Innovative conservation approaches for monitoring and protecting ancient and historic metals collections from the Mediterranean Basin

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Abstract

The paper outlines a three-year European funded project, acronym PROMET, under the auspices of Sixth Framework Programme, priority INCO. This will start in October 2004, and sets out to establish and promote a conservation strategy designed for the Mediterranean region by developing an approach to monitor and to protect metal artefact collections using state of the art portable analytical techniques and new corrosion inhibitors and/or coatings safe and effective to use. There are 23 partners involved from 13 different countries in Europe and in the Mediterranean Basin, with a total budget of around 4 million Euros.

Keywords: metal artefacts, Mediterranean Basin, Laser-induced breakdown spectroscopy, micro X-ray Fluorescence, corrosion inhibitors, coatings.

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1. Introduction

The European Commission under the Sixth Framework programme supports research in several priorities, one of which is specific measures in support of INCO International Cooperation (INCO,2003), and includes measures related to research in the protection and conservation of Cultural Heritage. Under these auspices, two projects related to the preservation of archaeological and historic metals collections were submitted in May 2003, acronyms PROMET and APHRODITE. Both projects passed the evaluation phase, and the experts recommended merging into one project. The project co-ordinators of PROMET and APHRODITE, Vasilike Argyropoulos and Emma Angelini respectively spent considerable time in merger negotiations, and were successful in unifying both projects under common objectives and deliverables.

In particular, the problems and needs of metal artefacts made of precious metal alloys (including gilded materials), iron and copper alloys from the Mediterranean Basin will be identified. New prototype portable techniques, Laser-induced breakdown spectroscopy and micro X-ray Fluorescence will be developed as complementary analytical tools for metals characterization. Also commonly applied analytical techniques will be used for quickly surveying large metals collections. These

analytical tools together with statistical methods will be applied to survey collections in the different countries in the Mediterranean Basin specifically Egypt, Greece, Italy, Jordan, Malta, Morocco, Spain, Syrian Arab Republic, Tunisia, and Turkey, and pilot studies will be carried out to highlight the problems and needs of the collections. In parallel, safe corrosion inhibitors, derived from vegetable oils, mature tobacco, tannins from wood, Physical vapour deposition (PVD) and Plasma enhanced chemical vapour deposition (PECVD) barrier films, synthetic microcrystalline or polyethylene-based waxes will be developed and tested on artificially and naturally aged metal coupons. Finally, the most effective products that meet conservation standards will be tested on a selection of artefacts specifically for the environmental conditions of the Mediterranean Basin.

The paper outlines these objectives, activities, and expected deliverables of one of the highest funded projects under the INCO measures for Cultural Heritage, and highlights the importance of this research related to metals in the conservation field.

2. Main Objectives

The project aims to establish and to promote a conservation strategy to protect Mediterranean archaeological or historical metals collections exhibited or stored in buildings without the benefit of a controlled environment. The overall scientific and technological objectives of the project are categorized under the two main actions:

Monitoring

- To optimize existing portable scientific instruments and documentation methodologies for the characterization and classification of large numbers of metal artefacts.
- To develop new non-destructive or on-line micro-destructive analytical techniques for analysing in-*situ* the compositional variations of metal artefacts.
- To identify the conservation problems and needs of metals collections situated in the Mediterranean Basin.
- To develop a codified approach in establishing procedures for conservation and restoration of metallic artefacts.

Protecting

- To determine the long-term effectiveness of past treatments (coatings and/or corrosion inhibitors) used to preserve metals collections in the Mediterranean Basin in terms of their success in protecting the metal substrate, inertness and reversibility.
- To determine**,** by means of a systematic scientific approach**,** the most compatible, reversible, and environmentally-friendly corrosion inhibitors and/or coatings to protect objects made of precious metals, copper and iron alloys.

The main conservation problems that metal artefact collections face in the Mediterranean Basin may be attributed to the high relative humidity and to the presence of aggressive agents in the atmosphere. Conservation strategies have to be tailored to take into account the different environmental conditions and the degradation causes occurring in the countries of the Mediterranean Basin. To decrease the rate of the degradation phenomena, it is not possible to protect the metal collections by placing them in strict environmentally controlled areas or by treating them on a regular basis, due to the large number of objects and the heavily cost of repeated maintenance. Furthermore, many of these artefacts are contaminated with soluble salts, such as chlorides, and can only be saved by proper documentation/analyses, stabilization treatment, and protecting them with an appropriate corrosion inhibitor and/or coating. Our project aims to establish and

promote a conservation strategy designed for the Mediterranean region by developing portable monitoring systems and protection methods, including the identification of degradation phenomena, for collections of precious metals, iron and copper alloys.

Portable techniques, as Laser-induced breakdown spectroscopy (LIBS) and micro X-ray Fluorescence (μ-XRF) will be optimized and proposed as analytical tools for characterizing metal artefacts and for identifying degradation phenomena. The technological development of non-destructive techniques for the characterization of metal artefacts of artistic and historical interest is of outstanding importance due to the difficulties in obtaining permissions for removing bulk material for destructive analyses. These advanced analytical methods will be applied to survey collections of archaeological or historical metal objects in different countries in the Mediterranean region, such as Egypt, Greece, Italy, Jordan, Malta, Morocco, Spain, Syrian Arab Republic, Tunisia, and Turkey, and to identify the conservation problems.

In parallel, safe corrosion inhibitors and chemical agents as well as Physical vapour deposition (PVD) and Plasma enhanced chemical vapour deposition (PECVD) barrier films and synthetic microcrystalline or polyethylene-based waxes will be either developed and/or validated for use on artificially and naturally aged metal reference alloys.

A maintenance policy for metals collections will be highlighted through dissemination-related activities, such as workshops, conference, an English-Arab web-site and the publication of a book.

3. The Consortium

The objectives of the proposed project could only be tackled by uniting the efforts of a Consortium made up of representative group of scientists, conservators, and archaeologists from across Europe and the Mediterranean Basin. Table 1 summarizes the participants involved in the project, which come from 13 different countries of Europe and of the Mediterranean Basin. The key element of this Consortium is the collaboration in innovative research between European and South Mediterranean Institutions. For example, the Institute of Electronic Structure & Laser (IESL), Foundation for Research & Technology, Heraklion, Greece and the National Institute of Laser Enhanced Sciences (NILES), Cairo University, Egypt will cooperate to produce a prototype portable LIBS for analyzing metal objects. Moreover, European Institutions as Malta Centre for Restoration, SVUOM Ltd, Czech Republic, Laboratory of Research on Historic Monuments, France, Politecnico di Torino, Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Italy, will cooperate with southern Mediterranean institutions as Laboratoire des Matériaux Minéraux et Composites, Université de Boumerdes, Algeria, and IBN TOFAIL University-Faculty of Science, Department of Chemistry, Morocco to develop new corrosion inhibitors and barrier films. In the consortium end-users, museums and conservation training institutions are also represented and will participate in the design and testing of the analytical techniques and restoration products.

Table 1. Participants involved in the project.

Role*	Partic. No.	Participant name	Partic. short name	Country	Participation in Workpackages (WP)
CO	1	Technological Educational Institution of Athens	TEI	Greece	WPL: WP1 and 4, WP 2, 3
CR	2	Foundation for Research & Technology- Hellas	FORTH-IESL	Greece	WP 1,2,3,4
WPL	3	Malta Centre for Restoration	MCR	Malta	WPL: WP3 WP 1,2,4
CR	4	Department of Metallurgy and Material Engineering, University of Malta	DMME	Malta	WP3
CR	5	Laboratoire des Matériaux Minéraux et Composites. Université de Boumerdes	LMMC	Algeria	WP1,3,4
CR	6	SVUOM Ltd	SVUOM	Czech Republic	WP1,3,4
CR	7	National Institute of Laser Enhanced Science	NILES	Egypt	WP1,2,3,4
CR	8	The Laboratory of Research on Historic Monuments	LRMH	France	WP1,3,4
CR	9	Laboratory for Material Analysis Institute of Nuclear Physics. NCSR Demokritos	Demokritos	Greece	WP1,2,3,4
CR	10	Institute of Archaeology and Anthropology	IAA	Jordan	WP1,2,3,4
CR	11	Royal Scientific Society	RSS	Jordan	WP1,2,3,4
WPL	12	Politecnico di Torino, Dipartimento di Scienza dei Materiali ed Ingegneria Chimica	POLITO-SMIC	Italy	WPL: WP2 WP 1,3,4
CR	13	Consiglio Nazionale delle Ricerche, Istituto per lo Studio dei Materiali Nanostrutturati	CNR-ISMN	Italy	WP1,2,3,4
CR	14	National Technical University of Athens, School of Chemical Engineering	NTUA	Greece	WP1,2,3,4
CR	15	Consejo Superior de Investigationes Cientificas, Centro National des Investigaciones Metalurgicas	CSIC-CENIM	Spain	WP1,2,3,4
CR	16	National Research Center, Physical Chemistry Department	NRC-EC	Egypt	WP1,2,3,4
CR	17	Egyptian Museum, Cairo	EM-MC	Egypt	WP1,2,3,4
CR	18	Jordan University of Science and Technology, Faculty of Computer and Information Technology	JUST	Jordan	WP1,2,3,4
CR	19	Institute National du Patrimoine, Conservation Laboratory	INP-CL	Tunisia	WP1,2,3,4
CR	20	IBN TOFAIL University- Faculty of Science, Department of Chemistry	IBN-DC	Morocco	WP1,2,3,4
CR	21	EGE University, Department of Protohistory and Near Eastern Archaeology	EGE-PNEA	Turkey	WP1,2,3,4
CR	22	Ministry of Culture- Directorate General of Antiquities and Museums, Chemistry Laboratory	MC-DAM	Syrian Arab Republic	WP1,2,3,4
CR	23	University of Aleppo, Department of Materials Engineering	ALP-ME	Syrian Arab Republic	WP1,2,3,4

***CO** = Coordinator, **WPL**=Workpackage leader, **CR** = Contractor
WP1: Project Management, **WP2**: Documentation and monitoring of metals collections
WP3: Development of safe coatings and corrosion inhibitors for the protection of metals
WP4: Preventive Strategies for saving metals collections

4. The Impact of the Project

The significance of this project is not only the size of the research group, amount of funds, deliverables, but also the extent of the experimental studies to be carried out for developing tailored strategies for the conservation of metal artefacts collections. A noticeable amount of funds in Europe is mainly devoted to 'hot' topics such as stone/ marble, mosaics, or wall-paintings degradation and conservation. Thus, the conservation knowledge for metal artefacts is underdeveloped in the Mediterranean region, including southern Europe. As a result, conservators from this region hesitate or delay to properly care for these types of artefacts, because of a supposed lack of knowledge and know-how to take measures to prevent against the artefacts unwanted damages. This is understandable, since the conservation problems and needs for metals collections are complex and can vary, e.g., the original surface of a metal artefact varies greatly depending on the technology of the object, the burial conditions, and its care after excavation. Furthermore, most archaeologists in the region are more interested in the information that ancient coins can provide, and care for these metal objects first, leaving in most cases other metal finds stored away and uncared for many decades.

The pilot studies for surveying metals collections in the Mediterranean Basin will be adopted as a strategy as well as a cost model for implementing maintenance programs for similar collections owned by museums, or historical sites in the Mediterranean region. The portable techniques, LIBS, and micro-XRF will be optimized within the project for monitoring large collections in a reproducible, reliable, and non-destructive way in order to implement maintenance programs for museums and historical sites.

The development and optimization of the most effective and environmentally-friendly corrosion inhibitor(s) and/or coating(s) to protect metals collections in the Mediterranean region will promote viable solutions when conservators cannot house their collections in strict environmentally controlled areas or retreat objects on a regular basis. The Consortium will consider the different environmental effects on the metal artefacts collections specific to the Mediterranean region, such as less rain but higher humidity containing sea salt than in other European countries; the new corrosion inhibitors and/or coatings studied for the proposed project will be tailored for use against these environmental conditions. These coatings and/or corrosion inhibitors, which can withstand the effects of soluble salts and high relative humidity will provide an improvement to the conservation field, since these are the most detrimental causes for corrosion of metal artefacts. A test site will be set-up also in the Czech Republic to compare the results with the ones obtained in the test sites in the Mediterranean Basin.

In summary, developing and testing environmentally friendly corrosion inhibitors and coatings will produce a noticeable advancement for the international conservation community, because it provides alternative choices to already existing practices of using toxic corrosion inhibitors and/or coatings.

5. Project Design

The workpackages (WP) involved in the project design, and the participation of each partners in the associated WP, along with the project leader for each WP are also given in Table 1. The approach taken in the project is described below:

5.1 The approach for the study of metallic artefacts collections

Precious alloys artefacts: The activities will be focused on the systematic identification of the degradation causes of Ag, Ag-Cu, Au, Au-Ag-Cu based artefacts, including Ag and Au coated or joint metal objects from pre-Roman to Medieval periods, selected on the basis of cultural, artistic or economical consideration and also taking into account the nature of the archaeological context of their finding. Advanced laboratory analytical techniques (XPS, FEG-SEM-EDS, XRD, GDOES, XRF, DTA-TG, EIS and OM and also in situ XRD, XRF and electrochemical portable instruments) will be used for the microchemical and microstructural characterisation of the corrosion products and of the bulk nature of the artefacts and for evaluating the protectiveness of restoration materials.

Copper and iron based artefacts: Three types of collections made of copper and/or iron alloys will be studied for the project:
In Greece, a collection of about 3000 classical archaeological artefacts made up of copper and iron alloys (not including coins) from the archaeological site of Messene near Kalamata in Greece will be studied. In Jordan, a collection of ancient artefacts made of copper alloys will be studied. Finally in Malta, a collection of steel metal armours from the Palace Armoury in Valletta will be studied.

A conservation survey will be conducted for each of these collections. The approach designed for the project will be used to select a representative sample for further non-destructive analyses**.** This approach will begin with the design and distribution of a questionnaire to all partners for the classification of the surveying collection. This classification will be based on the chemical and microstructural characteristics of the artefacts and on their conservation conditions. The aim of this step is to produce an overview of the identified collection and to select a representative sample of artefacts for further analyses. The statistical analysis will allow a classification of the artefacts, same frequencies (based on the characteristics that have been collected from the questionnaire), probabilities, and other measures of summary statistics. If our data provides information about different methods of conservation (for example occurrence, effectiveness of the method) it will be possible for a statistical comparison of these methods using statistical "tools", as "Factor Analysis" or "Regressions" or "ANOVA tables". This approach will provide for systematic determination of the characteristics that make up a metals collection in order to determine the 'actual' problems and needs.

5.2 The Technological Developments

5.2.1 The Techniques

A major technological advancement for this project will be the development of LIBS (by FORTH-IESL and NILES groups) and μ-XRF (by Demokritos group) into prototype transportable analytical techniques and thus the improvement of the quality and the speed of the information taken when these techniques are applied to metals collections *in-situ.* The potential use of Mass Spectroscopy techniques (e.g. Time Of Flight- Mass Spectroscopy, **TOF-MS**) in combination with LIBS analysis will also be considered in order to enhance the information obtained. The need for such development is due to the existing limitations of portable analytical techniques in determining compositional variations for metal artefacts with different mineralised

layers that make up the original surface, and the different shapes or intricate surface details that define the artefact. Thus, our research will have an impact in this field as to the analytical information that can be obtained from metal artefacts in-*situ* by upgrading the following criteria:

- *Fast*, so that a large number of artefacts may be analysed or a single artifact investigated at various locations.
- *Versatile,* allowing to obtain average compositional information but also permitting local analysis of small microscopic areas
- *Sensitive and multi-elemental on-line analysis,* making possible the use of trace-element fingerprints.

LIBS and µ-XRF will be developed as complementary analytical tools. The former provides on-line in-depth analysis of the various layers of the studied surface by laser ablation of a minute amount of material (1-10µm in depth and ~100µm in diameter). On the other hand, µ-XRF offers non-destructively compositional information of the superficial surface layer. The combination of these techniques will allow an integrated analytical study of both the outer surface as well as the stratigraphy of the corrosion layers, with minimum material loss. This innovation will improve the in-*situ* analytical characterisation of metal collections.

5.2.2 The Corrosion Inhibitors and Coatings

In parallel with artefact analyses, new environmentally friendly corrosion inhibitors and barrier coatings will be tested for use in protecting metals collections in the Mediterranean Basin. These products exist on the market, but were developed for protection in industrial environments, and are usually tested and applied on non-corroded metal surfaces for short-term protection (less than three years). By contrast, archaeological or historical metal artefacts are generally covered by corrosion layers of different composition and thickness, and due to the lack of funding in the conservation field, the restoration treatments must be able to protect the artefacts as long as possible (5-10 years). Few data are available on the protective effectiveness of these products on corroded metals over the long-term in the Mediterranean region.

The following types of corrosion inhibitors will be studied in this project:

- For copper and iron alloys: salts of linear aliphatic organic acids, which are derived from vegetable oils such as olive, colza, sunflower oils, products extracted from mature tobacco, and new products found from our market survey.
- For iron alloys: products extracted from wood as tannins.

- For silver alloys: nitrogen-based and sulphur–based innovative inhibitors.

Many of these patented corrosion inhibitors, are widely employed for industrial purposes. For example, aliphatic organic acids are applied with zinc coatings in the car industry (e.g., ATOFINA, ARCELOR, TUBEUROP). Tobacco extracts as inhibitors of metallic corrosion have already been patented (INHIBITEX). Tannins are commonly used in industry for tannin-based rust converters.

However, in the conservation field, only tannin-based products are commonly used for iron-based artefacts. Aliphatic organic acids or extracts from mature tobacco have not been tested for protecting copper or iron-based artefacts. In this project, short-term and long-term testing of the above-mentioned corrosion inhibitors both on naturally and artificially aged copper, iron, and silver alloy coupons and real artefacts

will be performed. A major advance in the conservation field will be the replacement of toxic inhibitors currently used by conservators, which often need special care in application or for disposal, (e.g., benzotriazole, ethylenediamine).

The following types of coatings will be studied in this project:

- PVD coatings.
- Organosilicon coatings by PECVD or by sol-gel technique.
- Synthetic microcrystalline or polyethylene based waxes; and
- New products found from our market survey.

The thin film technology concerning a large variety of non-equilibrium processes for leading-edge surface modifications of materials is gaining popularity, because it allows the design of substrate by means of the deposition or modification of thin films in an extremely versatile and environmentally friendly way, i.e. by employing low pressure plasmas, also called cold plasmas or glow discharges.

Environmental considerations are becoming more and more important as a consequence of the Kyoto Earth Summit. World-wide initiatives such as EU IPPC Directive (Integrated Pollution Prevention and Control – 96/61/CE), has identified targets for different industrial sectors, including corrosion protection, the development of 'best available techniques' (BAT).

A wide variety of void-free, high-adherence thin films (100-10.000 angstrom) deposited by PECVD are one of the most important technological results of thin film technology.

Two other important aspects of the research are the application of technology for the modification of the very top surface layers of solid materials by grafting chemical functionalities, so called Plasma Treatments (PT), and the ablation of materials by reactions with active species generated in the plasma to form volatile products, so called 'Plasma Etching' (PE).

Among the various applications, PECVD deposition of silicon containing organic compounds (i.e. organosilicons) appears particularly promising for corrosion protection of metallic materials. Since, PECVD a highly versatile technique in that the production of a variety of coatings with a wide range of properties simply by means of a proper selection of the experimental conditions is easily achieved. For example, the SiO_2-like coatings are characterized by high chemical and thermal stability, good dielectric properties, low gas permeability, etc.

The experimental apparatus employed for PECVD allows various operations to be carried out in the same reactor, before the deposition step, including the possibility of removing surface contaminants or performing surface modifications, like oxidation, reduction, etc. The deposition of complex multi-layers of different chemical composition and properties may also be carried out. Recent literature shows more and more studies devoted to this PECVD using organosilicon precursors for various substrates, mainly steels, light alloys and to a lesser extent artistic alloys and this also appears particularly promising for corrosion protection of metallic artefacts.

Although the PVD technique is often considered to be irreversible, the challenge of our project is to apply it to metal plates covered with corrosion layers and for which a compromise has to be found between a good protection and lower adherence performance. The technique has been in existence for 10 years, with a multitude of applications for industry. The main goal of our research is to adapt the technique for the production of a coating with very low permeability to oxygen and water, which is easily deposited onto a metal surface at low temperatures and which could be removed to some extent. Thus, a low melting point ceramic would be

chosen for both short-term and long-term testing to provide a dense but 'soft' coating to the metal surface. The coating process will be plasma assisted (magnetron sputtering) in order to further lower the deposition temperature. Initial short-term tests, such as mechanical and electrochemical assessment will be used to determine the optimal coating conditions. Then long-term testing of this type of coating will be required on aged coupons, and finally real artefacts, to determine its overall effectiveness to the conservation field.

Many types or combinations of synthetic microcrystalline or polyethylene waxes are used for the protection of both outdoor monuments and indoor metal artefacts, although not specific for use in the Mediterranean Basin. Few data may be found on the effectiveness of these coatings on artefacts situated in environments that usually have higher temperatures, and/or humidity containing sea salt than in northern Europe, and North America. This research will provide tailored new coatings for application to metal artefacts in the Mediterranean Basin.

A three-year project is needed due to the requirements for field tests of metal coupons with corrosion inhibitors and coatings based on international standards (e.g., EN ISO 8565 *General requirements for field tests),* and can be justified by summarising the design as follows:

1st Year:
-Survey of treated collections in the Mediterranean Basin
-Selection of metal coupons for testing based on the characterization of real artefacts
-Preparation of test metal coupons by accelerated ageing
-Market survey of corrosion inhibitors and coatings commonly employed in industry and selection of protective coatings and corrosion inhibitors for study
-Development of innovative coatings and corrosion inhibitors
-Development methods of application of coatings and corrosion inhibitors for the pre-weathered coupons (by accelerated ageing)
-Short-term testing of corrosion inhibitors and coatings
-Preparation of test coupons by natural ageing at test sites in the Mediterranean Basin.

2nd, 3rd Years:
-Removal schedule of naturally-aged test coupons after 3, 6 and 12 months of exposure at selected test sites in the Mediterranean Basin
-Application of coatings and corrosion inhibitors to pre-weathered coupons and scientific analysis prior to exposure in order to determine their adhesion properties
-Exposure of coupons with coatings and corrosion inhibitors for natural weathering at selected test sites in the Mediterranean Basin
-Monitoring of coupons during the 12 months exposure
-Scientific analyses of coupons with corrosion inhibitors or coatings after removal from natural weathering
-Testing of highly rated corrosion inhibitors and coatings (determined after short-term testing and results from batch 1 of outdoor testing) on a selection of real artefacts with a 6-month exposure
-Ratings for all the coatings and corrosion inhibitors.

6. Expected results and outcomes

The project will deliver two prototype portable equipments: LIBS and μ-XRF to the market, which will be able to carry out non-destructive or micro-destructive analyses of ancient metal artefacts.
The surveys conducted will provide an accurate description of the different degradation phenomena occurring on metallic artefacts in the Mediterranean basin.
The project will formulate new products, i.e., corrosion inhibitors and barrier coatings for the protection of metal artefacts. On the basis of the project results, it will be possible to provide effective tools for the protection of culture heritage by offering reliable solutions that are easily used and environmentally friendly. Furthermore, this project will investigate the legislative policy for conservation of metallic artefacts collections in each participating country.

In addition, PhD theses, scientific publications, conservation guidelines, and new environmentally-friendly conservation products for metal artefacts will be the expected outcomes of this project.

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