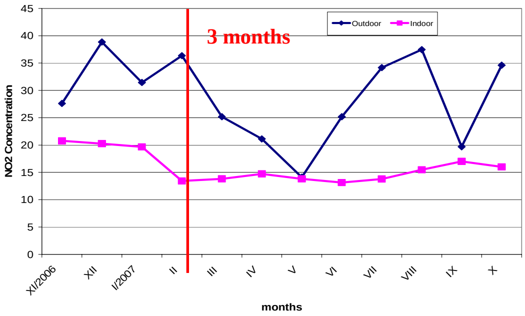


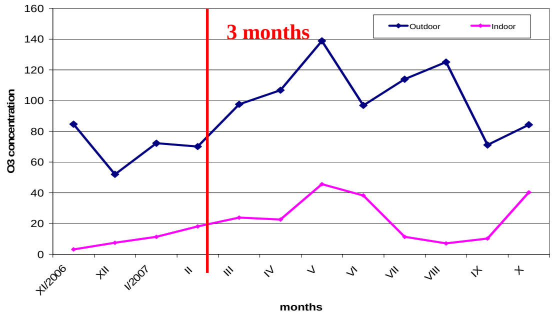
Figure 28 RH and T monitoring at the Palace Armoury, Valletta during the 12 months of exposure.

- <u>Gaseous pollutants</u>

Passive tubes[2] for SO_2, NO_2 and O_3 were considered by HM and SVUOM in addition to H_2S by YU-FAA and NRC-EC. Figure 29 gives the indoor and outdoor monitoring for NO_2 (a) and O_3 (b) at the Palace Armoury, Valletta.

[2] Principle based on the passive diffusion of the gas on an absorbent. During sampling, one of the ends of the tube is open and the other contains the absorbent. The gas molecules diffuse from the area of high concentration





a/ b/

Figure 29 Concentration of NO_2 (a) and O_3 (b) outdoor and indoor the Palace Armoury, Valletta.

A comparison of the indoor pollutant gaseous concentrations against the recommended pollutant levels inside the museum environment was carried out. For the whole period of measurement, NO_2 levels were above the recommended value of 5.03µg/m^3. During the summer months, the indoor level of O_3 would go above the recommended 25µg/m^3 limit. The indoor monthly SO_2 readings were for the most part within range of 1.01µg/m^3. An anomalously high value was recorded in August, when the SO_2 concentration reached 8.65µg/m^3. According to ISO 11844-1, the air pollutions in the Palace Armoury exhibition hall were on different levels (SO_2 – level II, NO_2 – level IV and O_3 - level IV) but were considered as rather corrosive.

Active sampling[3] of pollutants and dust were carried out by the Air Quality Group at Environmental Research Laboratory at DEMO in TEI's case. Two measurements for a one-week period in each museum (Benaki museum and museum of Criminology), one for winter and one for summer time were taken. Daily measurements for a week's interval gave representative results on the pollutant concentrations and their fluctuations (Figure 30).

a/ b/

Figure 30 (a) Active sampling at the museum of Criminology and (b) detail of the equipment used for active sampling of SO_2.

RSS monitored on a seasonal level (and during three hours) SO_2, NO_2 and NH_3 levels using multi gas detector with electrochemical cells. Total volatile organic compounds (TVOC) were determined by photo ionised detection (PID) with a portable gas analyser.

In addition to the monitoring protocols described above the corrosivity of the environment was assessed by SVUOM in the same way as during the natural ageing of the coupons (Knotkova *et al.* 2007). As regards coupons, colour changes as well as weight measurements were carried out. Elemental analysis of the surface was also performed after 12 months of exposure to detect any corrosion developments.

(open end) towards the area of low concentration (absorbent). The one-way flow of gas follows Ficks law, which states that the flow is proportional to the concentration gradient in the tube.

[3] The movement of the gas is forced (using a pumping system) through a collecting device

- <u>Dust particles</u>

Dust particles were studied by HM, TEI, SVUOM and YU-FAA. In the depositary of the National museum of Prague, the amount of dust particles deposited on the coupons was measured and found negligible to perform detailed evaluation. In the case of HM, intermittent (0-3 months, 3-6 months, 6-9 months and 9-12 months) and cumulative (0-3 months, 0-6 months, 0-9 months and 0-12 months) sampling were carried out using a Perspex support with dust collector tapes. Following dust collection, the samples were examined under SEM-EDS. Table 7 presents the results of elemental analysis. The composition of particles deposited throughout the year suggests that they are mainly constituted of calcium, silicon and chlorine. Calcium comes from calcium carbonate (limestone dust), silicon from alumino-silicates (clays), while the presence of chloride is due to marine salts.

	Point 1		Point 2		Point 3	
Major/minor elements	M	m	M	M	M	m
I 0-3	Ca	S, Cl	Ca, Si, Mg	Ti	Si, Ca, Mg - Cl	Cl
I 3-6	Ca	Si	Ca	Si	Ca, Si	
I 6-9	Ca, Si		Ca, Si	Mn, Cl	Ca, Si – Cl, S	Cl, S
I 9-12	Si, Al	Ca	Ca	Fe, Si, Cl	Cl, Ca, S	
C 0-3	Ca	S, Cl	Ca, Si, Mg	Ti,	Si, Ca, Mg - Cl	Cl
C 0-6	Ca		Ca, Si	S, Mg, Fe	Ca, Cl	
C 0-9	Ca, Cl		Ca, Si	Cl, Mg	Ca, Cl, Si	
C 0- 12	Ca, Si, Cl, K		Ca, Si, Mg	Cl, Fe	Ca, S, Al – Mg, Fe	Mg, Fe

Table 7 Major (M) and minor (m) elements analysed on three particles selected randomly from intermittent (I) and cumulative (C) sampling tapes.

1.5.4.2.c. <u>Progression of the corrosion on the coupons</u>

1.5.4.2.c-1. *Steel coupons*

Each set of coupon photographs (photographed at progressively increasing periods of time) taken by HM team were compared using Canon Utilities Zoom Browser EX 4.5, Version 4.5.1.148 software to detect slight surface modification. Figures 31 and 32 present the results obtained on non-protected coupons, coupons treated with carboxylatation solution, protected with Paraloid B72® and Poligen ES 91009®. Only coupons pre-corroded during a three-month period and half cleaned at regular intervals are considered here to visualise better the alteration of the metal surface during the 11months exposure time and see the possible effect of dust particles on the failure of the protection systems.

The results obtained at macro-level were confirmed at micro-level. Observations at a micro-level were considered useful particularly when new forms of corrosion were developing (filiform corrosion). Nevertheless, the microscopic observation is time consuming if all areas of the coupon are surveyed. By choosing to monitor only one area systematically, there was the possibility to miss some important new forms of corrosion that develop elsewhere. Therefore, a quick observation of the surface of the coupons was still required at micro-level in order to photograph areas of interest; the same procedure was carried out on the coupons covered with Paraloid when the formation of filiform corrosion was suspected.

At the end of the monitoring period it appeared that some of the protection systems behaved better than others. In what follows, we highlight some important points about the protection systems tested by HM. The protection of the coupons was definitively required since new localised corrosion developed during the first three months (winter period) on unprotected slightly pre-corroded coupons (Figure 31). New overall corrosion developed between three and six months (spring time). During that period, the indoor RH and O_3 levels increased. New corrosion seemed to develop faster when the metal surface had a higher coverage of pre-corroded areas.

PVD coating did not offer any protection. There was no improvement of the corrosion progress during the first three months of site exposure on slightly pre-corroded coupons and beyond three months the new forms of corrosion developed much faster with zones of active corrosion. The new corrosion forms progressed slower (patchy areas) with a higher coverage of pre-corroded areas. The back of the coupons was affected by new corrosion faster than in the case of other protection systems.

The corrosion inhibition provided by carboxylatation solution appeared quite promising. Although similarly to the unprotected coupons new localised corrosion developed during the first three months on slightly pre-corroded coupons, overall corrosion was clearly retarded for a few months (Figure 32a). Furthermore, corrosion on coupons developed slower when the metal surface was more corroded with a higher coverage of pre-corroded areas.

Poligen ES 91009® gave the best results. The metal surface remained more or less the same after application of the coating whatever the degree of pre-corrosion (Figure 32b). Some localised corrosion was observed after 11 months of exposure. However, because of the dust that seemed to be adhered on the surface, macroscopic observation was not often possible to provide a real picture.

Paraloid B72® gave quite satisfactory results, although the film applied seemed to fail on the edges of the coupons (edge effect – Figure 32c). The slightly pre-corroded metal surfaces appeared quite shiny. No new forms of corrosion developed on slightly, moderate or high pre-corroded metal surfaces during the first three months of exposure. Filiform corrosion worms grew from the edges after nine months of exposure on lightly pre-corroded coupons and between nine and 12 months exposure period on coupons with a medium and/or high coverage of pre-corroded areas.

The role of dust particles on the corrosion progress was not very clear. It seemed that they had no effect on coupons covered with either Paraloid B72® or Poligen ES 91009®. However, they seemed to accelerate the corrosion progress on unprotected coupons and coupons covered with PVD coating. The unusual behaviour of coupons treated with the carboxylatation solution (more corrosion in the half-cleaned area) might be due to the loss of the protection system during the cleaning process.

The coating testing at the Criminology museum did not show substantial coating failure. The exposure period was not enough to show significant changes or failure patterns among the coatings. Small corrosion patches, most of the times visible under the microscope, were observed in few coupons, but were, nonetheless, trivial. No colour changes were recorded during colour measurements either.

Other partners confirmed the good behaviour of Paraloid B72® at macro-level on steel coupons (IBN-DC for the Rabat Museum) during the whole period of exposure. SEM-EDS examinations showed that FPTS and OTH CIs failed during that time and seemed to be less effective than the treatment with carboxylatation solutions.

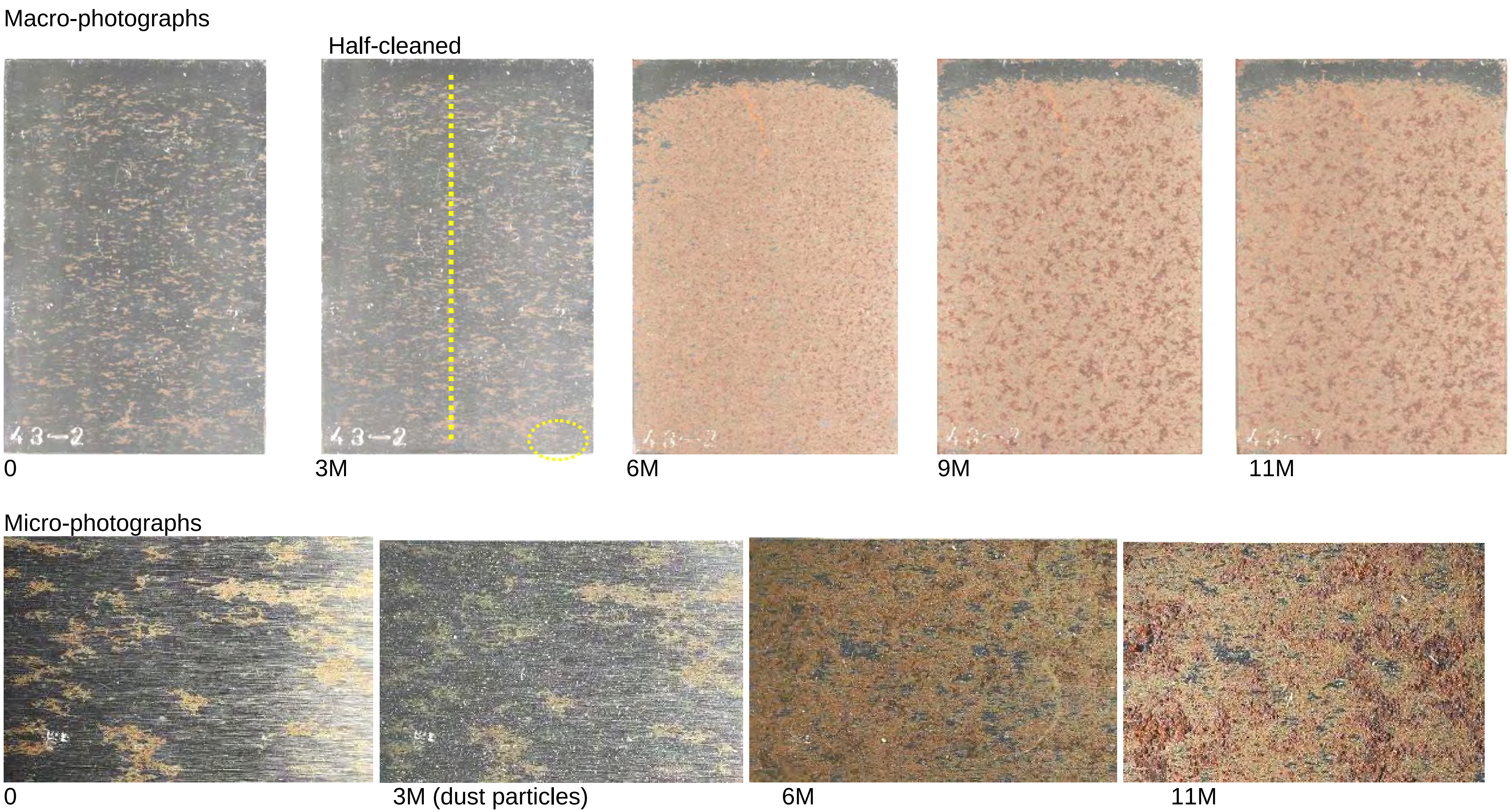


Figure 31 Monitoring with macro and microphotographs of non-protected steel coupon 43 (pre-corroded three months, exposure time: 11 months, half-cleaned (left side) every three-month exposure interval starting at the three-month exposure mark) during long-term ageing.

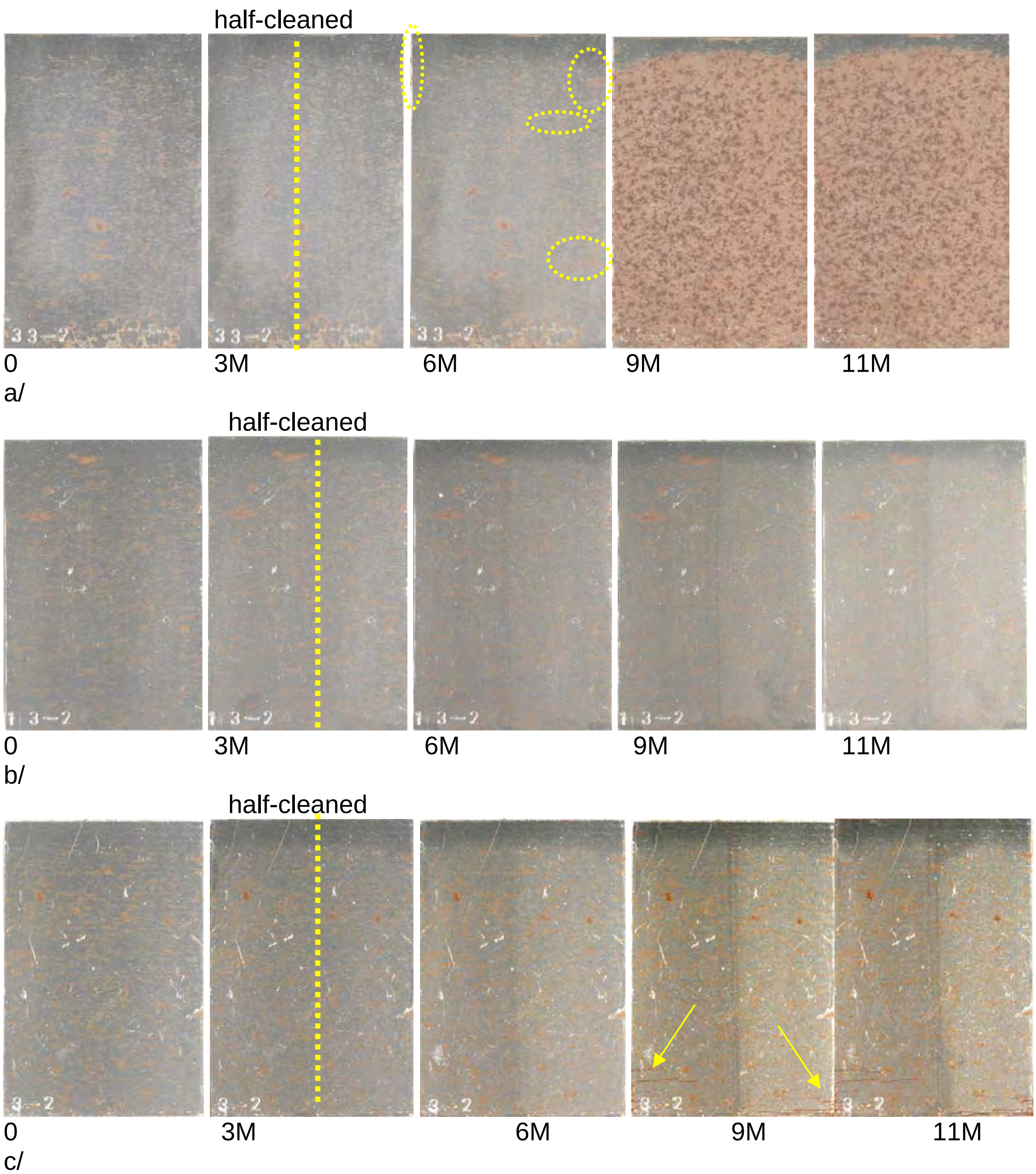


Figure 32 Monitoring with macrophotographs of protected steel coupons after carboxylatation treatment (coupon 33, a), with Poligen ES 91009® wax (coupon 13, b) and Paraloid B72® (coupon 03, c) during long-term ageing. The coupons considered were pre-corroded for three months. Exposure period: 11 months. half-cleaned (left side) at three-month exposure intervals starting at the three-month exposure mark.

1.5.4.2.c-2. *Bronze coupons*

Similarly to the steel coupons, no changes were observed on the bronze coupons of TEI for neither of the coatings applied. Longer exposure periods are necessary to evaluate the coating performance.

Bronze coupons protected with Paraloid B72®, CIs such as FPTS and bitriazoles and exposed by IBN-DC for one year on their rack at Rabat museum behaved well since SEM-EDS examination showed that none of these protection systems failed.

Bronze coupons protected with Paraloid B72®, NaC_7 and NaC_{10} and silane A were exposed for one year by SVUOM in depositary 103 of the National museum, Prague, and were examined every month. Figure 33 shows macrophotographs taken at three-month intervals. Almost no change was observed on the unprotected coupon and the coupon protected with silane A. Dark spots developing at casting pores appeared on the coupon protected with Paraloid B72®. The coupons treated with sodium carboxylates kept the very thin and matte white-grey layer that formed during the application.

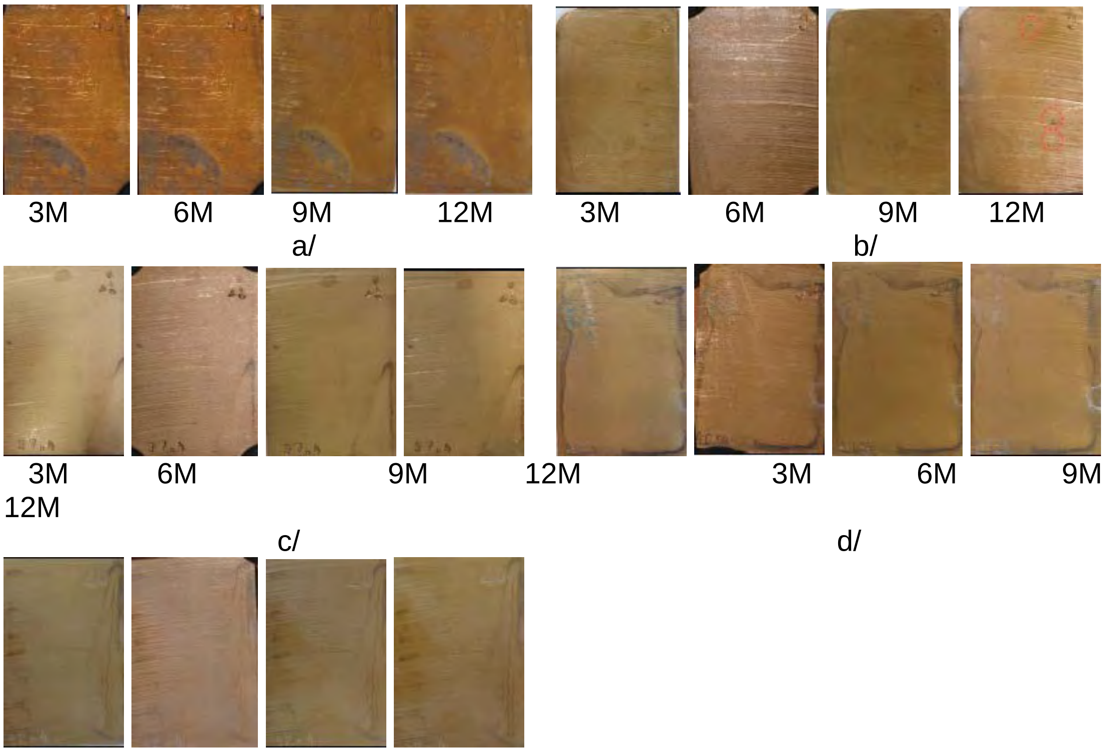


Figure 33 Monitoring with macrophotographs of protected bronze coupons: (a) reference, (b) protected with Paraloid B72®, (c) silane A coating, (d) 0.1M NaC_7 and (e) 0.1M NaC_{10} after three, six, nine and 12 months of exposure in depositary 103 of the National museum, Prague.

Additional examination of the coupons (colour and weight changes, elemental analysis after 12 months) showed more clearly that coupons protected with silane A remained unchanged (apart from the formation of microcracks) compared to those protected with Paraloid B72® or sodium carboxylates, where the aesthetic appearance of the coupons was considered as unacceptable.

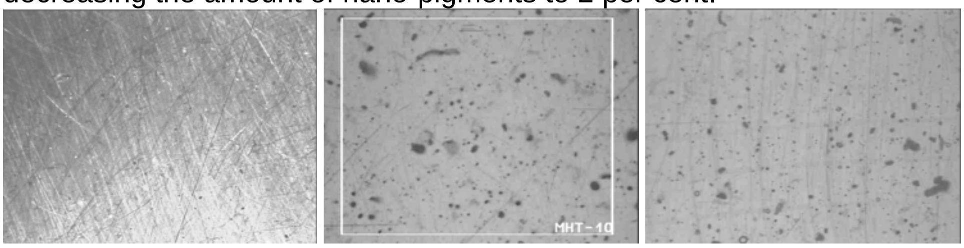
Silane A was also evaluated by RSS at Umm Qais museum in comparison to Paraloid B72® + M109 and FPTS CI. It was found that all protection systems (including Paraloid B72®) darkened during the seasons when the levels of SO_2 and TVOC (total volatile organic compounds) were the highest (autumn and summer). When removing the coupons from the rack, local failure of all protection systems could be observed on the coupons under binocular and SEM at casting pores where high levels of S could be detected by EDS.

However, among all protection systems tested, silane A gave the least darkening and thus seems to be the most protective.

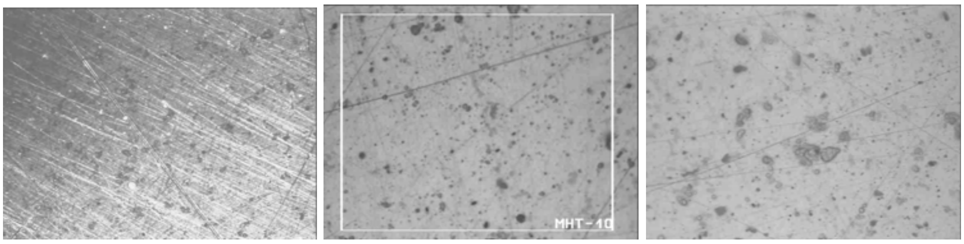
1.5.4.2.c-3. *Silver coupons*

Paraloid B72® and silane A were tested by YU-FAA on different silver alloys coupons at the Museum of Jordanian Heritage, Irbid. Both coatings were 3 to 7µm thick (Eddy currents measurements). None of them failed.

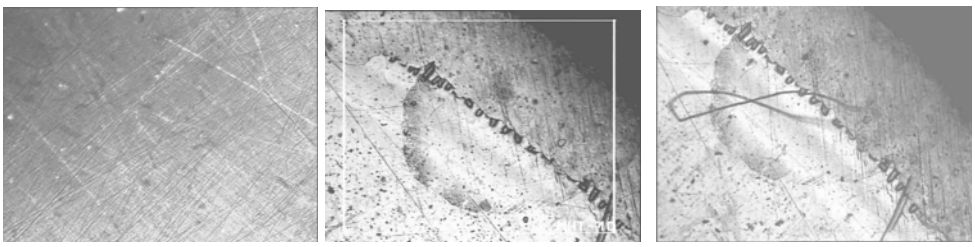
NTUA carried out macrophotographs on naturally aged silver alloy coupons (CNR92, 141 and 152) covered with plain Paraloid B72® or B44® and pigmented with nano-alumina and exposed one year in a showcase at the Technology Museum of Athens (Figure 34). For coupons CNR92, plain Paraloid B72® or pigmented with nano-alumina behaved quite well, although the protective film of the latter seemed to be slightly damaged after one year (Figure 34b). The protection failed though for plain Paraloid B44® (filiform corrosion developed) after six months (Figure 34c) and a little later for the pigmented varnish (Figure 34d). The failure of the protection was not so visible on coupons CNR141 (Ag 92.5%, Cu 7.5 %) and 152 (Ag 96.5%, Cu 3.5%). Several parameters caused the failure: the presence of nano-pigment agglomerates in the film formed, dust particles and the nature of the substrate. From these experiments it appeared that the system 10% Al_2O_3-Paraloid B72 was the most effective in protecting the silver-based alloys tested. Better protection could be obtained by decreasing the amount of nano-pigments to 2 per cent.



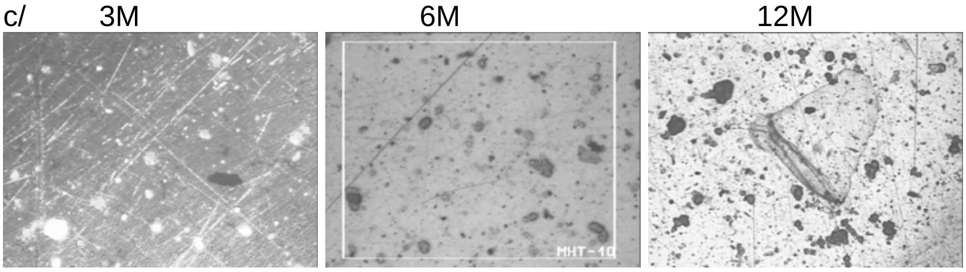
a/ 3M 6M 12M



b/ 3M 6M 12M



c/ 3M 6M 12M



d/ 3M 6M 12M

Figure 34 Monitoring with macrophotographs (x100-x200) of protected naturally aged silver coupons (CNR 92: Ag 92%, Pb 1.5%, Cu 6.5 %) after three, six and 12 months of exposure in a showcase at the Technology museum, Athens. (a): plain Paraloid B72®. (b): 10% nano-alumina pigmented Paraloid B72®. (c): plain Paraloid B44®. (d): 10% nano-alumina pigmented Paraloid B44®.

1.5.4.2.d. Discussion and conclusion of long-term testing

Complementary results to those obtained during short-term testing were obtained by long-term testing on the different protection systems used.

Although Paraloid B72® behaved quite well within the first three to six months, it appeared that beyond this period the acrylic varnish failed in aggressive environments such as in Valletta (MT) on the edges of the coupons. As indicated in the literature (Argyropoulos *et al.* 2007b), filiform corrosion formed then on steel coupons and tended to expand to the whole surface. As shown on tests performed by NTUA, SVUOM and RSS, alteration of the acrylic coatings is also expected on silver and copper alloys coupons. Considering the high risk of edge effects on historic artifacts (armour elements, swords, guns), the damage provoked to the metal surface and the difficulty to renew the varnish on a regular basis (at least once a year), Paraloid B72® alone should not be considered as a possible protection system in Mediterranean countries. Additions of nano-alumina pigments seem to decrease the risk of alteration as observed by NTUA on silver-based coupons but more testing is required to further support these preliminary results.

PVD coatings are still not an option for steel objects since the corrosion resistance offered by this innovative protection system was lower than for all the other systems tested. A lot of research is thus needed to solve problems such as the colour effects and the reversibility of the coating. PECVD coatings gave interesting results on bronze and silver-based alloys. In case the required equipment is locally available, the application of colourless and reversible PECVD coatings may be proposed.

As shown by long-term testing carried out at the Palace Armoury, Valletta and the Archaeological Museum, Rabat, carboxylatation treatment (HC_{10} + H_2O_2 or $NaBO_3$) could be considered as an interesting temporary protection for partly oxidised historic steel objects. This corrosion inhibition treatment seemed to delay the development of corrosion and was more efficient when the metal surface was covered with more pre-corroded areas. However, it would be required to determine more precisely the period of efficiency of the corrosion inhibitor according to the condition state of the metal surface. Our tests showed that on slightly oxidised surface and after nine to 12 months a new application of solution would be needed to maintain the protection of the metal surface. Such "repair" would be impossible with acrylic varnishes and makes carboxylatation solutions a good option for temporary protection of partly oxidised iron-based collections in the Mediterranean region. The fresh protection system is easily removed with alcohol, but its reversibility would need to be confirmed after some months of exposure (three to six months).

Although short-term testing seemed to indicate that the OTH CI could protect well partly oxidised steel surfaces, even when they are active, this protection system appeared less effective than the carboxylatation solution at Rabat museum. FPTS CI was not effective either and NaC_{10} CI, which seemed to be an interesting option during the short-term testing, should be further studied during long-term testing for possible application.

As regards historic bronze objects, FPTS and bitriazoles CIs could be a good solution for temporary protection, but further testing would be required, particularly in S-rich environments. NaC_7 and NaC_{10} CIs behaved well too but the formation of a thin white film when the CIs are applied was considered as aesthetically unacceptable.

Poligen ES 91009® was certainly the most interesting protection system tested for the long-term protection of historic steel objects. It gave sufficient protection during long-term testing and thus confirmed the good results of the short-term testing. However, in order for it to be considered in the future as a possible protection for historic objects, further work is required, especially as regards the role of the CI additives. Indeed the long term chemical stability of Poligen ES 91009® wax alone or with CI additives has to be proved. Furthermore, the removal protocol has to be refined to make the application of these protection systems fully reversible. Indeed the current procedure for Poligen ES 91009® proposed by the supplier (immersion in NaOH solutions) cannot be considered for all metal artifacts (in what follows, we will see that acetone too seems to be effective in removing this protection system).

Poligen ES 91009® alone and with CI additive did not perform well on patinated bronze surfaces due to the non adherence of the protection systems. Silane A too proved to be a good alternative not only for bronze but also for silver-based objects, as shown by SVUOM at the National museum of Prague and YU-FAA at the Museum of Jordanian Heritage, Irbid. Its reversibility is problematic since it can only be achieved in strong alkaline solutions.

1.5.4.3. Testing on real objects

The final testing step was to apply some of the most effective protection systems on real objects. Each partner involved in this task selected protection systems already tested on site on naturally aged coupons and accepted by the persons responsible of the collections. As it was impossible to move real objects from one country to another, only innovative CIs and coatings that could be easily applied by any of the partners had to be considered. Chemicals used to formulate the protection systems were made available to the partners. Poligen ES 91009 ® (with or without corrosion inhibitor additives) was considered for iron-based historic objects (arms and armours) and carboxylatation solutions for slightly to heavily corroded archaeological iron objects. FPTS CI and silane A were considered for historic and archaeological bronze objects. 2% nano-alumina pigmented Paraloid B72® and silane A were chosen for silver-based objects.

Depending on the objects, only one part of their surface or the whole object was covered with the tested protection system. In the first case the other part was protected with a standard protection system (such as Paraloid B72® 15% w/v in acetone) and/or a reference area was left unprotected. In the second case and considering that the group of objects tested had the same composition and were covered with the same corrosion products, each object was covered entirely by one coating / CI tested, so that edge effects or overlapping coatings would be avoided.

Table 8 gives the list of objects selected by the partners and the protection systems applied and Figure 35 shows some of them.

Partners	Object(s) to test	Protection systems tested
TEI	Objects from the Islamic collection of the Benaki museum (bronzes) and knives and bayonets from the museum of Criminology (iron objects)	Paraloid B72® and Poligen ES 91009® with or without CI additives applied by brush
HM	Steel fake armour elements, Palace Armoury, Valletta	Poligen ES 91009® applied by brush
LRMH	Wrought iron anchor chain, steel torpedo and bronze propeller from the Maritime museum of Romainville Fortress, near Paris	0.25M NaC_{10} on bronze / carboxylatation solution (HC_{10} + H_2O_2 and HC_{10} + $NaBO_3$) on iron-based objects, both applied by brush
YU-FAA	Silver Abbasid coins, from the Museum of Jordanian Heritage, Irbid	silane A applied by brush
RSS	Copper-based coins from Umm Qais museum	silane A and FPTS CI applied by brush
POLITO	Roman and Phoenician Punic coins	SiO_2-like layers by PECVD
NTUA	Silver medallions from the Technology museum, Athens	Paraloid B72® + Al_2O_3 nanopigments applied by immersion
CSIC	Iron and copper-based archaeological objects from the Department of Prehistory and Archaeology of the Universidad Autónoma de Madrid	Poligen ES 91009® applied by brush

NRC-EC	Old silver coins and other silver objects dated back to 1916 and 1923 during the period of Sultan Hussien Kamel and King Fouad.	Paraloid B72® + Al_2O_3 nanopigments applied by brush
IBN-DC	2 bronze objects from the Archaeology museum, Rabat	FPTS CI applied by immersion
EGE-PNEA	Bronze and iron objects from Van museum	FPTS and NaC_{10} applied by brush

Table 8 “Real” objects chosen to test the selected innovative protection systems.

Figure 35 Some of the objects selected for final on-site testing of the innovative protection systems.

In what follows, first we consider the protection of historic objects and then move on to consider the protection of archaeological artifacts.

1.5.4.3.a. <u>Historic objects</u>

1.5.4.3.a-1. *Iron-based objects (HM case study): Paraloid B72® versus Poligen ES 91009®*

- <u>Documentation</u>

HM selected three fake gauntlets used in the past in the exhibition hall of the Palace Armoury, Valletta, as decorative ends of the poles employed to hang banners above the windows. These steel surfaces protected in the same way as the real objects had then been exposed to the same environmental conditions (uncontrolled atmosphere). The metal surface was covered with a thick polyurethane varnish that yellowed with time. Extensive filiform corrosion had developed underneath (Figure 36).

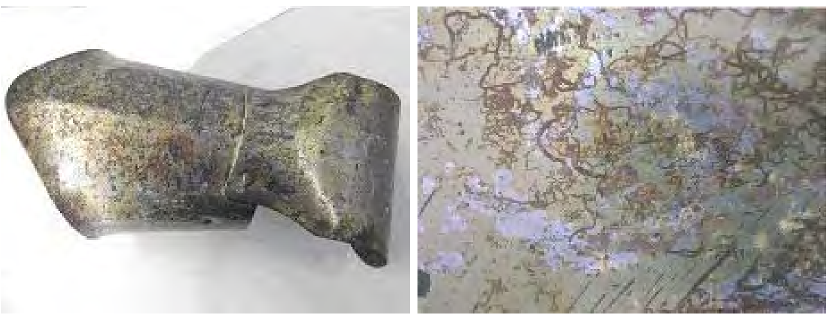


Figure 36 Condition state of one of the three fake gauntlets of the Palace Armoury, Valletta before intervention. Filiform corrosion developed under the polyurethane varnish.

- <u>Cleaning and application of the protection systems</u>

After the removal of varnish (poultices with acetone) and mechanical cleaning of powdery corrosion products, the two protection systems selected were applied by brush (two layers of criss-cross, with 12h of drying in between) on two areas on the end and the arm of each gauntlet as indicated in Figure 37.

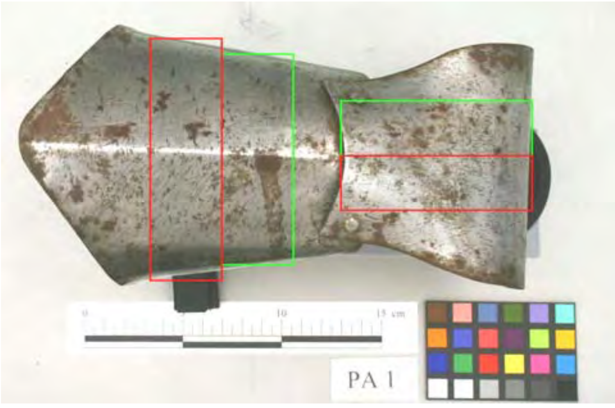


Figure 37 Location on the gauntlets of the zones protected by Poligen ES 91009® (in red) and Paraloid® B72 (in green). Each object was treated in the same way.

- Monitoring

The fake gauntlets were exposed seven months next to the coupon rack at the Palace Armoury, Valletta. The objects were removed periodically (after two, five and seven months) to document any alteration by visual observation and standardised photography (objects photographed on their four sides). Although the period of exposure was shorter than for the long-term ageing tests, we could observe that localised forms of corrosion started developing within two months of exposure in the non protected zones of the three objects. Extensive corrosion was observed after five months as expected on areas where dust particles had deposited. Central zones protected with Paraloid B72® and Poligen ES 91009® seemed to be unaffected (Figure 38). Filiform corrosion was observed though for the three objects on the edges of the areas protected with Paraloid B72® as soon as after five months of exposure (Figure 39). During the same period, Poligen wax remained efficient. Furthermore, dust particles seemed to be more attracted to surfaces protected with Poligen ES 91009® than with Paraloid B72®.

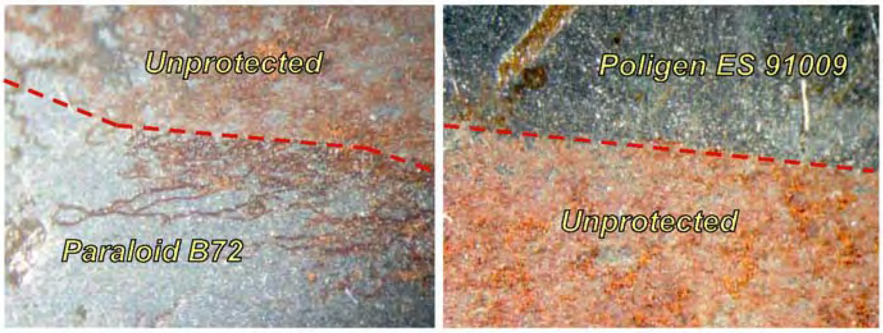

a/


b/


c/


d/

Figure 38 Corrosion progress on one of the fake gauntlets (upper side) from the start of the exposure test (a), after two months (b), five months (c) and seven months (d) of exposure. The same was observed on the two other objects.



a/ b/

Figure 39 Filiform corrosion detected on the edges of the areas protected with Paraloid B72® on the fake gauntlets after seven months of exposure at the Palace Armoury, Valletta (a). No similar failure was observed along the edges of the areas protected with Poligen ES 91009® (b).

1.5.4.3.a-2. *Iron-based object (TEI case study): Paraloid B72® versus Poligen ES 91009® with or without CI additives*

- Documentation

In collaboration with the C-R of the museum of Criminology, 35 objects (bladed weapons) of seven different types were chosen for comparative testing with four different protection systems (Table 9). Another group of seven objects were considered as a reference (not coated).

	Group 1	**Group 2**	**Group 3**	**Group 4**	**Group 5**
Protection system applied	Paraloid B72®	Poligen ES 91009®	Poligen ES 91009® + M370	Poligen ES 91009® + M435	No coating
“Caucasian”-like daggers (type A)	K 153	K 001	K 142	K 402	K138
Knives with a J-shaped handle / small (type B)	K 68	K 168	K 171	K 83	K189
Knives with a J-shaped handle / big (type C)	S 123	K 140	S 124	K 144	K72
“Caucasian” daggers (type D)	K 130	K 49	K 131	K 163	K158
“Caucasian”-like daggers (type E)	K 155	K 147	K 96	K 160	K 56
Small bayonets (type F)	B 109	B 86	B 75	B 92	B93
Big bayonets (type G)	B 95	B 89	B 98	B 217	B78

Table 9 Description of the different types of iron-based weapons from the museum of Criminology, Athens, with their respective protection systems tested.

Corrosion of the metal in the form of rust spots due to coating failure was in the past observed on several of the above mentioned objects. These objects were coated with Paraloid B72® (5 per cent in acetone) and Renaissance wax®, or oils alone. These rust spots appeared in a very short time period, namely in three months (Argyropoulos *et al.* 2005). SEM-EDX analyses on both the blades and handles revealed that the blades are made of steel alloys with a small percentage of carbon and manganese, whereas the handles are made of brass (copper-zinc alloy) and the joining material is a mixture of lead and tin. Regarding the corrosion products, large amounts of oxygen combined with calcium, silicon, sulphur and chlorine were detected both on the handles and the blades. Further XRF examination was carried out on clean areas of three knives that were taken to NCSRD laboratory and the analyses revealed that the metal of the bayonets was much purer than handmade knives that contained a lot of impurities. Similarly additional FTIR analyses on corrosion products found inside the engravings indicated that they were constituted of the following compounds: hematite (Fe_2O_3), calcium carbonate ($CaCO_3$) and Fe(III) oxy-hydroxides.

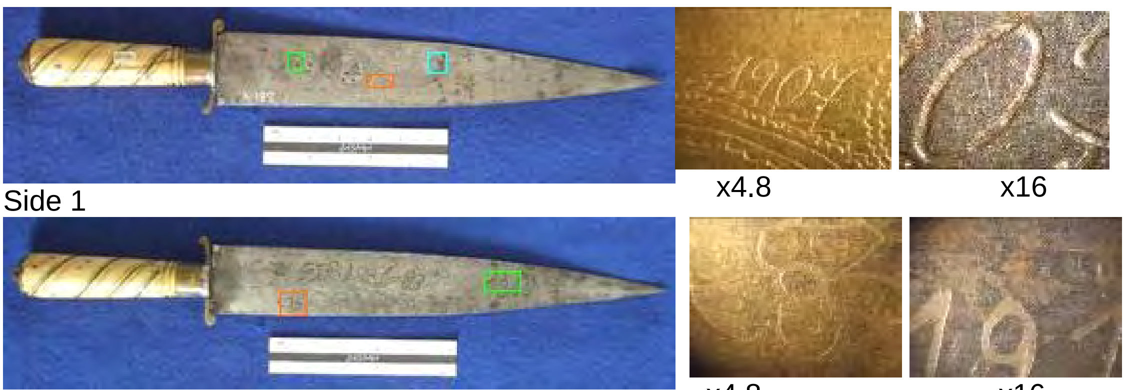
- Cleaning and application of the protection systems

Removal of the old coating with cotton swabs impregnated in acetone was the first action taken for these objects. No rust spot had appeared on any of these objects; however, the cleaning level was found to be insufficient. Re-cleaning by mechanical means to remove loose corrosion products was then carried out. The objects were again degreased by cotton swabs impregnated in acetone. All protection systems listed in Table 9 were applied by brush following the protocol given in Table 7.6. Two layers were applied (a different brush was used for each different coating). The second layer was applied after complete drying of the first layer (24h).

- Monitoring

Characteristic areas on each object were selected for monitoring any development of new corrosion processes. They were either engraved features of the objects or existing corrosion spots where it was assumed that further corrosion would be more likely to evolve. These areas were photographed using a digital camera adjusted on the ocular lens of the microscope. All objects were placed in the same showcase in the uncontrolled atmosphere of the museum.

After three months of exposure, no sign of coating failure, formation of corrosion on the iron alloys or any kind of degradation phenomena was visible on the coated knives, even in the case of Paraloid B72® (15 per cent in acetone), enhancing the assumption that previous coating failure was due to the very thin layer of the coating used or imperfect cleaning of the metal surface. Figure 40 shows the two sides of one of the knives with detailed photographs. No conclusion could be made during this short period of exposure on the benefit of adding CI additives to Poligen ES 91009® wax.



Side 1 x4.8 x16

Side 2 x4.8 x16

Figure 40 Surface appearance of knife K142 (group 3 – type A) with the blade protected with Poligen ES 91009® + M370 after three months of exposure at the museum of Criminology.

1.5.4.3.a-3. *Iron-based objects (LRMH case study): effect of the oxidising agent on the efficiency of the carboxylatation solutions*

- <u>Documentation</u>

The wrought iron anchor chain and the steel torpedo considered were stored in a boathouse within the Maritime museum of Romainville Fortress, near Paris. The environmental conditions were uncontrolled with fluctuations of RH and T on a daily basis (around 40 per cent). The metal surfaces were heavily oxidised (Figure 41).

a/ b/

Figure 41 Wrought iron chain (a) and steel torpedo (b) stored in a boathouse within the Maritime museum of Romainville Fortress, near Paris.

- <u>Cleaning and application of the protection systems</u>

Local chemical cleaning with nitric acid was carried out to approximate the metal surface of PROMET coupons. The carboxylatation solutions were applied by brush. To assess the effect of the oxidising agent in real conditions, the following solutions were considered:

Chain: HC_{10} (30g/L) + H_2O_2 (0.1M)
Torpedo: HC_{10} (30g/L) + $NaBO_3$ (0.1M)

Only half of the cleaned surface was treated with the carboxylatation solutions (green and blue squares on Figure 42).

a/ b/

Figure 42 Conditions of the chain element (a) and torpedo (b) surface after chemical cleaning and application of the carboxylatation solutions.

- <u>Monitoring</u>

A control of the surface aspect was carried out each month to evaluate the efficiency of the protection systems tested in this task.

Figure 43 Corrosion progress on the chain element surface after 1.5 (left) and 9 months (right) of exposure in the storage area of the Maritime museum of Romainville Fortress.

The efficiency of the carboxylatation treatment on iron-based surfaces was clearly demonstrated (Figure 44). After one and a half month of exposure in uncontrolled environmental conditions only the unprotected zones that had been pre-cleaned were covered with localised corrosion. After nine months, the corrosion in the same area was almost general. The protection applied on the other half zone was efficient during the whole period of exposure. Orange spots were visible on the chain element at the bottom of pits, certainly due to the growth of an iron carboxylate layer. No difference could be found during these tests on the particular effect of the two oxidising agents H_2O_2 and $NaBO_3$.

1.5.4.3.a-4. *Copper-based objects (TEI case study)*: *Paraloid B72® with or without CI additives versus Poligen ES 91009® + M370*

- Documentation

Due to the historical significance of the objects at the Benaki Museum and the fact that even uncoated coupons showed no signs of corrosion in both accelerated and natural ageing, three objects only were considered sufficient to test the coatings. The objects were part of the Islamic Art collection of the Benaki Museum, Athens. As indicated before, this museum is located in the centre of Athens and has uncontrolled exposure conditions. The selected objects came from the storage room of the museum which is situated on the ground floor, inside a wooden cupboard. Unfortunately, due to lack of equipment no monitoring was performed during the exposure period. No microscope was available either. Therefore the results are based on visual observations in artificial and natural light.

In collaboration with the metal conservator of the museum, three copper alloy objects were chosen. *"Object 1"* and *"Object 3"* appeared to be cast, having a more porous surface, whereas *"Object 2"* was most probably hammered and retained a glossy surface (Figure 45). All objects were in a good state of preservation: two (objects 1 and 3) were homogeneously covered by a thin dark layer of cuprite and only one (object 2) retained the yellow colour of copper alloys. No sign of active corrosion or any kind of deterioration were visible.

a/ b/ c/

Figure 45 Copper-based objects from the Islamic Art collection of the Benaki museum. Object 1 (a), Object 2 (b) and Object 3 (c).

- Cleaning and application of the protection systems

As mentioned before, since all objects are in good preservation state, no cleaning was necessary prior to coating application. Degreasing was performed with cotton impregnated in acetone. A very soft synthetic and flat brush was used for the application of the coatings on selected areas (see Table 8). Two layers were applied (a different brush was used for each different coating). The second layer was applied after complete drying of the first layer (24h).

Protection system applied	solvent	CI additive basic ingredient
Paraloid B72®	acetone	n/a
Poligen ES 91009® + M 370	n/a	Water solution of ammonium salts of tricarboxylic acid
Paraloid B72® + M109	acetone	Calcium sulfonate in mineral oil carrier
Paraloid B72® + M435	acetone	Alkaloamine salt of triazole
Reference coupons – not coated	n/a	n/a

Table 8: Description of the different protection systems tested on copper-based objects of the Islamic collection of the Benaki museum.

The application of the coating system Poligen ES 91009® + M370 was examined on all three objects. First a small part of each object was coated and was examined for coating failure during setting period. When no sign of failure was visible, a larger selected surface of each object was coated with one layer. At the first stages of drying, the objects still showed no sign of coating failure. However, as the drying period proceeded, coating failure (discoloration and exfoliation as observed on the coupons) appeared on tarnished *"Object 1"* and *"Object 3"* (Figure 46a). On the contrary, no sign of coating failure appeared on the metallic *"Object 2"*. However, the Poligen coating was easily removed on *"Object 1"* and *"Object 3"* with a brush and then cotton impregnated in acetone (showing that when Poligen ES 91009® + M370 is quite fresh, it can be considered as reversible). On "Object 1" the locally cleaned metal surface appeared a little lighter than the rest of the object (Figure 46b).

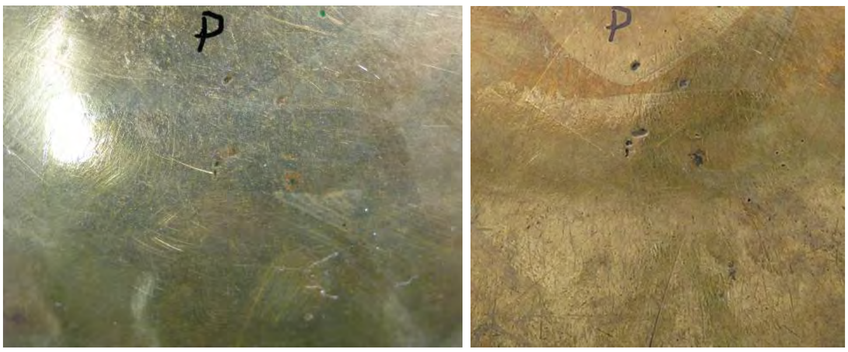
a/ b/

Figure 46 Failure of the protection system Poligen ES 91009® + M370 on Object 1 (a) and metal surface after the cleaning process (b).

As in the case of the coated coupons, the addition of M109 to Paraloid B72® made the coating easier to apply (maybe less viscous) and the brush strokes were not so apparent.

- <u>Monitoring</u>

Photographing using natural light was the only possible monitoring process available. No sign of coating failure, formation of corrosion on the copper alloys or any kind of degradation phenomena was visible on the coated areas after three months of exposure in the storage room of the museum. No additional protection was visible when comparing the coated and uncoated areas of *"Object 1"* and *"Object 3"*. For *"Object 2"* the application of coating offered protection of the metal surface since the first signs of a patina formation were apparent in the uncoated areas as indicated on Figure 47.



a/ b/

Figure 47 Detail of Object 2 protected with Paraloid B72®: after application (a) and after three months of exposure in the storage room of the Benaki museum. The unprotected areas became tarnished during the same period (see arrows).

1.5.4.3.a-5. *Copper-based object (LRMH case study): efficiency of sodium carboxylate*

- Documentation

The bronze propeller was stored in a gun powder house within the Maritime museum of Romainville Fortress, near Paris. In this room the temperature remained constant, while the RH still fluctuated but in lower ranges (10 per cent). The metal surface was slightly oxidised (Figure 48).

Figure 48 Bronze propeller stored in a gun powder house within the Maritime museum of Romainville Fortress, near Paris.

- Cleaning and application of the protection system

As a protection system NaC_{10} solution (0.25M) was applied by brush with a poultice without prior cleaning of the metal surface.

- Monitoring

A visual inspection of the surface was carried out each of the nine months of exposure to evaluate the efficiency of the protection systems tested.

a/ b/

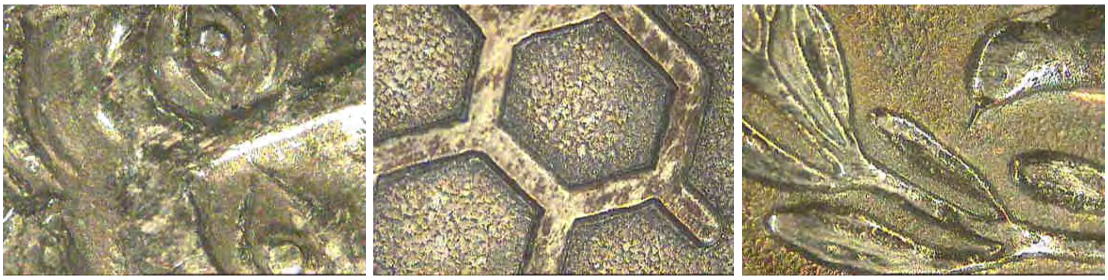
Figure 49 Corrosion progress on one of the blade of the bronze propeller after application of NaC_{10}: just after application (a) and after six months of exposure in the gun powder house of the Maritime museum of Romainville Fortress.

A thin white film appeared just after application of the corrosion inhibitor (Figure 49a), which had already been observed on the PROMET coupons. This film is made up of sodium carboxylate on top of a thin copper carboxylate layer. This effect could be reduced by cleaning the surface with a water solution. In this test, the thin white film was not cleaned since it was expected that it would disappear progressively. However, as became apparent, it did not.

1.5.4.3.a-6. *Silver-based objects (NTUA case study): Paraloid B72® versus nano-alumina pigmented Paraloid B72®*

- Documentation

NTUA tested nano-alumina pigmented Paraloid B72® versus Paraloid B72® on three medallions (Ref n° 14.2, 14.3 and 14.4) from the collection of the Technology museum, Athens. All were highly tarnished (Figure 50) in this uncontrolled environment. XRD analysis revealed the presence of acanthite (Ag_2S).



a/ b/ c/

Figure 50 Condition state of medallions 14.2 (a), 14.3 (b) and 14.4 (c) (details) before application of the protection systems tested.

- Cleaning and application of the protection systems

Tarnish removal was carried out with alkaline dithionite. Ag_2S was reduced to silver. No further cleaning was performed. The protection systems were applied as follows:

- medallion 14.3: plain Paraloid B72® by immersion
- medallions 14.2 and 14.4: 2% nano-alumina pigmented Paraloid B72® by immersion

- Monitoring

The medallions were exposed in the same conditions as the silver-based coupons considered before for the natural ageing. They were examined after three, six months and at the end of the exposure period (one year). No alteration was observed at macro- and micro-level on the surface of the three medallions, showing once again that Paraloid B72® applied correctly on a well cleaned metal surface offers a good protection on silver-based objects for a period of at least one year.

1.5.4.3.b. Archaeological objects

1.5.4.3.b-1. *Iron-based objects (CSIC case study): Poligen ES 91009® versus Paraloid B72®*

- Documentation

CSIC selected a group of two iron nails and one iron hook excavated from *El Saucedo* (Talavera de la Reina, Toledo, fourth to seventh centuries A.D., Figure 51a). Their condition was representative of the objects surveyed by CSIC within PROMET. They were covered with corrosion layers constituted of magnetite, goethite and lepidocrocite and contained a certain amount of Cl and S.

a/ b/

Figure 51 Condition state of three iron objects excavated from *El Saucedo*. (a) before application of Poligen ES 91009®. (b): after application and natural ageing (six months) in one of the laboratories of the UAM.

- Cleaning and application of the protection system

The objects had been preserved and treated in a conservation-restoration laboratory of the Department of Prehistory and Archaeology of the Universidad Autónoma de Madrid (UAM). Any trace of past protection (Paraloid B72®) was removed by immersion in acetone. Poligen

ES 91009® without CI additives was considered due to the good results obtained on artificially aged steel coupons. It was applied by a conservator of the UAM using a soft synthetic brush in two criss-cross layers, allowing 24h drying between applications. It yielded a slightly “plastic” aspect to the archaeological objects, not observed with Paraloid B72® (Figure 51b).

- Monitoring

The objects protected were stored in an open container in one of the laboratories of the UAM during six months (from summer to autumn 2007). The atmosphere was not controlled as indicated by the fluctuations of T and RH in summer: 18.9 to 28.3 ºC - 32 to 68 per cent and in autumn, 13.3 to 23.9 ºC - 22 to 56 per cent. Daily changes of T and RH were very important, especially during November, due to turning on and off the heating system.

Figure 52 shows corrosion outbursts that clearly indicated that Poligen ES 91009® was not effective in protecting active archaeological iron objects in an uncontrolled atmosphere. Similar results were obtained though with Paraloid B72® (not tested here but observations made from previous applications).

a/ b/

Figure 52 (a) Corrosion outbursts observed on one of the nail protected with Poligen ES 91009® of Figure 7.53b; (b) active corrosion observed on the iron hook.

1.5.4.3.b-2. *Copper-based objects (CSIC case study): Poligen ES 91009® versus Paraloid B72®*

- Documentation

CSIC selected a piece of a horse tack (gilded copper) and a hook (bronze) excavated from *Calatrava la Vieja* (Ciudad Real, eleventh to thirteenth centuries A.D., Figure 53a). Numerous gilded copper objects were recovered from that site. They are mainly small appliqués and ornaments of outstanding beauty and technique. They present a very heavy corrosion crust, sometimes containing the gold layer trapped inside, which further complicates the restoration processes.

a/ b/

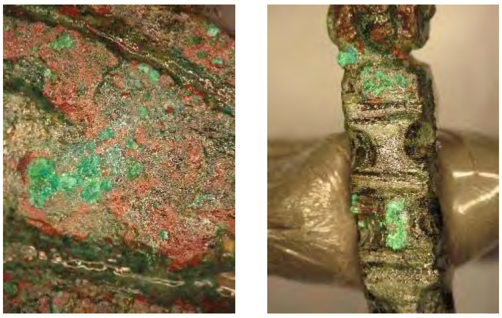
Figure 53 Condition state of two copper-based objects excavated from *Calatrava la Vieja*. (a) before application of Poligen ES 91009®; (b) after application and natural ageing (six months) in one of the laboratories of the UAM.

- Cleaning and application of the protection system

The piece of horse tack and the hook had been mechanically cleaned in a conservation-restoration laboratory of the Department of Prehistory and Archaeology of the UAM. The horse tack showed gold losses in some areas. Any trace of past protection (Paraloid B72®) was removed by immersion in acetone. Poligen ES 91009® without CI additives was applied on the whole of the objects by a conservator of the UAM using a soft synthetic brush in two criss-cross layers, allowing 24h drying between applications. It yielded a slightly "plastic" aspect to the archaeological objects, not observed with Paraloid B72®.

- <u>Monitoring</u>

The objects protected were stored in an open container in one of the laboratories of the UAM for six months. The same comments as above can be made about the uncontrolled atmosphere of the laboratory. Figure 54 shows corrosion outbursts that clearly indicated that Poligen ES 91009® was not effective in protecting active copper-based objects in an uncontrolled atmosphere. The same objects did not seem to show any trace of active corrosion when they were protected with Paraloid B72®. Therefore in the atmosphere of the laboratories of the UAM, Poligen ES 91009® appeared as less effective than Paraloid B72® for ensuring the protection of these objects.



a/ b/

Figure 54 (a) Corrosion outbursts observed on the gilded horse tack protected with Poligen ES 91009®; (b) active corrosion observed on the bronze hook.

1.5.4.3.b-3. *Copper-based objects (IBN-DC case study): efficiency of FPTS formulation*

- <u>Documentation</u>

IBN-DC selected a bronze female bust emergent from an acanthi leaf (ref Th 296) conserved in the bronze room of the Archaeology museum of Rabat. It was found in Thamusida (Roman Period (first to third century B.C.)). Its condition state was quite good, although the metal was heavily corroded and covered with black/green patina layer. Figure 55 shows the object before the application of the protection system chosen.

Figure 55 Condition state of a bronze female bust emergent from an acanthi leaf (ref Th 296) recovered from Thamusida (first to third century B.C.)).

- Cleaning and application of the protection system

The statuette was degreased with ethanol and an active spot (on the base) was cleaned mechanically. Only half of the metal surface was treated by immersion with FPTS: 0.07% in ethanol for three hours (Figure 56).

a/ b/

Figure 56 Application of FPTS on the surface of the female bust by immersion (a). Only the bottom part of the statuette was treated. The upper part remained unprotected (b).

- Monitoring

After application of the protection system, the object was placed back in its showcase and the monitoring of the protection systems in the uncontrolled atmosphere of the bronze room of the Rabat museum was carried out on a weekly basis by visual inspection. As shown on Figures 57a and 57b, no sign of alteration was detected during the next eight months of exposure.

a/ b/

Figure 57 Monitoring of the half-protected female statuette placed back in one of the showcase of the bronze room of the Archaeology museum of Rabat after four months (a) and eight months (b) of exposure.

1.5.4.3.b-4. *Copper-based alloys (RSS case study): FPTS CI versus silane A*

- Documentation

In collaboration with the Department of Antiquities (DoA), RSS selected five coins from Umm Qais museum to apply newly developed inhibitors. The coins were from the Roman period. They were copper-based with some silver, tin and lead as shown in Table 7.9.

	Cu	**Ag**	**Sn**	**Pb**	**Si**
Coin 0 (non protected)	85.14	2.23	1.69	9.56	1.36
Coin 1 (FPTS)	85.23	5.58	0.5	2.52	5.96

Coin 2 (FPTS)	88.11	3.27	0.55	4.39	3.52
Coin 3 (silane A)	89.44	2.7	0.41	3.61	3.85
Coin 4 (silane A)	90.40	3.23	0.54	2.93	2.79

Table 9 Analysis of Roman coins from Umm Qais museum used to compare the protection efficiency of FPTS CI and silane A.

- Cleaning and application of the protection systems

The coins were cleaned chemically by DoA staff using diluted 5% (w/v) citric acid during half an hour to remove adherent corrosion products. The coins were then washed thoroughly in distilled water and brushed to remove any acid residue. This process was repeated several times till corrosion products were minimised. At the end of this cleaning process, the coins were immersed separately in distilled water for three hours and then left to dry. The cleaning was finalised mechanically with a scalpel. One coin was kept as a reference, two coins (1 and 2, Figures 7.60a and 7.60b) were protected with FPTS CI and two coins (3 and 4, Figures 7.60c and 7.60d)) by silane A. Both protection systems were applied in two layers by a professional C-R from Yarmouk University and were followed by a 24h drying period.

a/ b/ c/ d/

Figure 58 Front side of the four coins of Umm Qais museum after chemical and mechanical cleaning. Coin 1 (a), coin 2 (b), coin 3 (c) and coin 4 (d).

- Monitoring

The coins were then put in the uncontrolled atmosphere of Umm Qais museum exhibition area, and photographed on a daily basis either by RSS or Umm Qais museum staff members for the first month to detect any change that could occur during exposure. The exposure lasted five months. The unprotected coin started darkening quite quickly and had darkened further at the end of the exposure time (Figure 59b).

a/ b/

Figure 59 Back side of the unprotected coin before (a) and after the five months of exposure (b).

Figure 60 shows the way the appearance of the front side of coin 1 covered with FPTS CI changed versus time during the first month of exposure. It is clear that after a few days the surface started darkening to acquire a dark mat appearance after a month.

a/ b/ c/ d/

Figure 60 Coin 1 after FPTS application (a) and 10 days (b), 18 days (c) and 26 days (d) of exposure in the exhibition room of Umm Qais museum.

Due to the failure of the protection system, the coin was re-cleaned by immersion in ethanol then in acetone with mechanical brushing and finally washed and sprayed with ethanol and dried during 24h. The coin was re-protected with FPTS CI twice using the same protocol as before. The duration of the second exposure lasted two months. The same darkening effect occurred (Figure 61). Reasons of the rapid failure might be attributed to the composition of FPTS that contains S and the presence of silver (from 3.27 to 5.58 %) in the two coins treated. The application in two layers might also have had an effect.

a/ b/ c/

Figure 61 Coin 1 after the second application of FPTS formulation. (a) after application; (b) after two days; (c): after three months.

Coins 3 and 4 coated with silanes were also exposed in Umm Qais museum exhibition room. As shown in Figures 62 and 63, the change in colour was minimal after five months of exposure.

a/ b/ c/

Figure 62 Coin 3 after silane A application (a), after three days (b) and five months (c) of exposure at Umm Qais museum (in the exhibition room).

a/ b/ c/

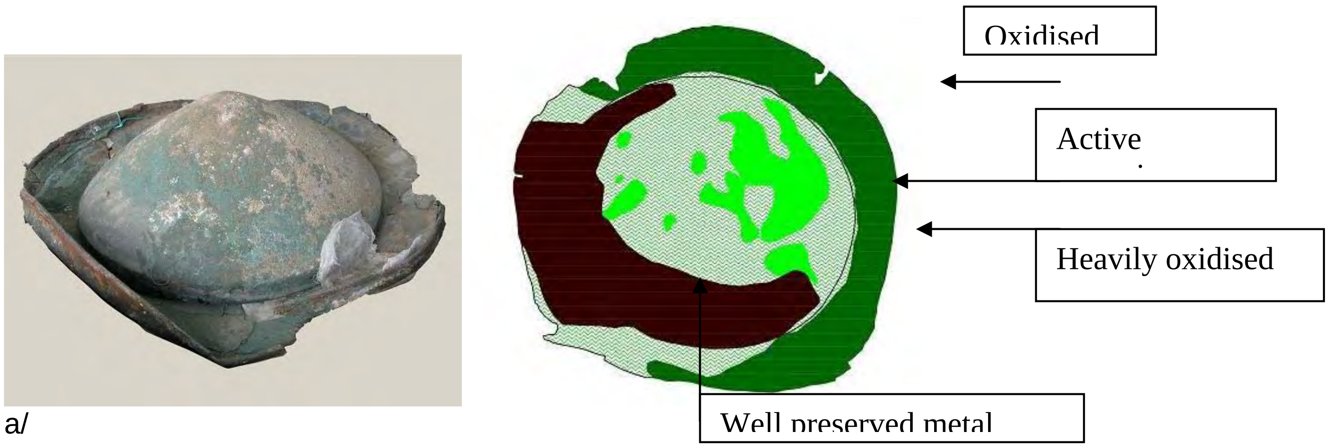
Figure 63 Coin 4 after silane A application (a), after three days (b) and five months (c) of exposure at Umm Qais museum (in the exhibition room).

Similar results to those obtained on the naturally aged bronze coupons protected with silane A and FPTS CI and exposed one year on the site of Umm Qais museum could be observed. Indeed the darkening of the coins covered with silane A is less pronounced than for the coins protected with FPTS. The compositions of the coins are different from those of the bronze coupons since the former have Ag and no Zn and less Sn. The bronze coupons have no Ag but contain equal amounts of Zn, Pb and Sn (5 %). The presence of Ag and the high reactivity of this element to S might be the main reason of failure of the FPTS formulation.

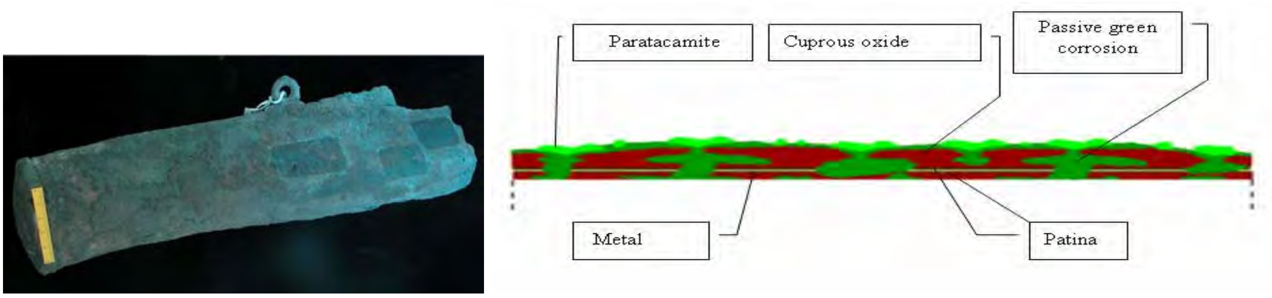
1.5.4.3.b-5. *Copper-based objects (EGE-PNEA case study): Paraloid B72® versus corrosion inhibitors (FPTS formulation and* NaC_{10}*)*

- Documentation

EGE-PNEA selected two pieces: a bronze shield and a bronze quiver excavated from Fortress of Ayanis, Van (Urartu, seventh century B.C.). Their physical condition was examined for corrosion. Figure 64 shows that they were heavily corroded.



a/



b/

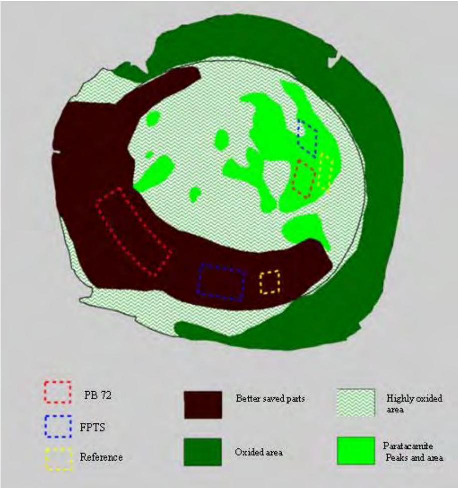
Figure 64 Condition state of a bronze shield (a) and a bronze quiver (b) excavated from Fortress of Ayanis, Van (Urartu, seventh century B.C.).

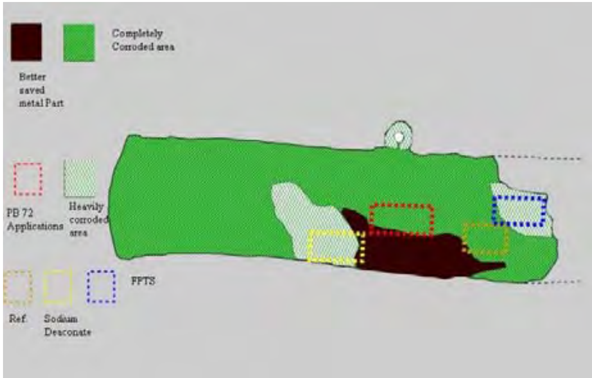
- Cleaning and application of the protection system

The bronze shield and bronze quiver had already been conserved during excavation before being handled to the Van Museum. Only mechanical cleaning was carried out. As indicated on Figure 65a, three windows were realised on the shield both on the better preserved part of the metal surface and active areas. In addition to the reference area, the two other areas were used for testing the following protection systems:
- 15% Paraloid B72® in acetone was applied by brush in December 2006
- two layers of FPTS were applied by brush in April 2007. Drying time was 48h.

Three additional windows were carried out on the active corrosion zone to test the same protection systems on this other substrate.

Four windows were realised on the surface of the bronze quiver (Figure 65b) in the heavily and completely corroded zones. This time Paraloid B72® was applied on the most corroded zone (like the reference area), parallel to FPTS and NaC_{10} which were applied on less corroded areas. The conditions of application of the protection are as follows:
- Paraloid B72® was applied by brush in December 2006
- Two layers of FPTS were applied by brush in April 2007. Drying time was 48h.
- 0.1M NaC_{10} was applied by brush in April 2007. Drying time was 48h





a/ b/

Figure 65 Condition state of the bronze shield (a) and bronze quiver (b) with location of the windows for testing the different protection systems.

- Monitoring

After application of the protection systems, the objects were kept three days in the small laboratory of Van museum and then moved to the uncontrolled conditions of the museum depot. Monitoring the objects involved visual observation and photographing of the windows tested.

Figure 66 shows the results obtained on the shield and the quiver after almost one and a half year of exposure for the window cleaned and protected with Paraloid B72® and 10 months of exposure for the windows cleaned and protected with FPTS and NaC_{10}.

Before exposure After exposure

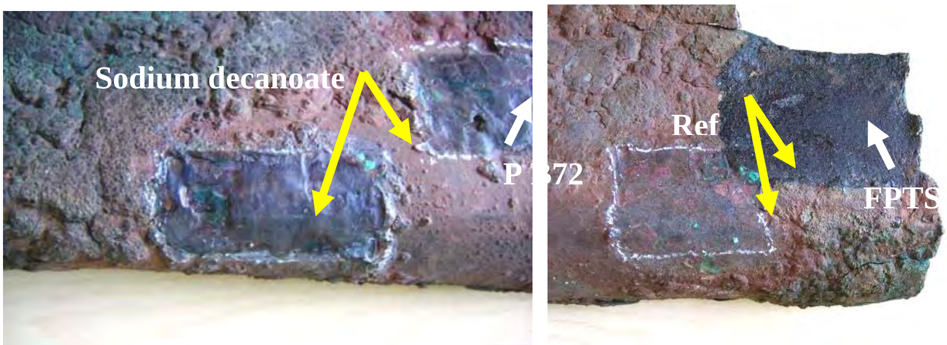
a/

Before exposure After exposure

b/

Figure 66 Condition state of the bronze shield (a) and bronze quiver (b) before and after exposure of ten months in the depot of the Van museum.

Paraloid B72® behaved very well on the two objects. No damage was observed between December 2006 and February 2008. It is important to note that Paraloid was applied on both slightly and heavily corroded surfaces. During the same time active corrosion developed on the quiver on the reference window cleaned similarly to the Paraloid window in a completely corroded area (Figure 67b). FPTS applied on both slightly corroded, active and heavily corroded areas gave good results too during the 10 months of the exposure period (Figure 67b).



a/ b/

Figure 67 Details of Figure 67b after exposure. Yellow arrows indicate areas of active corrosion.

NaC_{10} applied on a heavily corroded zone of the quiver seemed to be less effective than FPTS since active corrosion developed not only on the edge of the window cleaned and protected with NaC_{10} but also in the central area of the window (Figure 67a).

1.5.4.3.c. <u>Discussion and final conclusion on real objects testing</u>

The tests carried out on a maximum of a one-year period, which is a short period in conservation, confirmed that, in the uncontrolled atmospheres of the Mediterranean region, Paraloid B72® is not effective at protecting historic and archaeological metal objects. Depending on the environmental parameters (fluctuations of RH and T, level of pollutants, presence of dust particles) the acrylic varnish failed eventually, and when it did, localised and/or filiform corrosion developed and provoked serious damages on the metal surface. The addition of nano-alumina pigments to Paraloid B72® might solve the problem, particularly when the concentration is as low as 2% (w/w). This was tested successfully on silver and copper alloys coupons during a one-year period (Vassiliou *et al.* 2007). If the application of Paraloid B72® had to be considered it should be carried out by C-Rs to assure good preparation of the metal surface and good application. Additionally, every effort should be made to limit the fluctuations of the environmental parameters.

Another way to improve the protection of metal objects would be through the use of other protection systems tested / developed within the PROMET project. For short-term exposure, CIs such as the carboxylatation solutions applied by brush on corroded iron-based objects gave good results (at least from nine to 12 months of exposure in uncontrolled environments). No conclusion could be made though on the specific effect of the oxidation agent added to the decanoïc acid. The application of three layers was certainly beneficial, but more research is needed to determine the appropriate number of layers for a specific metal surface. Sodium decanoate (NaC_{10}) is an option for copper-based alloys, although the problem of the formation of the thin white film during application has to be solved. For large collections, the appropriate concentration should be determined more precisely but we might be able to lower it from 0.25 to 0.1M, depending on the level of active corrosion within the metal. Such CIs should be considered particularly when large collections have to be treated, since they are easy to apply and repair. Furthermore, they can be removed easily with ethanol. FPTS CI gave good results on copper-based objects (except when objects contained Ag), but here, too, some additional testing is required to determine the duration of their efficiency.

For long-term exposure, Poligen ES 91009® with or without CI additives gave good results on historic iron-based objects such as steel armour elements and weapons (for example, the knives and bayonets of the museum of Criminology, Athens). Poor results were obtained though with Poligen ES 91009® alone on active archaeological iron and copper-based objects since corrosion developed further. Additionally, the application on non active, patinated or slightly tarnished copper-based alloys should be avoided, since exfoliation of the coating (Poligen ES 91009® with or without CI additives) occurred when loose corrosion products were present. Silane A could be an option for historic bronze objects but apparently not for silver-based objects (YU-FAA results). More tests are needed to assess the long-term efficiency of these different coatings and in both cases (Poligen ES 91009® with or without CI additives and silane A) the removal protocol should be further studied to make sure that it does not provoke any harm to the metal surface.

1.5. 5 CONCLUSIONS

The work presented for WP3 was true collaborative work involving all PROMET partners. It is certainly the first time that so many partners in a whole geographical region have followed the same methodology, exchanged practices and benefited from transfer of knowledge in order to draw some preliminary conclusions on the most effective protection systems to use for ensuring the long-term conservation of our metal heritage. Our work is thus unprecedented in the field.

The methodology was based on the use of metal analogues, corroded artificially or through natural ageing and simulating real objects. The artificially corroded coupons were exposed to accelerated corrosion tests to compare traditional and innovative protective materials and methods in order to find the most effective ones for the indoor museum environments of the Mediterranean region. Additional ageing of a selection of the most effective protection systems on naturally aged coupons in real conditions was used to determine the most promising compounds that would finally be tested on real objects.

Accelerated corrosion tests in climatic chambers and through electrochemical measurements were particularly useful to compare the efficiency of the different protection systems under study. Such an approach was essential to discard most of the traditional protection systems commonly used in northern countries in the conservation field (Renaissance® and Cosmoloid® waxes, cellulose nitrate, polyvinyl acetate), adapt the composition of the innovative CIs / coatings developed to meet the needs of the Mediterranean region and study the effect of corrosion stimulators. The latter must definitely be removed (through stabilisation treatments) so as to prevent any rapid failure of the protection systems applied.

Natural ageing of the most effective coatings / CIs on naturally aged coupons (reflecting better the alteration of real objects) confirmed some of the results already obtained through short-term testing and further improved the assessment of the protection systems under study. Paraloid B72® gave poor results on steel coupons where filiform corrosion developed. Other forms of alterations were observed on copper and silver-based alloys. NTUA suggested that nano-alumina pigments are added to the acrylic resin, as this seems to decrease the risk of alteration on silver-based coupons; however, more testing is required to further support these preliminary results, especially on copper and iron-based alloys.

As regards innovative protection systems, it was found that PVD coatings, as prepared by DMME, should not be considered for steel objects. PECVD coatings gave interesting results on bronze and silver-based alloys. Concerning PVD coatings, more research is needed on the colour effects produced during the application and the reversibility of the coatings with time; the use of colourless and reversible PECVD coatings may be proposed if the required equipment is locally available. More research is needed to determine the durability of the coating.

A good replacement for Paraloid B-72® for temporary protection on partly oxidised historic steel objects was carboxylatation treatment (HC_{10} + H_2O_2 or $NaBO_3$). Other CIs tested (OTH, FPTS and NaC_{10}) were apparently less effective and would require more testing. Additional work would also be needed to confirm the efficiency of FPTS and bitriazoles CIs on copper-based objects and the application protocol of NaC_7 and NaC_{10} on these materials should improve to prevent the whitening of the metal surface.

Poligen ES 91009® could be suggested for the long term protection of historic steel objects. The role of CI additives should be studied further as well as the durability and reversibility of the coating alone or with the CI additives tested. Since the failure of these coatings was observed on oxidised copper-based objects an alternative could be the application of silane A, although its reversibility is problematic. This coating seemed to be an option for silver-based objects as well.

When testing the most promising protection systems on real artifacts and comparing them to the traditional Paraloid B72®, we found out that Paraloid B72® should not be fully removed from the list of possible protection systems to use in Mediterranean countries. It should be applied, though with care (by C-Rs and after a good cleaning of the metal surface), and efforts should be made to improve the conditions of exposure of the objects protected (limitation of the fluctuations of environmental parameters). We confirmed though that the addition of alumina nano-particles should be beneficial (at least in the case of silver-based objects).

The good behaviour of NaC_{10} CI (for historic copper-based objects) and carboxylatation solutions (for slightly oxidised iron-based objects) for short-term protection was confirmed. FPTS CI gave good results on archaeological objects (even active ones) except when these contain Ag, in which case rapid tarnishing was observed. NaC_{10} should not be considered though on active archaeological objects. These new temporary protection systems are easy to repair and reversible in ethanol. Still they should be further investigated to define precisely their field of application, durability and reversibility beyond several months of application. If applicable, they could be used during transfer of collections from one building to another where uncontrolled environments are involved, or to objects on loan for temporary exhibition that require specific protection during transport.

We also confirmed that Poligen ES 91009® alone or with CI additives and silane A were good candidates for long-term protection. Poligen ES 91009® systems were suitable for historic iron-based objects, but should not be considered for active archaeological objects. Furthermore the conditions of their application to copper-based objects should be further defined. Silane A might be an interesting alternative here that could also be applied to silver-based objects. In both cases, the removal protocol should be further studied to make sure that it does not provoke any harm to the metal surface. If applicable, these new protection systems would solve the problem of the safe storage or exhibition of large metal collections exposed to uncontrolled conditions in museums of the Mediterranean countries.

The PROMET project was too short to study the combination effect of some particularly effective coatings and additional CIs. Based on the good results obtained for Paraloid B72®, such testing should be carried out in future projects. Furthermore, at the time of writing this chapter, the assessment of the results for all the work performed, such as the assessment of natural ageing of protection systems on naturally aged coupons using reflectance FTIR, had not been completed.

It is too early to draw definitive conclusions on the real efficiency of the protection systems proposed by the PROMET partners. As stated before, the conservation community tends to be very conservative, and perhaps rightfully so, since innovative protection systems not tested enough and applied immediately to the field might provoke some new damages in the long-term that did not occur during our project because of its limited duration. Still some PROMET partners actively work in the conservation field and will hopefully be the promoters of the methodology followed in the project and of future testing experiments on the different protection systems suggested.

1.5.6 References

Al-Saad, Z. and Hani, M.B. 2007. “Corrosion behaviour and preservation of Islamic silver alloy coins”. In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 177-183, Athens: TEI of Athens.

Angelini, E., Fracassi, F., d’Agostino, R., Grassini, S. and Rosalbino, F. 2004. “PECVD protection of metals”. In *Trends in electrochemistry and corrosion at the beginning of the*

12th century, Costa J.M., Brillas Enric, Cabot, Pere-Lluìs (eds.) IV, 979-999. Collecciò, Publicacios UB.

Argyropoulos, V., Sakki, Z., Karydas, A.G., Zarkadas, C., Pouli, P., Melessanaki, K., Giakoumaki., A., Anglos, D. and Giannoulaki, M. 2005. “Problems in stabilising historic iron-bladed weapons displayed in an uncontrolled environment in the Criminal Museum of Athens, Greece”. In *Preprints of the ICOM-CC Triennial Meeting in the Hague*, 1, 293-300. London: James & James.

Argyropoulos, V., Charalambous, D., Kaminari, A. Karabotsos, A., Polikreti, K., Siatou, A., Cano, E., Bastidas, D.M., Cayuela, I., Bastidas, J-M., Degrigny, C., Vella, D., Crawford, J. and Golfomitsou, S. 2007a. “Testing of a new wax coating poligen ES 91009® and corrosion inhibitor additives used for improving coatings for historic iron alloys”. In *METAL07, proceedings of the ICOM-CC Metal WG interim meeting*, Amsterdam, C. Degrigny, R. van Langh, B. Ankersmit, I. Joosten (eds.), 5, 10-15, Amsterdam: Rijskmuseum.

Argyropoulos, V., Giannoulaki, M., Michalakakos, G. and Siatou A. 2007b. “A survey of the types of corrosion inhibitors and protective coatings used for the conservation of metal objects from museum collections in the Mediterranean basin”. In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 166-170, Athens: TEI of Athens.

Beale, S. and Smith., R. 1998. *Conservation of metal statuary and architectural decoration in open-air exposure*, 99-124. Rome: ICCROM.

Brostoff, L.B. 1995. “Investigation into the interaction of benzotriazole with copper corrosion minerals and surfaces”. *In METAL95*, proceedings of the International ICOM-CC Metal WG conference, Semur-en-Auxois, I. MacLeod, S. Pennec and L. Robbiola (eds.), 99-108, London: James & James.

Brostoff, L.B. 2003. *Coating strategies for the protection of outdoor bronze art and ornamentation*, PhD thesis, Amsterdam.

Cano, E., Bastidas, D.M., Argyropoulos, V. and Siatou, A. 2007. “Electrochemical techniques as a tool for testing the efficiency of protection systems for historical steel objects”. In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 121-126, Athens: TEI of Athens.

Crawford, J., Degrigny, C., Glorieux, Q., Bugeja, P. and Vella. D. 2007. “A Standardised Remote Monitoring Photographic Capture System (RMPCS) for in-situ documentation of corrosion protection system Tests”. In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 85-92, Athens: TEI of Athens.

d’Agostino, R., Favia, P. and Fracassi, F. 1997 *Plasma processing of polymers*, 3-46, Dordrecht: Kluwer Academics Publishers.

d’Agostino, R., Fracassi, F., Palumbo, F., Angelini, E., Grassini, S. and Rosalbino F. 2005. “Protection of silver-based alloys from tarnishing by means of plasma-enhanced chemical vapor deposition”, *Plasma Processes and Polymers*, 91-96.

Degrigny, C., Vella, D., Golfomitsou, S. and Crawford, J. 2007. “Characterisation of corrosion product layers on atmospherically corroded ferrous artifacts: application to the armour of the Palace Armoury, Valletta, Malta”, In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 31-39. Athens: TEI of Athens.

Dermaj, A., Chebabe, D., Hajjaji, N., Joiret, S., Rahmouni, K., Srhiri, A. Takenouti, H. and Vivier, V. 2005. “Etude de la corrosion du bronze Cu-8%Sn et l’effet inhibiteur de 3-phenyl-1.2.4- triazole -5-thione”, In the *Proceedings of the 17th Forum on the Electro-chemical Impedances*, C. Gabrielli (ed.) 257-268.

Dermaj, A., Chehabe, D., Hammouch, H., Goursa, M., Hajjaji, N. and Srhiri, A. 2007. “Atmospheric corrosion inhibition of historical steel by FPTS formulation based of triazole-thione”. In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 143-148. Athens: TEI of Athens.

Giannoulaki, M., Argyropoulos, V., Michalakakos, G., Panou, T., Kantarelou, V., Zarkadas, C., Karydas, A., Perdikatsis, V. and Apostolaki. C. 2007. “A conservation survey of museum metal collections using portable scientific techniques: a case study in the museum of Ancient Messene, Greece”, In *METAL07*, proceedings of the ICOM-CC Metal

WG interim meeting, Amsterdam, C. Degrigny, R. van Langh, B. Ankersmit and I. Joosten (eds.), 1, 67-72. Amsterdam: Rijskmuseum.

Hajjaji, N., El Harrif, F.Z., Kaouane, C., Srhiri, A., Takanouti, H. and Rahmouni, K. 2007. "Conservation problems and a new method of protection: the case of bronzes at the archaeological museum of Rabat, Morocco". In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 138-142. Athens: TEI of Athens.

Hallam, D., Thurrowgood, D., Archer, E., Otieno-Alego, V., Creagh, D., Viduka, A. and Heath, G. 2004. "Studies of commercial protective petrochemical coatings on ferrous surfaces of historical and museum objects". In *METAL01*, in Proceedings of the International ICOM-CC Metal WG conference, Santiago de Chile, Eds I. MacLeod, J.M.Theile and C.Degrigny, Western Australian Museum, Fremantle, 297-303.

Hammouch, H., Bennaghmouch, L., Srhiri, A. and Hajjaji, N. 2005. "Inhibition of iron corrosion using Opuntia extract", FAO CactusNet Newsletter.

Hammouch H., Dermaj, A., Goursa, M., Hajjaji, N. and Srhiri, A. 2007a. "New corrosion inhibitor containing Opuntia Ficus Indica seed extract for bronze and iron-based artifacts". In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 149-155. Athens: TEI of Athens.

Hammouch, H., Dermaj, A., Hajjaji, N., Degrigny, C. and Srhiri, A. 2007b. "Inhibition of the atmospheric corrosion of steel coupons simulating historic and archaeological iron-based objects by cactus seeds extract". In *METAL07*, proceedings of the ICOM-CC Metal WG interim meeting, Amsterdam, C. Degrigny, R. van Langh, B. Ankersmit and I. Joosten (eds.), 5, 56-63. Amsterdam: Rijskmuseum.

Hatchfield, P.B. 2002. *Pollutants in the Museum Environment*. London: Archetype

Hollner, S., Mirambet, F., Rocca, E. and Steinmetz, J. 2007a. "Environmentally-friendly treatments for the protection of iron objects of the cultural heritage against atmospheric corrosion". In *METAL07*, proceedings of the ICOM-CC Metal WG interim meeting, Amsterdam, C. Degrigny, R. van Langh, B. Ankersmit and I. Joosten (eds.), 5, 64-70. Amsterdam: Rijskmuseum.

Hollner, S., Mirambet, F., Texier, A., Rocca, E. and Steinmetz, J. 2007b. "Development of new non-toxic corrosion inhibitors for iron-and copper-based artifacts from cultural heritage". In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 156-161. Athens: TEI of Athens.

Horie, C.V. 1987. *Materials for Conservation.* London: Butterworth-Heinemann.

Hughes, R. and Row, M. 1991. *The Colouring, Bronzing and Patination of Metals*. London: Thames and Hudson Ltd.

Knotkova, D., Kreislova, K., Kreibichova, B., Kudlacek, I. 2007. "Indoor corrosivity in the National Museum Depositary". In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 64-71. Athens: TEI of Athens.

Letardi, P. 2005. Oral communication.

MacLeod, I.D. and North, N.A. 1979. "Conservation of Corroded Silver". *Studies in Conservation* 24: 165-170.

Mattox, D.M. 1998. *Handbook of Physical Vapour Deposition (PVD) Processing – Film Formation, Adhesion, Surface Preparation and Contamination Control*. USA: Noyes Publications.

Monnier, J., Bellot-Gurlet, L., Legrand, L., Dillmann, P., Reguer, S., Neff' D. and Guillot, I., "The long term indoor atmospheric corrosion of iron: rust layer characterisation". In *METAL07*, proceedings of the ICOM-CC Metal WG, Amsterdam, C. Degrigny, R. van Langh, B. Ankersmit, I. Joosten (eds.), 47-54, 2. Amsterdam: Rijksmuseum.

Plueddemann, E.P. 1991. *Silane Coupling Agents*, 2nd ed.. New York: Plenum Press.

Pouli, P., Melessanaki, K., Giakoumaki, A., Argyropoulos, V. and Anglos, D. 2005. "Measuring the thickness of protective coatings on historic metal objects using nanosecond and femtosecond LIBS depth profiling". *Spectrochimica Acta* Part B 60, 1163- 1171.

Selhofer, H., Ritter, E. and Linsbod, R. 2002. “Properties of titanium dioxide films prepared by reactive electron-beam evaporation from various starting materials”. *Applied Optics*, 41, 4, 756-762.

Pye. E. 2001. *Caring for the past. Issues in conservation for archaeology and museums*. London : James & James.

Siatou, A., Argyropoulos, V., Charalambous, D., Polikreti, K. and Kaminari, A. 2007. “Testing new coating systems for the protection of metal collections exposed in uncontrolled museum environment”. In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 115-120. Athens: TEI of Athens.

Turgoose, S. 1985. “Corrosion inhibitors in conservation”. UKIC Occasional paper 4; UK Institute for conservation, S. Keene (ed.), 13-17.

Van Ooij, W.J., Zhu, D., Palanivel, V., Lamar, J.A. and Stacy, M. 2002. “Potential of silanes for chromate replacement in metal finishing industries”. *Silicon Chemistry*, 3, 1-2, 11-30.

Vassiliou, P., Novakovic, J. and Samara, K. 1007. “Copper alloys and silver objects protection by coatings with nano-alumina pigments”. In *Strategies for Saving our Cultural Heritage*, V. Argyropoulos, A. Hein and M.A. Harith (eds.), 132-137. Athens: TEI of Athens.

Vella, D., Degrigny, C. and Grech., M. 2004. “Metallurgy of armour exhibited a the Palace Armoury, Valletta, Malta”, In *METAL04*, proceedings of the ICOM-CC Metal WG interim meeting, METAL04, J. Ashton & D. Hallam (eds) 215-233. Canberra: National Museum of Australia.

Vella, D., Degrigny, C. and Grech, M. 2005. “A preliminary study of the morphology of corrosion developing onto historic steel armour artifacts from the Palace Armoury Collection, Valletta, Malta”. In *Proceedings of the 14th triennial meeting of ICOM-CC, The Hague, Netherlands*, 317-325. London: James & James.

Vella, D., Grech, M. and Degrigny, C. 2007. “Application of titanium oxide thin films on polished and partly corroded mild steel substrate – an evaluation of vapour deposited coatings for the protection of historical steel objects”. In *METAL07*, proceedings of the ICOM-CC Metal WG interim meeting, Amsterdam, C. Degrigny, R. van Langh, B. Ankersmit and I. Joosten (eds.), 5, 123, Amsterdam: Rijskmuseum.

Walker R. 2000. “Aqueous corrosion of tin-bronzes and inhibition by benzotriazole”. *Corrosion*, 56, 1211-1218.

2. Dissemination and use (Workpackage 4)

2.1 Introduction and Summary

The deliverables of our research were designed to meet the demands of its end-users (museum and conservation professionals). The diagnostic portable techniques LIBS and microXRF is applicable for most materials constituting cultural assets, such as monuments or objects of archaeological, historic, and artistic value. Furthermore, our research has shown that there is a great demand for non-toxic corrosion inhibitors to stabilize metal objects, which is currently not being used by metal conservators.

PROMET prototypes were tested by 21 partners from 11 different countries in Europe and the Mediterranean basin, many representing end-users, such as museums and Ministries of Culture. Hundreds of publications have culminated from the research of these EU projects, and the results of PROMET have become well known to International Committee of Museums-CC Metal Working Group where 8 papers and 3 posters were presented and/or published at their interim meeting in September 2007. In the Arab world, an international conference was organized in Cairo, Egypt last year, as well as workshops in Damascus, Syria and Irbid, Jordan (October 2007) highlighting the results of these EU projects and/or demonstrating the prototype portable micro-XRF and LIBS techniques in-*situ*. Over 600 copies of its conference proceedings have already been distributed throughout Europe and the Mediterranean Basin, as well as can be found on its Internet portal www.promet.org.gr in English and in Arabic www.promet.just.edu.jo.

For PROMET's final meeting organized in Athens, over 200 people (archaeologists, conservators, scientists, embassy officials) came to an event organized at the Benaki museum on Feb. 15, 2008 to hear the achievement's of the PROMET project. The event was heavily covered in the Greek newspapers and TV media, as well as press releases were sent out to the foreign press. What struck the press was the application of such innovative and portable techniques such as LIBS and micro-XRF to analyse important artifacts (see "Laser show on ancient metals" http://www.e-tipos.com/multimedia accessed Feb. 19/2008). Also, the application of plant extracts from countries representing the Mediterranean basin being developed and tested to preserve their cultural heritage as opposed to toxic inhibitors sold by the metals industry made a huge impact on the sustainability of the results of these EU projects.

Below is a description of the overall strategy to gain public awareness of the PROMET research, through press releases and newsletters, as well as the publications on an academic level.

2.2 Press Releases

Press releases and contact with the press were made for all three major events that took place during the PROMET project and are discussed in detail below:

2.2.1 The Cairo Conference February 25-March 1.

The Cairo conference was a pivotal conference regarding dissemination of information to the press. Cairo is a unique city sitting at a crossroads with the "West" and the "Arab countries" and for this reason, every news media in the world has some type of correspondent in Cairo. In addition, the Cairo conference marked the first time that the two years of research data that had been being compiled by the PROMET partners had finally reached a stage where everyone had some definite information that could be described in "lay language" to journalists.

To reach the Cairo media, the international media, and the media in each partner's country, with the active cooperation with the coordinator of the conference, Dr. Mohammed Abdel Harith of NILES at Cairo University who edited the information, a series of press releases were emailed to Cairo media, international media, and media in each partner's country starting two weeks before the conference:

- **Between 6-15 February 2007** The first press release announced and described the conference, and invited Cairo news correspondents to attend the opening ceremonies. This was sent to all Cairo media as well as to international media that had a science reporter. Phone calls were made to certain media in Cairo to make certain the email addresses were correct, and to alert them personally. (See Attachment: Cairo Media 1) Media included: Agence France Presse, Daily Star Egypt (International Herald Tribune), the McClatchy newspapers, Mirror, Reuters, Guardian, Zaman, El Halal, Middle East News Agency, Science Now, NY Times, Times Online, AP, Middle East News Service, World News Network. (See Attachment "Cairo Media 1")

- **21 February** A second press release was sent to all Cairo media, stating the time and place of the Opening Ceremonies and inviting them to meet the PROMET Partners. This was also sent to media in the individual countries who might have a reporter or a liaison in Cairo. These included: International Herald Tribune, Science Now, Reuters, Science Now, The Times World News, Guardian, Mirror, NY Times, World News Europe, Middle East News Service, UNESCO Press, Daily Star, Egypt, McClatchy Newspapers, AP, Agence France, Middle East News Agency, Al Helal, Jordan Agence France Press, Jordan Times, Al Bawaba, Syrian Arab News Agency, Syria times, Syria Today News Agency, Topix.net, Champress, AP Greece, Hurriyet, Daily Telegraph Greece, El Tiempo, Spanish News Agency EFE, Sipa Press, National Radio of Egypt, Cairo, Reuters Greece, Athens News Agency, Milliet, Anadoulou News Agency, Turkish Daily News, Al Rayah Magazine Cairo Office, Aujourd'hui Le Maroc, Liberation, Maroc, La Nouvelle Tribune, Maroc,Le Matin Maroc, La Gazette, Maroc, L'Opinion, the Malta Independent, Malta Times, Malta Star, Malta Today, AGI-Agenzia Giornalistica Italia, ItalPress News Agency, Agencia Giornalista Online, La Stampa. (See Attachment "Cairo Media 2, "The Email Addresses")

- **22-24 February 2007** An announcement of the conference was emailed to the media of countries whose PROMET scientists were attending the conference. These were approved by the scientists in that country before they were sent. Some of the scientists didn't approve it in time, so theirs was reviewed with them at the conference, revised, and emailed as the fourth press release, see below. This press release including the names and contact details of the partners, local researchers involved in the project, and a brief statement as to their specific work in the project. (See "Jordan Press inside Jordan"; "Malta press inside Malta", "Cairo Conference for Greece, "Spain")

- A final press release was sent to all countries whose PROMET partners attended the Cairo conference, stating the names of those who attended and a description of the metal antiquities in their country that is being studied by these partners.

Press attending the Cairo Conference:
Primarily Egyptian media came to the Opening Ceremonies of the Cairo Conference. These included:

- two television stations, "Orbit", and "The National TV network" filmed the entire opening ceremonies speeches and interviewed the coordinator of the conference, Dr. Harith, as well as several of the other partners who spoke Arabic.

- one print media, "Akbar", printed the information about the conference for two consecutive days during the conference, 26-27 February.

- “Radio Cairo—the European Service in Egypt”. A woman journalist from Radio Cairo spent hours at the conference on the second day. She became interested in the topic of women scientists from the Arab countries, so she interviewed all of the Arabic-speaking women scientists as well as several of the women scientists from the European Union.

Review of the media in each country regarding the Cairo Conference
Researching the press activity in each partner country was done via internet search engines, and by asking partners if they had spotted their names in their local media.

2.2.2 Press Releases regarding the assessment collaboration between Greek PROMET physicists/chemists and Jordanian and Syrian scientists, October 2007.

1. Setting up a working plan
During the workshop/meeting at Herakleon, Crete, scientists from Demokritos and the FORTH institute in Greece discussed the possibility and logistics of carrying out a visit by Greek scientists to the Jordanian and Syrian archeological sites, in order to use Greek developed laser and x-ray portable devices to analyse the coatings of the ancient metal artifacts belonging to two Jordanian and Syrian collections. The date was tentatively set for this event.

Following this meeting, a series of media planning meetings was carried out in Athens by Professor Argyropoulos, the Greek scientists involved, and the people who will be disseminating the information to the public. The results of the meetings were:

- a set of articles were drafted about the proposed voyage. After these are approved, they were sent to science reporters in international journals several months/weeks before the trip.

- a set of press releases were drafted for Greek, Jordanian, and Syrian news media. Once approved, they will be sent the weeks before the trip.

The trip and collaboration to Syria was covered by Syrian National TV and newspapers covered by the Syrian Arabic news agency www.sana.sy in Syria which has also electronic web site. Also the story was covered by the Arabic news sites: www.Moheat.com, www.souria.com, and www.news.bdr130.net

2.2.3. The Final Conference in Athens 2008

One-day PROMET conference, 15th of February 2008, Benaki Museum, Athens

The conference opened by Prof M.Bratakos, Vice-President of TEI, Mrs. P. Vasilopoulou, Director General of the Directorate of Antiquities and Cultural Heritage of the Ministry of Culture, Greece and Mr. N. Minos, Director of the Directorate of Conservation of Ancient and Modern Monuments. Following the opening speeches, Prof. Argyropoulos gave a presentation on the achievements of PROMET. The conference included presentations from different PROMET partners and was open to the public. Around two hundreded people attended.

The Ambassadors and Cultural Attaches in Greece of all the participating in PROMET countries were also invited. His Excellency, Mr. R. Vella-Laurentis, ambassador of Malta, Mr. K. Al-Ayoubi of the Syrian Embassy, Dr. Tarek Radwan Cultural Attache of the Egyptian embassy, Mrs. H. Aoune of the Morrocco embassy and the Cultural Attaches of the Jordanian, Turkish, Czech, French and Italian Embassies attended.

Prior to the conference, press releases were sent to Greek and Foreign press making use of the media list compiled in previous years. In that list new journalists of Greek newspapers and radio shows were added. All of the journalists were contacted not only via email but also by phone and were persuaded about the importance of such event and project of that scale. As a result, the conference was announced as a forthcoming event in several high profiled Greek newspapers.

There were also two major articles on the event. Mr. P. Panagiotakos, of Eleytheros tipos wrote an article on the project and its objectives and the presentations of the conference (http://www.e-tipos.com/newsitem?id=26346). Ms M. Adamopoulou of Ta-Nea also wrote an article on the project and included an interview with Mrs. Wafaa El-Saddik of the Cairo Museum that was given to her on the day of the conference and appeared as a full page in the newspaper.

The conference press releases were also sent to journalists of the participating countries, by the PROMET partners.

34 ● ET2 ΤΕΧΝΕΣ

Ημερίδα για το πρόγραμμα «Promet» όπου συμμετείχαν 21 εργαστήρια από χώρες της Ευρώπης και της Μεσογείου με καινοτόμες μεθόδους συντήρησης αρχαιοτήτων που στηρίχθηκαν στην ελληνική τεχνογνωσία

Λέιζερ σόου σε αρχαία μέταλλα

II. Future actions regarding publicity of PROMET

A major press release is planned for the PROMET book entitled Metals and Museums in the Mediterranean, edited by V. Argyropoulos, in September 2008. We expect a number of articles on the achievements of PROMET and publicity about the book internationally.

2.3 Newsletters and English Internet portal and Arabic Internet Site

The PROMET project could not have succeeded without the development and implementation of the Internet portal www.promet.org.gr (currently with 185 registered users representing 38 countries worldwide), an integrated information system allowing communication, control and exchange of information between the partners, European and Mediterranean Museum and Conservation Institutions. This tool was used by all the partners for housing the results of the project as well as other important information needed to carry out the deliverables of the project. The co-ordinator was able not only manage the project more efficiently, but also edit the material for dissemination purposes in the form of Newsletters.

Newsletters were written to highlight the events of the project and then automatically sent out to the 185 registered users. The co-ordinator also sent out the newsletter to interested parties in the field of conservation.

Through the newsletter, there were many requests for a copy of the Conference Proceedings of the PROMET project, which was distributed ‘freely’ world-wide.

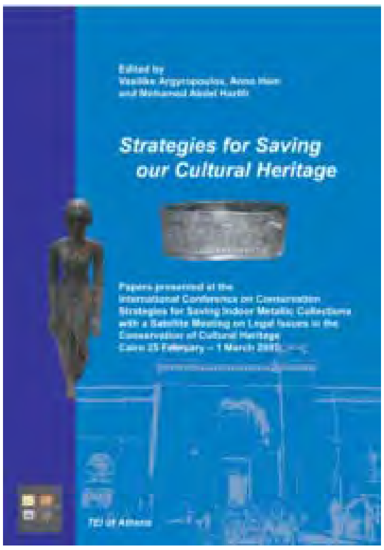
2.4 Consortium Publications

With such a large consortium and many project deliverables, it became important to highlight the project’s results in formal publications, one resulting from the project’s conference and the other an overall book directed toward museum professionals and the general public.

2.4.1 Conference Proceedings

The first *International Conference on Conservation Strategies for Saving Indoor Metallic Collections (CSSIM)* was held in Cairo from the 25 February to the 1 March 2007. Subjects of the CSSIM were development and applications of conservation strategies and related materials research with a special focus on new technologies in diagnostics of corrosion layers. The conference hosted a one day satellite meeting on *Legal Issues in the Conservation of Cultural Heritage* organized by the ICOM-CC Working Group Legal Issues in Conservation (LIC) as interim meeting with the subject *Realigning the Legal Vision*.

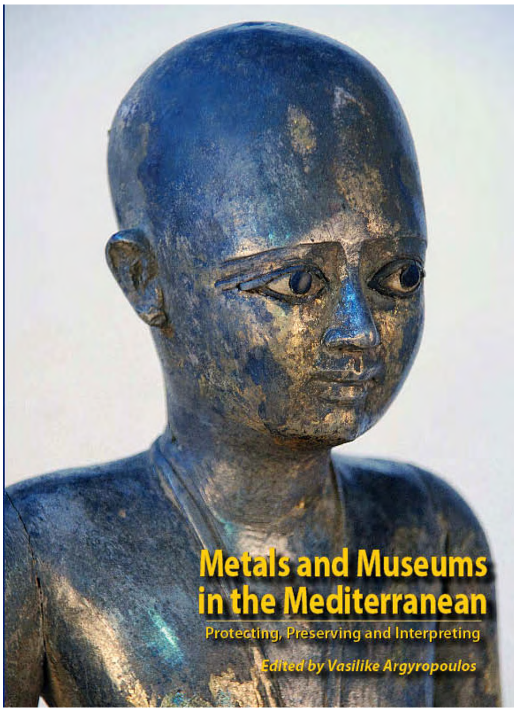
The international community was invited by Prof. Mohammed Abdel Harith from the Applied Laser Spectroscopy group (ALS) of the National Institute of Laser Enhanced Science at the Cairo University. Under the auspices of the European Union funded project PROMET Prof. Harith was chairing the conference together with the project's co-ordinator Prof. Vasilike Argyropoulos. The satellite meeting on Legal Issues in Conservation was coordinated by Sharon Little and Janet Hawley from the ICOM-CC LIC working group. 68 scholars from the Middle East, Europe, North America and Australia attended the conference, including conservation scientists, physicists, chemists and archaeologists. During the conference 42 oral presentations were given supplemented by 21 poster presentations. The proceedings present 42 full papers based on these presentations. The papers were all reviewed by members of the PROMET project. The papers for the section on Legal Issues in the Conservation of Cultural Heritage were reviewed by J. Hawley, S. Little and I.D. MacLeod.



1000 copies of the conference proceedings were produced by the TEI of Athens. Over 600 copies were distributed to all partners during the final meeting in Athens (February 2008) and worldwide. The partners were responsible for distributing the proceedings to libraries in their countries as well as interested parties. The coordinator was responsible for distributing the proceedings internationally to those who made a request in writing via email. The book was not sold and distributed freely.

2.4.2 PROMET Book

The book *Metals and Museums in the Mediterranean* was written to highlight the significance of ancient metallurgy and its products from the Mediterranean region, as well as its impact on world culture. Mediterranean experts from the field of Cultural Heritage collaborated together to examine, research, develop, and implement innovative products and materials to help preserve metals collections from the Mediterranean basin for future generations. Suitable conservation approaches that address the problems and meet the needs of these collections are essential to ensure that innovative products and materials developed and tested by research projects are sustainable.



The research strategy carried out by the international team for the PROMET project, who are specialists and stakeholders in the field of Cultural Heritage was implemented to improve the care of metal objects housed in museums according to the policies of their countries, with the available means to ensure sustainable results. Chapter 1 provides the state-of-the-art approach for the project. Chapter 2 discusses the impact of ancient metallurgy in the Mediterranean region by discussing three case studies in Anatolia, Egypt, and Syria. Chapters 3 and 4 of the book provide a context for the problems and needs of 12 museums and their metals collections under study for this project, as well as Chapter 4 presents the results of the survey of the collections. Chapter 5 gives a review of the application of routine non-destructive diagnostic techniques for assessing the condition of metal objects. The new and innovative techniques and safe corrosion inhibitors-coatings that were either developed or tested for this project are discussed in chapters 6 and 7 respectively. Finally, Chapter 8 summarises the conservation policies of the participating countries and available resources for the protection of their cultural property. An attached CD also provides a simple database for the documentation of metals objects from a collection, with some examples provided.

The editor of this book tried to ensure that the chapters of the book were written for any reader who is interested in the topic of Preservation of Cultural Heritage. However, Chapters 6 and 7 that discuss the innovative techniques and materials researched for this project were more technical in nature so as to satisfy the specialists in the field, who desire more information about our work that may not have been previously published in the scientific literature.

The book will be sold, but to date no signed agreement has been reached with a distributor. A publicity event is planned during the Fall of 2008 to highlight the closing of the project and the production of the book which highlights the results of the project.

2.4.3 Joint academic publications with contractors

Books

1. V. Argyropoulos, A. Hein and M.A. Harith (Eds.), *Strategies for Saving our Cultural Heritage - Papers presented at the International Conference on Conservation Strategies for Saving Indoor Metallic Collections with a Satellite Meeting on Legal Issues in the Conservation of Cultural Heritage, Cairo 25 February – 1 March 2007*, TEI of Athens, Athens, 2007.

2. V. Argyropoulos (Ed.), *Metals and Museums in the Mediterranean: Protecting, Preserving and Interpreting*, Athens, 2008.
CHAPTER 1 *by E. Angelini and V.Argyropoulos*
THE CONSERVATION PROBLEMS AND NEEDS OF MUSEUM COLLECTIONS
CHAPTER 2 *by V. Gouda, A. Çilingiroğlu, G.M. Ingo, T. De Caro and C. Riccucci*
THE IMPACT OF ANCIENT METALLURGY AND METAL CRAFTS IN THE MEDITERRANEAN REGION
CHAPTER 3 *by V. Argyropoulos*
PAST AND CURRENT CONSERVATION PRACTICES: THE NEED FOR INNOVATIVE AND INTEGRATED APPROACH
CHAPTER 4 *by V. Argyropoulos*
CONSERVATION DAMAGE ASSESSMENT OF METAL COLLECTIONS
CHAPTER 5 *by A. Hein and C. Degrigny*
THE APPLICATION OF NON-DESTRUCTIVE TECHNOLOGIES FOR THE DAMAGE ASSESSMENT OF METAL OBJECTS
CHAPTER 6 *by A.G. Karydas, D. Anglos and M.A. Harith*
MOBILE MICRO-XRF AND LIBS SPECTROMETERS FOR DIAGNOSTIC MICRO-ANALYSIS OF ANCIENT METAL OBJECTS
CHAPTER 7 *by C. Degrigny*
THE SEARCH FOR NEW AND SAFE MATERIALS FOR PROTECTING METAL OBJECTS
CHAPTER 8 *by V. Argyropoulos*
THE MAINTENANCE POLICY

Refereed Journals

3. E. Cano, D.M. Bastidas, V. Argyropoulos, S. Fajardo, A. Siatou, J.M. Bastidas and C. Degrigny, “Protection of steel artifacts using organic coatings doped with corrosion inhibitors”, Electrochimica Acta, *under review*.
4. Dermaj, N. Hajjaji, S. Joiret, K. Rahmouni, A. Srhiri, H. Takenouti,V. Vivier, “Electrochemical and spectroscopic evidences of corrosion inhibition of bronze by a triazole derivative”, Electrochimica Acta **52** (2007) 4654–4662
5. A. Elhassan, A. Giakoumaki , D. Anglos , G.M. Ingo , L. Robbiola , M. A. Harith, “Nanosecond and Femtosecond LIBS Analysis of Bronze Alloys”, Spectrochemica Acta B, **63** (2008) 504-511.
6. A. Elhassan, A. Giakoumaki , L. Fornarini , D. Anglos, R. Fantoni , M. A. Harith, ”Quantitative analysis of bronze alloys via nano and femto second LIBS”**,** submitted to Spectrochemica Acta B, *in press*.
7. A. Erdem, A. Cilingiroglu A. Giakoumaki, M. Castanys, E. Kartsonaki, D. Anglos and C. Fotakis, “Characterization of iron age pottery from Eastern Turkey by laser induced breakdown spectroscopy (LIBS)”, Journal of Archaeological Science, *in press*.
8. Ingo, G.M., Balbi, S., de Caro, T., Fragalà, I., Angelini, E., and Bultrini G., “Combined use of SEM-EDS, OM and XRD for the characterization of corrosion products grown on silver Roman coins”, *Applied Physics A*, 83 (2006) 493-97
9. Pouli, P., Melessanaki, K., Giakoumaki, A., Argyropoulos, V., Anglos, D., “Measuring the thickness of protective coatings on historic metal objects using nanosecond and femtosecond LIBS depth profiling”, Spectrochimica Acta B., Atomic Spectroscopy **60,** 7-8 (2005)1163-1171.

Conference Proceedings and Monographs

10. E. Angelini, S. Grassini, T. de Caro and G.M. Ingo, “Survey of the Italian Archaeological precious metal collections: characterization of the patina and study of the degradation phenomena”, in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 184-188.

11. *Argyropoulos, V., Giannoulaki, M., Anglos, D., Pouli, P., Harith, M.A., Elhassan, A., Karydas, A-G., Zarkadas, C., Kantarelou, V., Arafat, A., and Haddad, N., "Developing Innovative Portable Diagnostic Techniques and Approaches for the Analysis of Metal Artefacts from Museum Collections", In: Proceedings of the* 7th EC Conference*, Prague, May 2006.*
12. *Argyropoulos, V., Angelini, E., Al-Jarrah, O., Degrigny, C., Gouda, V., Ingo, G.M., and Giannoulaki, M, "The survey approach of museum collections: a priori step in the sustainable conservation for metal objects from the Mediterranean Basin", In: Proceedings of the* 7th EC Conference*, Prague, May 2006.*
13. *Argyropoulos, V., Angelini, E., and Degrigny, C., "Innovative conservation approaches for monitoring and protecting ancient and historic metals collections from the Mediterranean basin",* Metal04, *(eds. Ashton, J. and Hallam. D.), National Museum of Australia, Canberra, 2004, 43-52.*
14. Argyropoulos, V., Sakki, Z., Karydas, A.G., Zarkadas, C., Pouli, P., Melessanaki, K., Giakoumaki, A., Anglos, D., and Giannoulaki, M., "Problems in stabilizing historic iron-bladed weapons displayed in an uncontrolled environment in the Criminal Museum of Athens, Greece", *Preprints of ICOM-CC Triennial Meeting in the Hague*, Vol. 1, 2005, 293-300.
15. *V. Argyropoulos, D. Charalambous, A. Kaminari, A. Karabotsos, K. Polikreti, A. Siatou, E. Cano, D.M. Bastidas, I. Cayuela, J-M. Bastidas, C. Degrigny, D. Vella, J. Crawford and S. Golfomitsou. "Testing of a new wax coating poligen ES 91009 and corrosion inhibitor additives used for improving coatings for historic iron alloys", in C. Degrigny, R. van Langh, B. Ankersmit, I. Joosten (eds.)* METAL07, Proceedings of the ICOM-CC Metal WG interim meeting, Amsterdam, Book 5*, Amsterdam, 2007. 10-15*
16. E. Cano, J.M. Bastidas, V. Argyropoulos and A. Siatou, "Electrochemical techniques as a tool for testing the efficiency of protection systems for metallic artifacts", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 121-126.
17. Degrigny, C., Argyropoulos, V., Pouli, P., Grech, M., Kreislova, K., Harith, M., Mirambet, F., Karydas, A., Arafat, A., al Saad, Z., Angelini, E., Ingo, G., Vassiliou, P., Cano, E., Hajjaji, N., Almansour, A., and Letardi, P., "Innovative protection systems for large collection of metal artefacts conserved in the Mediterranean Basin – PROMET", In: Proceedings of the *7th EC Conference*, Prague, May 2006.
18. *C. Degrigny, V. Argyropoulos, P. Pouli, M. Grech, K. Kreislova, M.A., Harith, F. Mirambet, N. Haddad, E. Angelini, E. Cano, N. Hajjaji, A. Cilingoroglu, A. Almansour and L. Mahfoud, "The methodology for the PROMET project to develop / test new non-toxic corrosion inhibitors and coatings for iron and copper alloy objects housed in Mediterranean museums", in C. Degrigny, R. van Langh, B. Ankersmit, I. Joosten (eds.)* METAL07, Proceedings of the ICOM-CC Metal WG interim meeting, Amsterdam, Book 5*, Amsterdam, 2007, 31-37.*
19. *C. Degrigny, A.G. Karydas, S. Golfomitsou, V. Kantarelou, Ch. Zarkadas and D. Vella, "Methodology for the in-situ analyses of historic steel armours with portable milli and micro-XRF spectrometers", in C. Degrigny, R. van Langh, B. Ankersmit, I. Joosten (eds.)* METAL07, Proceedings of the ICOM-CC Metal WG interim meeting, Amsterdam, Book 2*, Amsterdam, 2007, 26-34.*
20. A. Elhassan, G. Cristoforetti, S. Lengaioli, V. Pallischi, A. Salivitti, E. Tognoni, G. Ingo, M.A. Harith, "LIBS Calibration Curves and Determination of Limits of Detection (LOD) in Single and Double Pulse Configuration for Quantitative LIBS Analysis of Bronzes", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 72-77.
21. M. Giannoulaki, V. Argyropoulos, G. Michalakakos, T. Panou, V. Kantalerou, C. Zarkadas, A.G. Karydas, V. Perdikatsis, and C. Apostolaki, "A conservation survey of museum metals collections using portable scientific techniques: A case study in the Museum of Ancient Messene, Greece". In Degrigny, C., R. van Langh, B. Ankersmit, I. Joosten (eds.)*METAL07 - Proceedings of the ICOM-CC Metal WG, Amsterdam Vol. 1*, Amsterdam: Rijksmuseum., 2007, 67-72.

22. S. Grassini, E. Angelini, R. D'Agostino, F. Palumbo, G.M. Ingo, "Advanced plasma treatment for cleaning and protecting precious metal artifacts" in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 127-31.
23. *H. Hammouch, A. Dermaj, N. Hajjaji, C. Degrigny and A. Srhiri., "Inhibition of the atmospheric corrosion of steel coupons simulating historic and archaeological iron based objects by cactus seeds extract", in C. Degrigny, R. van Langh, B. Ankersmit, I. Joosten (eds.)* METAL07, Proceedings of the ICOM-CC Metal WG interim meeting, Amsterdam, Book 5*, Amsterdam, 2007, 56-63.*
24. G.M. Ingo, G. Padeletti, E. Angelini, S. Grassini, T. de Caro, C. Riccucci, G. Guida, "Microchemical investigation of ancient silver and gold plated objects: coating techniques and degradation mechanisms", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 9-13.
25. V. Kantarelou, A.G. Karydas, Ch. Zarkadas, M. Giannoulaki and V. Argyropoulos, " Micro-XRF analysis of high tin bronze mirrors at the museum of Ancient Messene in Greece", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 93-99.
26. V. Kantarelou, Ch. Zarkadas, A. Giakoumaki, M. Giannoulaki, A.G. Karydas, D. Anglos and V. Argyropoulos, "A novel approach on the combined in-situ application of LIBS and µ-XRF spectrometers for the characterization of copper alloy corrosion products", in C. Degrigny, R. van Langh, I. Joosten and B. Ankersmit (eds.) *METAL07, Proceedings of the ICOM-CC Metal WG interim meeting, Amsterdam, Book 2*, Amsterdam, 2007, 35-41.
27. A.G. Karydas, X. Brecoulaki, Th. Pantazis, E. Aloupi, V. Argyropoulos, D. Kotzamani, R. Bernard, Ch. Zarkadas and Th Paradellis. "Importance of in-situ EDXRF measurements in the preservation and conservation of Material Culture", in M. Uda, G. Demortier and I. Nakai (eds.) *X-Rays for Archaeology*, Springer, 2005, 27-53.
28. Vella, D., Degrigny, C., Grech, M. and Williams, A., "Metallurgy of armour exhibited at the Palace Armoury, Valletta, Malta." In *Proceedings to the ICOM-CC Interim Metal Working Group meeting, Metal 2004*, Canberra, Australia, 3rd-8th October, 2004, 215-233
29. Vella, D; Degrigny, C., Grech, M., "A preliminary study of the morphology of corrosion developing onto historic steel armour artefacts from the Palace Armoury Collection, Valletta, Malta", in *Proceedings of the 14th triennial meeting of ICOM-CC,* The Hague, Netherlands, 2005, 317-325.
30. Williams, A., Vella, D., Giumlia-Mair, A., Degrigny, C. and Grech, M. "A novel *in-situ* approach for the examination of the microstructure of metal artifacts: Principles and application to iron-based armour elements". In A. Denker, A. Adriaens, M. Dowsett and A. Giumlia-Mair (eds.) *COST Action G8: non-destructive testing and analysis of museum object*, Stuttgart: Fraunhofer IRB Verlag, 2005, 9-15.

2.4.4 Individual academic publications per contractor

Refereed Journals

1. A. Brysbaert, K. Melessanaki, D. Anglos, "A new non-destructive approach to the pigment analysis of Bronze Age Aegean and Eastern Mediterranean painted plaster by means of LIBS" Journal of Archaeological Science 33, 1095-1104 (**2006**)
2. K. Essalah, F. Said, M. Benlmassoud, N. Hajjaji, M. Aouial, H. Takenouti, A. Srhiri, "Corrosion of copper nickel alloy in 3% NaCl solution in presence of bitriazole." *Phys. Chem. News* **23** (2005) 108 – 118.
3. A. Giakoumaki, I. Osticioli, D. Anglos, "Spectroscopic analysis using a hybrid LIBS-Raman system"; Appl. Phys. A 83, 537-541 (**2006**)
4. J. Goujon, A. Giakoumaki, V. Pinon, O. Musset, D. Anglos and E. Georgiou, *Comparison of single and double pulse LIBS measurements with a new compact laser for portable applications*, Spectrochimica Acta B, *in press*.
5. B. Kanngießer, A.-G. Karydas, R. Schütz, D. Sokaras, I. Reiche, S. Röhrs, L. Pichon, J.h Salomon. *3D Micro-PIXE at atmospheric Pressure: A New Tool for the Investigation of*

Art and Archaeological Objects, Nucl. Instr. and Meth. In Phys. Res. B, 264 (2), 383-388, (2007)

6. A.G. Karydas. "Self-Element Secondary Fluorescence Enhancement in XRFA." *X-Ray Spectrometry* **34**, (2005) 426.
7. A.G. Karydas. Application of a portable XRF spectrometer in the analysis of museum metal collections. Annali di Chimica 97 (7), pp. 419-432, (**2007**)
8. A.G. Karydas, D. Sokaras, C. Zarkadas, N. Grlj, P. Pelicon, M. Žitnik, R. Schütz, W. Malzer and B. Kanngießer 3D Micro PIXE – a new technique for depth resolved elemental analysis, J Anal At Spectrom **22**, (2007) 1260–1265.
9. M. Kavčič, A.G. Karydas and Ch. Zarkadas. Chemical state analysis employing sub-natural linewidth resolution PIXE measurement of Ka diagram line. X-Ray Spectrometry, 34, 310, (2005).
10. Ingo, G.M., Balbi, S., de Caro, T., Fragalà, I., Riccucci C., and Bultrini G., "Microchemical investigation of Greek and Roman silver and gold plated coins: Coating techniques and corrosion mechanisms", *Applied Physics A*, 83 (2006) 623-29.
11. M. A. Ismail, H. Imam, A. Elhassan, W. T. Youniss and M. A. Harith, "Study of LIBS limit of detection and plasma parameters of some elements in two different metallic matrices", *Anal. At. Spectrom*. **19**, 2004, 489 – 494.
12. L. Pappalardo, A. G. Karydas, N. Kotzamani, G. Pappalardo, F. P. Romano and Ch. Zarkadas. "Non-destructive, *in-situ* characterization of gemstones on museum jewels. The complementary use of PIXE-alpha and XRF portable system." *Nucl. Instr. Meth. B* **239**, (2005) 114.
13. V. Pinon, C. Fotakis, G. Nicolas, D. Anglos, *Double pulse LIBS with femtosecond laser pulses*, Spectrochimica Acta B, under review
14. Potiriadis, A.G. Karydas, Ch. Zarkadas, A. Clouvas. "A Study of PIXE Continuum Polarization Properties." X-Ray Spectrometry **34**, (2005) 335.
15. S. Tzortzakis, D. Gray, D. Anglos, "Femtosecond laser filaments enable remote LIBS analysis with potential applications in the monitoring of sculpture and monuments" Optics Letters 31, 1139-1141 (**2006**)

Conference Proceedings and Monographs

16. O. Abdel-Kareem and Z. Al Saad, "Conservation strategy of metal embroidery threads in textile objects in Museum of Jordanian Heritage" in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 23-30.
17. Z. Ait Chikh, D. Chebabe, A. Dermaj, N, Hajjaji and A. Srhiri, "Study of the dezincification of alloy 60Cu-Zn in 3% NaCl solution using spectroscopic techniques", *Proceedings of the 10^th European Symposium on Scale Inhibitors (10 SEIC)*, Ann.Univ. Ferrara, N.S., Sez. V, Suppl. N. 12, 2005. 819-830.
18. Z. Al-Saad and M. Bani Hani. "Corrosion behavior and preservation of Islamic Silver Coins", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 177-183.
19. A. Alshami, N. Haddad and A. Arafat, "The Role of the Department of Antiquities of Jordan in Preventing the Illicit Trade of Cultural Heritage", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 194-198.
20. Angelini E., Grassini S., Corbellini S. and Parvis M., "Monitoring of patinas and coatings protective effectiveness by means of a new EIS portable instrument", *Proceedings of Art 2005* (8^th International Conference on " Non-destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage), Lecce 15-19 May 2005.
21. Angelini E., Grassini S., Corbellini S. And Biscontin G., Evaluation of the conservation state of the railing of Palazzo Reale in Torino, *Proceedings of Eurocorr 2005, Lisboa (Portugal), 4-8 september 2005*.

22. Angelini E., d'Agostino R., Fracassi F., Grassini S., Laera S., Palumbo F. and Rosalbino F., Plasma processes as new conservation treatment for works of art. The case of precious metal artefacts, *Proceedings of 17th ISPC, International Symposium on Plasma Chemistry, 7-12 August 2005, Toronto Canada*.
23. V. Argyropoulos, M. Giannoulaki, G.P. Michalakakos and A. Siatou, " A survey of the types of corrosion inhibitors and protective coatings used for the conservation of metal objects from museum collections in the Mediterranean Basin"**,** in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 166-170.
24. S. Chlouveraki, K. Melessanaki and D. Anglos*, "*LIBS as an identification and documentation tool in the conservation process: applications at the W.D.E. Coulson Conservation Laboratory, INSTAP-SCEC*"***,** in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 46-52.
25. J. Crawford, C. Degrigny, Q. Glorieux, P. Bugeja and D. Vella. "A Standardised Remote Monitoring Photographic Capture System (RMPCS) for in-situ documentation of corrosion protection system Tests", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 85-92.
26. C. Degrigny, D. Vella, S. Golfomitsou and J. Crawford. "Characterisation of corrosion product layers on atmospherically corroded ferrous artefacts: application to the armour of the Palace Armoury, Valletta, Malta", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 31-39.
27. A. Dermaj, D. Chebabe, N. Hajjaji, S. Joiret, K. Rahmouni, A. Srhiri, H. Takenouti, V. Vivier., "Etude de la corrosion du bronze Cu-8%Sn et de l'effet inhibiteur du 3-phényl 1,2,4-triazole-5-thione", *Acte du 17ème Forum sur les Impédances Electrochimiques*, C. Gabrielli (ed.), Paris (2005) 257-268.
28. A. Dermaj, D. Chebabe, H. Hammouch, M. Goursa, N. Hajjaji and A. Srhiri, "Atmospheric Corrosion inhibition of historical steel by FPTS formulation based of triazole-thione". in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 143-148.
29. M. Giannoulaki, V. Argyropoulos, T. Panou, A. Moundrea-Agrafioti, and P. Themelis, "The feasibility of using portable X-ray radiography for the examination of the technology and the condition of a metals collection housed in the Museum of Ancient Messene, Greece". In Szmelter, B. and A. Lopuska (eds.) *Art Conservation-Restoration: Studies and Practice Vol VII*, Torun: Nicolaus Copernicus University, 2007, 163-176.
30. V.K. Gouda, E.Elbradie, M. Eldamaty, "Survey of Precious Metal Production in Ancient Egypt", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 14-22.
31. N. Haddad, A. Arafat and B. Sallam, "Current Conservation Practices of Metallic Objects at Archaeological Sites in Jordan", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 162-180.
32. N. Hajjaji, F. El Harrif, C. Kaouane, A. Srhiri, H. Takenouti and K. Rahmouni, "Conservation Problems and New Method of Protection: Case of Bronzes at the Archaeological Museum in Rabat", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 138-142.
33. H. Hammouch, A. Dermaj, M. Goursa, N. Hajjaji and A. Srhiri, "New corrosion inhibitor containing Opuntia ficus indica seed extract", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 149-155.
34. S. Hollner, F. Mirambet, E. Rocca, A. Texier, and J. Steinmetz, **"**Development of new non toxic inhibitors for iron and copper based artefact from cultural heritage**"**. in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 156-161.
35. S. Hollner, F. Mirambet, E. Rocca, J. Steinmetz, "Environmentally-friendly treatments for the protection of iron artefacts of the cultural heritage against atmospheric corrosion". in C. Degrigny, R. van Langh, B. Ankersmit, I. Joosten (eds.) *METAL07, Proceedings of the ICOM-CC Metal WG interim meeting, Amsterdam, Book 5*, Amsterdam, 2007, 64-70.

36. D. Knotkova. K. Kreislova, B. Kreibichova and I. Kudlacek, "Indoor corrosivity in the National Museum Depository, Prague, the Czech Republic", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 64-71.
37. J. Novakovic and P. Vassiliou, "Corrosion of Silver Alloy Artefacts in Soil", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 58-63.
38. J. Novakovic, P. Vassiliou and Kl. Samara, "Copper Alloys And Silver Artefacts Protection By Coatings With Nano-Alumina Pigments", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 132-137.
39. J. Novakovic and P. Vassiliou, "Environmental effects on silver artifacts", in *Proceedings of the 6th Hellenic Chemical Engineering Conference*, Athens, 2007, pp. 185-188
40. J. Novakovic and P. Vassiliou, "Marine and Urban Environment Effects on Silver Alloy Artefacts", in *Proceedings of the IX YUCORR Conference, Tara, Serbia, 21-25 May 2007*, p. 162
41. P. Pouli, A. Nevin and A. Andreotti, "Lasers in the analysis and conservation of Cultural Heritage; state of the art and new trends", in M. Perla Colombini and L. Tassi (eds.) *New Trends in Analytical, Environmental and Cultural Heritage Chemistry*, 2008.
42. Siatou, A., Argyropoulos, V., and Charalambous, D., "Testing new corrosion inhibitor additives and coating for the long-term protection of metal collections in indoor uncontrolled environment", In Szmelter, B. and A. Lopuska (eds.) *Art Conservation-Restoration: Studies and Practice Vol VII*, Torun: Nicolaus Copernicus University, 2007, 177-191.
43. A. Siatou, V. Argyropoulos, D. Charalambous, A. Kaminari and K. Polikreti, "Testing new coating systems for the long-term protection of metal collections exposed in uncontrolled museum environment", in V. Argyropoulos, A. Hein and M.A. Harith (eds.) *Strategies for Saving our Cultural Heritage*, Athens, 2007, 115-120.

3. Final Plan for using and Disseminating the knowledge

3.1 Exploitable Knowledge and its Use:

Exploitable Knowledge (description)	**Exploitable product(s) or measure(s)**	**Sector(s)** of application	Timetable for commercial use	Patents or other IPR protection	**Owner** & Other Partner(s) involved
1. Methodology for LIBS analysis of metal objects and common corrosion layers		**1.** Cultural Heritage objects **2.** Industrial inspection	By the end of the PROMET project (31 Oct. 2007)		Participant **P2,** IESL-FORTH Participant **P8,** NILES
	2. A fully-portable LIBS instrument ($LM_{NT}II$) that enables analysis of the objects at their location	**1.** Cultural Heritage objects **2.** Industrial inspection	By the end of the PROMET project (31 Oct. 2007)		Participant **P2** IESL-FORTH
3. Methodology for combination of LIBS analysis with other alternative analytical techniques, such as laser Raman spectroscopy and/or laser ablation mass analysis for the analysis of metal objects of CH value	A set-up that enables LIBS and Raman analysis	**1.** Cultural Heritage objects **2.** Industrial inspection	By the end of the PROMET project		Participant **P2** IESL-FORTH
4. Methodology for the complementary use of the portable LIBS and μ-XRF analytical instruments developed through PROMET		**1.** Cultural Heritage objects **2.** Industrial inspection	By the end of the PROMET project		Participant **P2** IESL-FORTH Participant **P10** Democritos
5. Methodology for measuring the thickness of the protective coatings applied on metal objects using LIBS analysis	A descriptive and well established protocol to measure protective coatings thickness by means of LIBS	**1.** Cultural Heritage objects **2.** Industrial inspection	By the end of the PROMET project		Participant **P2** IESL-FORTH in collaboration with **P1, P3, P4, P7, P9, P13, P15, P16, P17, P20, P22**
Manufacturing of artificial coupons that mimic the behaviour of real artefacts for the study of corrosion mechanisms and application of coating	Steel alloys in the form of coupons that can be artificially or naturally corroded in any environmental conditions	1.Corrosion science 2. Engineering / Tooling 3. Materials & Metallurgy	N/A	N/A	DMME, HM,
Artificial accelerated corrosion tests	Steel alloys in the form of coupons				DMME
Protection of surfaces of steel components against corrosion	Steel alloys (Coupons & Engineering Components)	1.Conservation 2.Engineering / Tooling 3.Restoration 4.Archaelogical			DMME
Manufacturing of artificial coupons that mimic the behaviour of real artefacts for the study of corrosion mechanisms and application of coating	Steel alloys in the form of coupons that can be artificially or naturally corroded in any environmental conditions	1.Corrosion science 2. Engineering / Tooling 3. Materials & Metallurgy	N/A	N/A	DMME, HM,

Artificial accelerated corrosion tests	Steel alloys in the form of coupons				DMME
Protection of surfaces of steel components against corrosion	Steel alloys (Coupons & Engineering Components)	1.Conservation 2.Engineering / Tooling 3.Restoration 4.Archaelogical			DMME
Manufacturing of artificial coupons that mimic the behaviour of real artefacts for the study of corrosion mechanisms and application of coating	Steel alloys in the form of coupons that can be artificially or naturally corroded in any environmental conditions	1.Corrosion science 2. Engineering / Tooling 3. Materials & Metallurgy	N/A	N/A	DMME, HM,
Artificial accelerated corrosion tests	Steel alloys in the form of coupons				DMME
Production of silver based reference alloys whose chemical composition and metallurgical features are similar to the ancient ones	*Silver based reference alloys*	- Conservation of metal ancient objects. - Standard materials	2009	---	ISMN-CNR, NTUA, POLITO
Production and use of degraded silver based reference alloys whose chemical composition, metallurgical features and corrosion products are similar to the ancient ones and can be used for testing materials and methods for conservation	*Degraded silver based reference alloys*	- Conservation of metal ancient objects. - Standard materials.	2009	---	ISMN-CNR, NTUA, POLITO
Understanding silver based artefacts degradation occurring during archaeological burial	*Contribution to the design of inhibiting materials*	Conservation of metal ancient objects	2009	---	ISMN-CNR
Production of silver based reference alloys whose chemical composition and metallurgical features are similar to the ancient ones	*Silver based reference alloys*	- Conservation of metal ancient objects. - Standard materials	2009	---	ISMN-CNR, NTUA, POLITO
Production and use of degraded silver based reference alloys whose chemical composition, metallurgical features and corrosion products are similar to the ancient ones and can be used for testing materials and methods for conservation	*Degraded silver based reference alloys*	- Conservation of metal ancient objects. - Standard materials.	2009	---	ISMN-CNR, NTUA, POLITO
Use of artificial coupons that mimic the behaviour of real artefacts for the	Steel, copper and silver based alloys in the form of coupons that can	- Corrosion science - Conservation science	N/a	N/a	**HM, SVUOM, CNR-ISMN and NTUA**

study of corrosion mechanisms and the development of conservation treatments	be artificially or naturally corroded in any environmental conditions				
Protection of silver surfaces by nano aloumina in Paraloid protective coatings	Copper alloys Silver alloys	-Conservation -Protection of silver objects -electronics -Art sector	-	-	**NTUA**
Artificial accelerated ageing of silver alloys	Silver alloys				**NTUA**
Protection of silver surfaces by nano aloumina in Paraloid protective coatings	Copper alloys Silver alloys	-Conservation -Protection of silver objects -electronics -Art sector	-	-	**NTUA**
Protection of silver surface by the use of SUVOM Silane A-coating	Silver – Copper Alloys, Silver alloys, silver	Metal Conservation			**SVUOM, YU-FAA**
Use of artificial coupons that mimic the behaviour of real artefacts for the study of corrosion mechanisms and the development of conservation treatments	The possibility of studying the effect of various environments on metals and metals alloys	- Conservation of cultural héritage & Metal corrosion	-	-	
Artificial accelerated ageing of silver alloys	Different types of silver alloys				**YU-FAA** ***(see procedure for sulphur test developed by YU-FAA)***
Use of electrochemical techniques for the characterization of protection systems for metallic heritage		*Conservation science* *Corrosion science*	*n/a*	*n/a*	***CENIM-CSIC***
Use of Poligen ES91009 for the protection of iron based historical artifacts	Poligen ES91009	Conservation and restoration	n/a	n/a	TEI, CENIM-CSIC and other PROMET partners
Methodology for optimizing the micro-XRF analysis of metal alloys		**1.** Cultural Heritage objects **2.** Industrial inspection	By the end of the PROMET project (30-4-2008)		Participant **P10,** NCSR DEMOKRITOS
Analysis protocols for the characterization of metal corrosion products		**1.** Cultural Heritage objects (Diagnosis and preventive conservation) **2.** Industrial inspection	By the end of the PROMET project (30-4-2008)		Participant **P10,** NCSR DEMOKRITOS with partners involved P1, P2, P3, P7P, P12, P13, P15, P24, P25
Experimental procedure for the determination of the X-ray lens transmission efficiency	**4.** Software that supports the determination of the X-ray lens transmission efficiency	Industrial-Manufacture sector of XRF spectrometers and of X-Ray optics			Participant **P10,** NCSR DEMOKRITOS
Methodology for optimizing the micro-XRF analysis of metal alloys		**1.** Cultural Heritage objects **2.** Industrial inspection	By the end of the PROMET project (30-4-2008)		Participant **P10,** NCSR DEMOKRITOS
	5. Software for the quantitative micro-XRF analysis	Industrial-Manufacture sector of XRF spectrometers	By the end of the PROMET project (30-4-2008)		Participant **P10,** NCSR DEMOKRITOS
	6. A transportable	**1.** Cultural			Participant **P10,**

	micro-XRF instrument with implemented analysis and data evaluation software	Heritage objects **2.** Industrial inspection **3.** Geoscience **4.**Environmental samples (Toxic element assessment)			NCSR DEMOKRITOS
Methodology for the complementary use of the portable LIBS and μ-XRF analytical instruments developed through PROMET		**1.** Cultural Heritage objects **2.** Industrial inspection	By the end of the PROMET project (30-4-2008)		Participant **P10** Democritos with Participant **P2** IESL-FORTH

3.2 Dissemination of knowledge

Overview table

Planned/actual Dates	**Type**	**Type of audience**	**Countries addressed**	**Size of audience**	**Partner responsible /involved**
May 2006	*Conference* **7th EC Conference** "Safeguarded Cultural Heritage. Understanding & Viability for the Enlarged Europe"	Research, *Professionals in conservation* European committee officers	European		*All PROMET*
Sep2006	*Conference* **LIBS 2006**	*Research*	Worldwide		*P2, P8*
Sep 2007	*Conference* **METAL 2007**	*Professionals in Metals conservation*	Worldwide	*400*	*P2, P1, P10*
Sep 2007	*Conference* **LACONA VII**	*Applied Research on the use of lasers in conservation, Professionals in conservation*	Worldwide	*500*	*P2, P1, P10*
Sep 2007	*Conference* **LIBS 2007**	*Research*	Worldwide		*P2, P8*
May 2007	*Conference* **EMRS 2007**	*Research*	European	*300*	*P2, P1, P10*
Feb 2007	*Conference* ***CSSIM***	*Professionals in Metals conservation*	Worldwide		*All partners*
Nov 2005	*Exhibition* **CER2005**	Research, European committee officers	European		*P1,P2, P10*
2004-2008	*Publications*	*Research*	Worldwide	*unlimited*	*P2, P1, P8, P10, P16, P15, P23*
Apr 2005	Press:The Times (Malta)	General public	Malta	?	HM
May 2005	Press: TheTimes (Malta)	General public	Malta	?	HM
Sep 2005	Triennial conference of ICOM-CC / paper	Conservation professionals	Worldwide	50	HM
2004-2008	ICOM-CC web-site and Metal homepage: regular update on PROMET outcomes	Conservation professionals	International	750	

Apr 2005	Press:The Times (Malta)	General public	Malta	?	HM
Oct 2005	Two contributions presented at the European Materials Research Society, Spring Meeting Symposium dedicated to “Materials Science and Cultural Heritage”, Strasbourg (France) 28 May-2 June 2005 + two papers submitted to Applied Physiscs A	Conservation professionals and material scientists	Europe et al	400	ISMN-CNR, POLITO
Oct 2008	One paper submitted to the !7th International Corrosion Congress in Las Vegas	Corrosion scientists	USA	2000	ISMN-CNR, NTUA
Apr 2008	Paper submitted to MetalEspaña 08, Congreso de Conservación y Restauración del Patrimonio Metálico	Conservators-restorers, conservation scientists, curators	Spain	~180	**CENIM-CSIC** / TEI
2007-2008	Several informal meetings with curators and conservators of Spanish museums and institutions	Conservators-restorers, curators	Spain		**CENIM-CSIC**
Mar 2007	Public Presentation	University Staff, Academics, and students	Syria	200	ALP-ME
Apr 2007	Report in Arabic	University Board	Syria	50	ALP-ME
Oct 2005	European Workshop on Quantitative Analysis in X-Ray Fluorescence Spectrometry, Ghent, Belgium	Research	Worldwide, but mostly European	*50*	*P10*
Jun 2006	European X-Ray Spectrometry Conference		Worldwide, but mostly European	*300*	*P10*
Feb 2008	*Press release, Eleutheros Typos*	*General Public*	Greek	*200000*	*P10, P1, P2*
Jun 2008	*Press release, Eleutheros typos*	*General Public*	Greek	*200000*	*P10*

2.3. Publishable results

1. Optimization of LIBS analysis following studies on different laser parameters (operative wavelength, laser pulse duration), set-ups (i.e. double pulse configurations) and methodologies (i.e. investigation on quantitative results).

- Possible market application

The optimisation of the LIBS analysis conditions and parameters is significant not only for applications on Cultural Heritage analysis but also on industrial inspection and scientific advance.

- Stage of development
- Collaborators

This work was a collaborative effort of FORTH with NILES

- Intellectual property rights

N/A

2. The design, development and construction of a portable and user-friendly LIBS system for metal surface analysis which was able to overcome many practical issues and successfully take LIBS technology outside the research laboratory into real case archaeological analysis applications.

- Possible market application

The development of a portable and user-friendly LIBS system for metal surface analysis is important not only for applications on Cultural Heritage analysis but also on industrial inspection and scientific advance.

- Stage of development

The developed prototype, LMNT II, has been successfully tested on site.

- Collaborators

FORTH only

- Intellectual property rights

FORTH holds the intellectual property rights for the design, construction and development of the Portable LIBS system, LM NT II.

3. Research on the development of a hybrid LIBS-Raman system, aiming to combine LIBS analysis with laser Raman spectroscopy.

- Possible market application

The possibility to combine LIBS analysis with laser Raman spectroscopy in a hybrid LIBS-Raman system is expected to have an impact not only for applications on Cultural Heritage analysis but also on industrial inspection and scientific advance.

- Stage of development

Under research

- Collaborators

FORTH only

- Intellectual property rights

N/A

4. The potential of using the LIBS analytical methodology to measure the thickness of the various protective coatings usually encountered on metal objects.

- Possible market application

The potential use of LIBS analytical methodology to measure the thickness of various protective coatings usually encountered on metal objects is expected to have an impact not only for applications on Cultural Heritage analysis but also on industrial inspection and scientific advance.

- Stage of development

Under research

- Collaborators

This work is a collaborative effort of FORTH with TEI

- Intellectual property rights

N/A

5. Use of artificial coupons that mimic the behaviour of real artefacts for the study of corrosion mechanisms and the development of conservation treatments and materials
Possible market application:
- Corrosion science and conservation science

Stage of development:
complete
Collaborators:
POLITO, CNR-ISMN and NTUA
Intellectual property rights: -

6. Protection of silver surfaces where bronze disease is occurring by organic inhibitors

Possible market application:
Conservation -Protection of silver objects
Stage of development:
complete
Collaborators: -
Intellectual property rights: -

7. Artificial accelerated ageing of silver-based alloys
Possible market application:
Corrosion and conservation science
Stage of development: complete
Collaborators: NTUA, POLITO
Intellectual property rights: -

8. Protection of iron and copper based samples with new non
toxic corrosion inhibitors
• Possible market application: Conservation -Protection of iron and copper based objects,
• Application industriel
• Stage of development: complete
• Collaborators: LRMH
• Intellectual property rights: -

9. Methodology for optimizing the micro-XRF analysis of metal alloys

- *Possible market application*

The methodology can be implemented in commercial micro-XRF spectrometers providing analysis protocols to be used by end-users in various disciplines.

- *Stage of development*

The analysis protocols have been already applied and assessed in numerous of applications. The next stage is to incorporate them in commercial analysis software.

- *Collaborators*

NCSR “Demokritos” only

- *Intellectual property rights*

N/A

10. Analysis protocols for the characterization of metal corrosion products

- *Possible market application*

The methodology can be implemented in commercial micro-XRF spectrometers providing analysis protocols to be used by end-users (conservators).

- *Stage of development*

The analysis protocols have been already applied and assessed in numerous of applications related to the characterization of metal corrosion products. The next stage is to integrate them in commercial analysis software.

- *Collaborators*

NCSR “Demokritos” only

- *Intellectual property rights*

N/A

11. Experimental procedure for the determination of the X-ray lens transmission efficiency and software that supports the determination of the X-ray lens transmission efficiency.
Possible market application
The methodology can be implemented in commercial micro-XRF spectrometers in order the end-user to be able with simple steps to determine experimentally the lens transmission efficiency. The benefit of the proposed methodology is that it does not require any removal of the X-ray lens from the set-up in order to measure its transmission efficiency, so that there is no risk for producing any misalignment by putting the lens back in the XRF configuration. That’s why it seems very attractive for commercial developers.

- *Stage of development*

The methodology has been almost completed, but few aspects are still under research. Nevertheless, the methodology established up to now is ready to be adapted in commercial micro-XRF spectrometers.

- *Collaborators*

NCSR “Demokritos” only

- *Intellectual property rights*

N/A

12. A transportable micro-XRF instrument with implemented analysis and data evaluation software

- *Possible market application*

Analysis and data evaluation software are ready to be adapted in commercial units.

- *Stage of development*

The application of the micro-XRF for metal alloys has been completed and carefully assessed. For other type of materials the work is in progress.

- *Collaborators*

NCSR “Demokritos” only

Appendix

Workpackage progress of the third reporting period

Work-package No[4]	Workpackage title	Lead contractor No[5]	Person-months[6]	Start month[7]	End month[8]	Deliv-erable No[9]
1	PROJECT MANAGEMENT	1	22	1	43	15
2	DOCUMENTATION AND MONITORING OF METALS COLLECTIONS	14	418	1	43	20
3	DEVELOPMENT OF SAFE COATINGS AND CORROSION INHIBITORS FOR THE PROTECTION OF METALS COLLECTIONS	3	401.5	1	43	24
4	PREVENTIVE STRATEGIES FOR SAVING METALS COLLECTIONS	1	164.5	1	43	7
	TOTAL		1006			

[4] Workpackage number: WP 1 – WP n.
[5] Number of the contractor leading the work in this workpackage.
[6] The total number of person-months allocated to each workpackage.
[7] Relative start date for the work in the specific workpackages, month 0 marking the start of the project, and all other start dates being relative to this start date.
[8] Relative end date, month 0 marking the start of the project, and all ends dates being relative to this start date.
[9] Deliverable number: Number for the deliverable(s)/result(s) mentioned in the workpackage: D1 - Dn.

List of Deliverables for the third reporting period

	Deliverable name	Work Package	date due	delivery date	esimated person months	used person months	lead contractor
D 1.5	Interim Activity reports	1	30	30	1	1	1
D 1.9	21 Audit certificates	1	36	43	1	1	1
D 1.15	Periodic Internal Evaluation reports	1	30	30	1	1	1
D 2-1	A detailed database of spectra and collections of characteristic finger print atomic emission lines for each substrate and encrustation type	2	24	24	24	24	2
D 2-2	Optimized ready to use working parameters	2	24	24	24	24	2
D 2-3	Software for the integration of the individual components to the system	2	24	24	63	63	2
D 2-4	A functional prototype LIBS instrument for reliable analysis of metal objects in-*situ*.	2	36	36	63	63	2
D 2-5	The technical file of the prototype LIBS instrument	2	36	36	63	63	2
D 2-6	Laboratory set-up for complementary characterisation of relevant metal objects using optical emission (LIBS) and Mass Spectrometric analysis.	2	36	36	24	24	2
D 2-7	A prototype µ-XRF portable spectrometer, optimised for the compositional analysis of metal objects	2	27	28	30	39.9	10
D 2-8	Quantification procedures supported by appropriate software packages for fast and almost real time-basis compositional analysis	2	30	31	30	39.9	10
D 2-9	Analytical methodologies for the non-destructive µ-XRF characterisation of various metal-corrosion surface layers	2	27	28	12	13	10
D 2-10	Database of XRF spectra from various metal-corrosion products	2	32	32	12	13	10
D 2.14	Analytical and/or documentation reports that analyze and document a representative sample of the collection to determine the problems and needs. (month 20 and 30)	2	30	30	79.5	83.5	14
D 2.15	Comparative reports to determine the advantages, complementarity and limitations of the analytical techniques developed through WP2	2	31	31	79.5	83.5	14
D 2.16	Analytical and/or documentation reports that compare the results and findings of the survey in Task 2.7.	2	30	30	44.5	46	14
D 2.17	Report on the physical-chemical characterisation of the selected artefacts of the Mediterranean Countries participating to the project	2	25	25	63	73	14
D 2.18	Data base with the results of the characterization of the artefacts and the results of the investigation carried out using laboratory and portable equipments with the comparison between the results obtained using different techniques	2	30	30	63	73	14
D 2-19	Data on the ancient manufacturing techniques employed for the production of the selected artefacts	2	31	31	25	30	14
D 2.20	A report that identifies the problems and needs for each collection surveyed.	2	32	36	27	31	14
D 3-5	Protocols for the acceleration corrosion tests according to the materials considered	3	7	26	16	17	3
D 3-15	Protocols for the conditions of application of new coatings and corrosion inhibitors	3	35	30	60.5	70	3
D 3.16	rating of coatings and corrosion inhibitors	3	35	35	51	54.5	3
D 3.17	definition of protocols of application for protection systems selected	3	35	35	51	54.5	3

D 3.19	exposure in real conditions of coupons aged naturally and covered with protection systems	3	33	33	25	27	3
D 3.20	definition of a monitoring program during exposure to control the effectiveness of the protection systems	3	33	33	25	27	3
D 3.21	assessment of the protection systems tested	3	35	35	36.5	42	3
D 3.22	rating of corrosion inhibitors and coatings according to the participating countries	3	35	35	36.5	42	3
D 3.23	assessment of the protection systems tested in real conditions	3	35	35	63	70	3
D 3.24	report with guidelines on which protection system to use according to the countries and the materials considered (database)	3	35	35	63	70	3
D 4.3	Conference on a Preventive Strategy for Saving Metals Collection	4	30	28	20.5	21	1
D 4.4	1000 Books for distribution	4	36	39	12.5	13.5	1
D 4.5	Report of the studies from each participating country	4	32	44	24	24	1
D 4.6	Publication of 1000 Guides with accompanying CD ROMs for distribution.	4	36	44	29.5	34	1
D 4.7	PROMET website in English and Arabic	4	30, 36	30,36	47	57	1

List of Milestones for the third reporting period

Milestone	Milestone name	Workpackage	Date due	Actual delivery date	Lead contractor
M 1.4	Two review meetings Functional monitoring and reporting to the Commission	1	30,36	28,40	1
M 2.1	To explicitly state the operational parameters of the LIBS set-up for the analysis of various metal surfaces and their corrosion products	2	24	24	2
M 2.2	To investigate the operational parameters (e.g. fibre optics, integration soft- and hard-ware and user interface) and their optimisation for the integration and portability of the LIBS demo unit	2	24	24	2
M 2.3	To verify that the proposed methodology is capable for the proposed operation (lab demo)	2	36	36	2
M 2.4	Optimized operational parameters (X-ray tube, X-ray detector, optical unit, microscope device etc.) for the portable μ-XRF spectrometer	2	30	30	10
M 2.9	To determine the suitability of the developed methodology and instrumentation for the surveyed collections	2	36	36	14
M 3.8	A list of protection systems submitted to accelerated corrosion tests to be used in the participating countries involved in Task 3.9	3	36	36	3
M 3.10	A preliminary idea of the time of effectiveness of protection systems applied on naturally pre-aged coupons in real conditions of exposure	3	33	33	3
M 3.11	A definitive rating of the protection systems applied on naturally pre-aged coupons in real conditions of exposure in terms of the most compatible, reversible or retreatable and durable after exposure	3	35	35	3
M 3.12	A confirmation of the rating obtained in Task 3.11 when protection systems are applied on artefacts and monuments.	3	35	35	3
M 4.3	Presentation of Preventive strategies for saving metals collections in the Mediterranean region	4	30	28	1
M 4.4	Dissemination of Preventive strategies for saving metals collections in the Mediterranean region	4	36	39	1
M 4.5	Providing a maintenance program for outdoor and indoor metals collections in the Mediterranean region	4	32	44	1
M 4.6	Distribution of the Guide in European and International level.	4	36	44	1
M 4.7	Presentation, dissemination of information and results of the project in the wide scientific community and the public through the internet in European and international level.	4	30,36	30,36	1