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NON - DESTRUCTIVE PHYSICOCHEMICAL ANALYSIS AND CONSERVATION OF METALLIC BOOK COVERS OF ECCLESIASTICAL BOOKS FROM SAINT MAVRA AND TIMOTHEOS CHURCH IN ZAKYNTHOS (GREECE)

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ABSTRACT

In this article, six metallic book covers of ecclesiastical books and a metallic pair of church ornaments, used as a decorative in the church, are studied. These objects are dated in the 19th century and derive from Saint Mavra and Timotheos Church in Zakynthos Island in Greece. Physicochemical analysis provided information, such as the construction metals, which was brass (copper and zinc alloy) in five of them with nickel as coating, one was made of silver along with the pair of church ornaments and specimens of enamels in various colors (blue, green, red), in order to proceed to the collection's conservation. Specifically, Stereo Microscope was used in order to provide information about the microscopic features and X-ray fluorescence to grant with both quantitative and qualitative results of the chemical composition. The conservation method based on the results of the physicochemical analysis was decided, aqueous solutions of chemicals and pastes were used after the proper cleaning tests, as the procedure was completed the objects were in a stable state, protected by a varnish coating from further corrosion. The results of the study and the conservation process are documented, providing important information about metalwork in the 19th century in Zakynthos Island and the conservation approach.

KEYWORDS: Metallic book covers, Zakynthos, physicochemical analysis, Stereoscope, X-ray fluorescence analysis (XRF), conservation, Christian church

1. INTRODUCTION

The metallic book covers are categorized by the type of ecclesiastical book they decorated, there are three covers from a Gospel, three from an Apostle book and a metallic pair of ornaments. In 2005, a fire broke out in the church and burnt almost everything, including the books that the metallic covers were attached. Each object was studied separately but also as a part of a collection, the results were assembled and compared.

The history of metals unfolds through the ages in relation to the technological development and skills of past (prehistoric) societies. Gold and silver, were the first metals that the first men discovered in nature before 3.000 B. C, along with copper. Gold and silver's shine and slow corrosion rate made them easy to trace from men. Copper is an important chapter in human history, with bronze and brass to follow along, around 2.000 B. C. Iron in different forms was easy to use and was discovered combined with nickel in meteorite deposits (Treister 1996; Kirk et al., 2003; Tolcin, 2008; Rosenberg, 1968).

Metalwork includes various techniques of metal processing. The ecclesiastical metalwork refers to objects that have a kind of use in a church, either liturgical, or decorative. The metallic covers of ecclesiastical books are of particular aesthetic value, and vary in construction techniques and decoration, such as glazing, plating, patination, leaf decorations etc (Lasseter – Clare et al., 2008).

The objects' basic construction metals are silver, copper, zinc and nickel, determined by the physicochemical documentation held by X-ray fluorescence (XRF) and provided further information about the construction materials, the collection's surface features were documented by the Stereo – Microscope. The quantitative and qualitative analysis of the objects not only gave information on the historical background, but also in the procedure to be followed during conservation. The non-destructive physicochemical analysis was critical due to the variety of their visible features such as color, shimmer, surface etc. In addition, the lack of documentation of artifacts similar to the collection, and the minimum bibliography about metalworking techniques of that time and a conservation approach to such items, made it clear that physicochemical analysis was the only source of further information.

Metal corrosion is a natural process, which converts a refined metal mechanically and chemically, and it depends on the metal and its environment. Studying on the reactions of each metal, contributed in the understanding of their preservation status.

Finally, spot tests were conducted in order to find proper conservation methods and materials. The conservation process is presented, along with the materials that were used. A concise report on preventative conservation of metal objects was made. The results were studied and conclusions were made regarding the metalwork in the area and the conservation process.

***Figure 1** Map of the Balkan States 1899 Map from "Stanford's Compendium of Geography and Travel: Europe" Volume 1, 1899 and the island with the objects*

2. DESCRIPTION OF THE COLLECTION, HISTORICAL DATA

The collection that is studied was saved from a fire that took place in the church, and that is the reason that only the metallic covers from the books exist. The collection includes three metallic covers from a Gospel, three metallic covers from an Apostle Book and a pair of church ornaments, which thought to be books' ornaments at first (Figs 2, 3 & 4). The covers' designs are embossed and look intaglio in their backside (average maximum dimensions 25 cm X 35 cm). The pair of the ornaments portray faces of angels decorated with wings, (9-8,5 cm X 4,5-4,5 cm), with hanging ledges (3,9 cm – 3,4cm).

Figure 2. Metallic book covers AM1 and AM2.

Figure 3. Metallic book covers AM4, AM6 and the metallic pair of church ornaments AM5.

Figure 4. Metallic book covers AM7 and AM8.

3. METALWORKING

Metallic materials are a combination of metallic elements that are composed by inorganic compounds. An alloy is a mixture of metals, a combination of metals may reduce the overall cost of the material while preserving important properties (Anderson et al., 2003; Callister, 2000).

The art of metalworking, that is the various techniques used to process metals, start to appear in the ancient times. This art originated categories of specialization according to the kind of the metal and the objects that were to be constructed. The most common metals are gold, silver, copper, brass and less of all lead (Zora, 1980).

Luxurious metallic bindings have been found in holy books. A Gospel with a silver or a gold binding always gave a hint of splendour in a church. Rarely there was a New Testament and later on 19th century A.D there are metallic bindings in Apostoles' books. Important criterion of possession of luxurious ecclesiastical objects is the economic prosperity and the reputation of the temple.

It is important to note that the sacred objects are not always works of art, even if their manufacturing metal is precious. Usually catalytic role is played by the origin, the craftsman and the style, which is the only evidence to verify the lab and the craftsman, and the person making each donation to the temple.

The art of metalworking of silver and gold is divided into chronological phases, the first phase is the post-Byzantine (until the early 18th century), the second is the Modern Greek and includes works created from the early 18th to the early 20th century, which is quite affected from the west (Ikonomaki-Papadopoulos, 1990, 1991).

In Zakynthos Island there is a tremendous tradition in metalworking, mostly with silver and gold, there was a variety of objects that sadly didn't survive all the natural disasters that the island suffered. Everything that was found is just a specimen of the work that locals did. Kallarites is a village in Epirus that had a lot of metal workers and a great tradition in working with silver, they are those who brought new techniques in Zakynthos (Kousouni et al., 2017).

In order to manufacture a metallic book cover, a metal sheet must be processed. The starting material is a rolled sheet, in the formation procedure the thickness of the work - piece does not change drastically. The pressure is applied to the metal sheet by a press, the process is known as stamping. Other techniques are shearing (cutting), drawing (pressing in a cylindrical shape), bending (deformation of a sheet into an angle) and spinning (pressing in order to form hollow shapes) (Creese, 1999).

The techniques and the materials used to construct such covers are various, different metals and they were mainly forged with cast elements, incised, impressed or embossed with additional elements, such as gold plating, enamels (which are used as decoration in object AM4, manufactured according to Clossoine technique), niello coatings, precious and non-precious stones, wire decorations, metal clasps and detailed carved inscriptions. Bookbinding slabs of wood with leather lining (usually dark brown) or cloth, nailed with metal plates, are mentioned (Zora, 1980).

The techniques used to attach the metallic covers to the books were various. In this collection it seems that an adhesive was used. During the 17th century was used a gelatine mixture (slurry wheat boiled or rice) with alum, which is a double salt of aluminum sulfate and potassium, while in the early 18th century, rosin was used too, either in pure form or in combination with alum. Information indicate that the bindings of books in the 19th century, using various kinds of organic adhesives.

The craftsmen who had influences from the east, used an organic glue made from wheat or rice, the so called gelatine, which they dissolved in water and then added alum. Those with western influences, used organic adhesives using animals' bones, cartilage (except pig) and skin, such as rabbit-skin glue. There was a kind of fish glue which was not particularly used (Young, 1995; Diehl, 1980; NPCS Board of Consultants & Engineers, 2016; Kousouni et al., 2017).

4. PRESERVATION STATUS

The objects are in their entirety in a critical preservation status. The documentation of their state is a key part towards the understanding of the mechanisms of the preservation of the materials, but also the environment in which they were exposed or stored. In this way the proper conservation materials and methods can be selected.

All items had suffered mechanical strain, they had apertures, distortions, deformities, material loss and deposits such as dust, soot and remains of some kind of adhesive (Fig. 5). The most important difference between the metallic covers and the pair of church ornaments, is the kind of oxidation that each one of them produced, and that varies as a result to their different metals and alloying and coating process. A fact to mention is that the metallic pair of ornaments have not any severe mechanical strain, except a small aperture in one of an angel's face.

Studying the construction metals of the objects, copper, silver, nickel and zinc, gives us information about their basic corrosion products. The basic oxides of silver (Ag) are, the silver sulphide or argentite, Ag_2S (black) and cerargyrite or silver chloride, AgCl (purple - gray), of copper (Cu) are, tenorite, CuO (black), cuprite, Cu_2O (reddish - orange), nantokite, CuCl (white) and atakamite $CuCl_2$ (green), (also known as copper's disease), of nickel (Ni) is the nickel oxide, NiO, (green-black) and the oxidation of zinc (Zn) is the formation of a basic carbonic coating (Hamilton, 1999; McNeil et al., 1992; Copper Development Association 2016; Callister, 2000; Porter, 1991; Lide, 2004; Chatterjee, 2001).

Figure 5. Various decays from the metallic book covers and the metallic pair of church ornaments.

5. PHYSICOCHEMICAL ANALYSIS

Material identification through physicochemical analysis is an important and necessary step, as it covers details of the historical background of an object, but also gives a specific direction for the conservation process, to choose appropriate materials and methodology. The main objective of this study was the observation of objects, as well as the quantitative and qualitative analysis of the manufacture materials (construction metals and their concentration).

The stereoscope is a very useful detailed observation instrument, particularly for the collections' objects, because of the embossed and intaglio surfaces (Figure 6). The procedure was non-destructive and was done with Stereo Microscope Leica M205FA (160x), with fixed focus 7,8x, on all shots (Hodges, 2003).

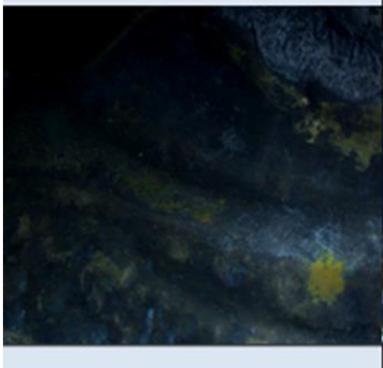
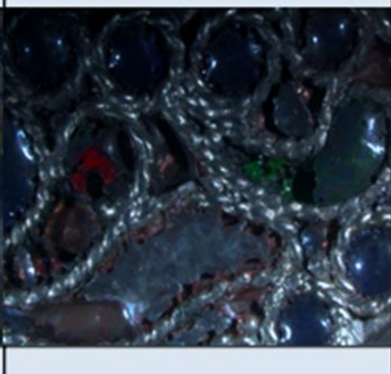
AM2_2B	AM4_3	AM5_1
		
The surface is completely covered with soot deposits, except for some areas that the metal can be seen (possibly gold leaf coated brass). The intaglio surfaces are apparent.	Enamel residues in red and green color are in the cells, as well as traces of burnt material. In the picture shown, a part of decoration, that the pattern is changed, in circular cells.	The embossed surface is a part of the wing. Small incisions in the left are a part of the object. The surface is completely coated by soot, however, oxidation products appear, that either belong to the object and are derived from the small quantity of copper, or they are transferred through contact with another object.

Figure 6. Shots from the Stereo Microscope

Methods that are based on the X-Ray functions, based on the structure of a material (elemental atomic structure or microcrystalline structure), can provide information on solid materials and can identify traces. The purpose of the analysis with X-ray fluorescence spectroscopy, is a quantitative and qualitative documentation of the objects in the collection. The verification of the alloy components, in the construction metals of the objects, provide information, that are a criterion for the proper selection of the conservation materials and method, though constituting a mean for finding historical information. The analysis was carried out with XRF, Thermo Scientific Niton XL3 + GOLDD (Mantler et al., 2000; Beckhoff et al., 2006; Liritzis, 2011).

Table 1 Qualitative and quantitative XRF results (Source: NCSR Demokritos, Laboratory of Archaeometry, Athens)

CODES - OBJECTS	Sb	Sn	Cd	Ag	As	Au	Pb	Zn	Cu	Ni	Co	Fe	Al	P	S
AM1_68 Gospel Metallic Cover		1,2%				0,3%		27,3%	58,3%	11,4%		0,3%		0,3%	0,9%
AM1_69 Gospel Metallic Cover						0,5%		33,3%	65,0%					0,5%	0,6%
AM2_70 Gospel Metallic Cover						0,6%		24,4%	52,3%	18,2%				2,7%	1,8%
AM2_71 Gospel Metallic Cover		0,1%				0,8%		33,2%	61,1%					2,6%	2,1%
AM4_72 (blue enamel) Gospel Metallic Cover	3,0%	1,2%			3,9%		37,1%	0,4%	26,5%	11,3%	3,1%	0,4%	2,0%	0,3%	10,9%
AM4_73 (red enamel) Gospel Metallic Cover			0,6%	0,1%	8,4%		39,7%	0,1%	24,7%	13,9%	0,1%	0,4%	1,7%	0,3%	10,0%
AM 4_74 (green enamel) Gospel Metallic Cover			1,3%	0,1%	6,4%		26,2%	0,1%	37,4%	18,4%	0,2%	0,3%	1,6%	0,2%	7,7%
AM4_75 (metal surface) Gospel Metallic Cover				0,1%		0,4%			50,8%	46,3%			0,5%	1,0%	0,9%
AM5_79 Metallic pair of church ornaments				88,7%		0,9%	0,9%	0,1%	5,4%				0,7%	0,4%	2,9%
AM5_80 Metallic pair of church ornaments				88,4%	0,1%	0,6%	1,2%	0,2%	5,2%			0,1%		0,2%	3,9%
AM6_76 Apostle book metallic cover						0,1%		22,6%	64,8%	10,4%			0,4%		1,7%
AM 7_77 Apostle book metallic cover				94,6%			0,2%		4,9%						0,3%
AM8_78 Apostle book metallic cover						0,2%		28,3%	56,2%	14,7%				0,1%	0,4%

The results from the X-ray fluorescence analysis (Table 1), were very enlightening as 5 of the metallic covers are an alloy of copper and zinc, the well-known brass, and only one of the covers and the metallic pair of church ornaments are made by silver. The range of copper varies in percentage as it comes from 4,9% to 65%, high amounts of copper are in items made of brass, with zinc to follow along as a part of the alloy from 22,6% to 33,3%. Silver is the construction metal of 3 objects in amount of 88,4%, 88,7% and 94,6%, copper and zinc are in small amount in these items. Nickel as the plating metal in brass objects comes from 10,4% to 46,3%, with none traced in the pair of church ornaments. In some items there are small amounts of gold, iron, silver, lead, aluminium, phosphorus, and others, and in all of them there is sulphur.

The basic construction metals of the collections' objects are brass (copper and zinc alloy) with nickel plating and silver. Brass and silver are really common in ecclesiastical metalwork, although nickel was not to be expected its presence was justified as a protection coating and placing the objects in the 19th century. Brass was easy to process but susceptible to oxidation, nickel plating provided with protection and a silver color look that made the objects appear more luxurious.

In enamels there are various elements such as copper 20-40%, nickel 10-20%, phosphorus 25-40%, sulfur 7-11%, arsenic 3-9%, aluminum 1,5-2%. In the blue enamel, the pigment is made by cobalt (3,1%) and copper (26,5%), the red enamel is made by iron (0.4%), copper (24,7%) and lead (39,7%), the green enamel is made by copper (37,4%), nickel (18,4%), iron (0,3%), cadmium (1,3%) and cobalt (0,2%). The specific concentrations of the elements in the enamels give in each of them their distinctive colour.

6. CONSERVATION PROCESS

Cleaning tests (spot tests) were made on small areas of the item's which had deposits and oxidations with primary goal to choose the most suitable conservation method. Aqueous solutions of chemicals were used by using cotton swabs, applied with circular motion and alternate the friction and time needed, and patches of the solutions or cleaning pastes. Aqueous solutions were made using deionized water, and after the spot test, they were well washed with deionized water (the same method was used in the conservation process). Afterwards, the proper methods were decided and implemented for each item, as a criteria was the impact of the materials on each object and the reaction of deposits and oxidations. The following table (Table 2), demonstrates the materials that were used.

Table 2 Conservation materials

<table>
<tr><th>ITEMS' CODES</th><th colspan="8">CONSERVATION MATERIALS</th></tr>
<tr><th></th><th colspan="2">Acetone
(C3H6O)</th><th>Ethanol
(C2H6O)</th><th>Ammonium bicarbonate paste patch</th><th>Aqueous formic acid solution 8% w/w</th><th>Aqueous formic acid solution 10% w/w</th><th>Aqueous formic acid, thiourea and Desogen biocide solution</th></tr>
<tr><td>AM1</td><td colspan="2">Removal of residues from adhesive substance</td><td>Removal of dust and dirt deposits</td><td>Removal of oxidation from the surface in front</td><td>Removal of oxidation from the surface of the backside</td><td>Removal of intense deposits</td><td>-</td></tr>
<tr><td>AM2</td><td>Removal of dust and soot deposits</td><td>Removal of residues from adhesive substance</td><td>-</td><td>Removal of oxidation from the surface in front</td><td>Removal of oxidation from the surface of the backside</td><td>Removal of intense deposits</td><td>-</td></tr>
<tr><td>AM4</td><td colspan="2">Removal of dust and soot deposits</td><td>Removal of dust and soot deposits</td><td>-</td><td>-</td><td>Removal of copper and nickel's oxidation products ($CuCl_2$, NiO)</td><td>-</td></tr>
<tr><td>AM5</td><td colspan="2">Removal of dust and soot deposits</td><td>-</td><td>Removal of oxidation from the surface</td><td>-</td><td>-</td><td>Removal of oxidation was more effective.</td></tr>
<tr><td>AM6</td><td colspan="2">-</td><td>Removal of dust and soot deposits</td><td>-</td><td>Removal of oxidation from the surface</td><td>Removal of oxidation from the surface</td><td>-</td></tr>
<tr><td>AM7</td><td colspan="2">Removal of dust and soot deposits</td><td>-</td><td>-</td><td>-</td><td>-</td><td>Removal of silver and copper's oxidations.</td></tr>
<tr><td>AM8</td><td colspan="2">Removal of dust and soot deposits</td><td>Removal of dust and soot deposits</td><td>-</td><td>Removal of oxidation from the surface</td><td>Removal of oxidation from the surface</td><td>-</td></tr>
</table>

The main oxides that were removed from the items were nickel's oxide (NiO), copper's oxides (atakamite $CuCl_2$ and cuprite Cu_2O) and silver sulphide or argentite (Ag_2S). Even though the collection was eventually cleaned, there were a lot of spot tests, in order to find the proper materials. Various tests were carried out in object AM2, one of them was with aqueous solution of nitric acid 3-7% w/w that was not quite effective. In object AM6 aqueous solutions of 5% ammonium thiosulfate, of glycerol with sodium hydroxide and of Rochelle Salt with sodium hydroxide, were used, which, while they were effective in removing oxidations, lead to the weakening of the nickel plating.

Dust and soot deposits were not an easy matter, as they were hardened by the fire, such as the residues from an adhesive substance that was used to attach the metallic covers on the books (the substance was not identified by the XRF analysis, due to the alteration of the material, that was caused from the fire). Probably workers from the church had made an effort to clean soot deposits from the objects, although the embossed or intaglio surfaces and melted material, did not made it possible (Scott, 2002; Ashton, 2004; Cronyn, 1990).

A varnish coating concluded the conservation process (Figs. 7 & 8), with an acrylic resin solution of Paraloid B72 5% w/v in acetone, with a soft brush. The choice of Paraloid B72, was a safe option to create a protective film, mainly because the manufacturing alloys of the objects, contain various proportions of metals and alter their expected reactions (Ready et al., 1999).

Figure 7. The collection after varnish coating.

Figure 8. The collection after varnish coating.

7. PREVENTATIVE CONSERVATION

The main goal when preventative conservation's parameters are taken, is to reduce the chance of any further damage for the object. Therefore, any object should be displayed or stored in a controlled area, with proper preservation conditions. Metallic items require physical and chemical stability by a configured climate. Display units should be manufactured by compatible materials such as aluminium, stainless steel, sulphur and chlorine free fabrics, acrylic resins as coatings or adhesives that are chemically stable, impervious, and do not attract dirt.

Environmental conditions should be controlled strictly. Humidity RH should be below 40%, although it can even reach 15% depending on the metal and lighting in 200 - 500 lux, apart from metallic items combined with sensitive materials, in that case 150 lux are recommended. Temperature cannot cause immediate damage. Many objects are transported from place to place, but when it comes to safety there should be a secure plan, that will maintain the stability needed. Metallic items are transported in boxes (metallic or antacid cardboard boxes), that are stabilized with polyethylene sheets (Ethafoam) and wrapped with antacid paper (Watkinson, 2010; Hatchfield, 2002; King et al., 1992; Stolow, 1987). As a result such integrated approach aids sustainability via archaeometrical-conservation applications (Liritzis, 2001).

8. CONCLUSION

The collection consists of 6 metallic covers of ecclesiastical books, and a metallic pair of church ornaments. The church ornaments, were speculated by the church of Saint Mavra, that are part of the collection, perhaps as shutters for the church books. The features, however, such as weight, the purity of the constructions' metals, as shown in the results of the X-ray fluorescence analysis (silver in amount 88%) and the references in castings from various matrices, classify them as church decorative in candles, candelabra etc.

The physicochemical documentation of the objects, by non – destructive methods, had a particular role in the course of the study, answering key questions. The materials of the collection were not clearly based on visual observation and scientific bibliography. The conservation was based on the result of the qualitative and quantitative analysis of the construction materials, through X-ray fluorescence analysis (XRF), as well as metals requires different treatment depending on the material. Non-destructive methods were used in order to preserve the artifacts without any unnecessary interventions.

To summarize, the results from the physicochemical analysis by XRF, the main construction metals are brass (copper and zinc alloy), AM1, AM2, AM4, AM6, AM8, with nickel used as a coating and silver AM5, AM7.

Studying the enamels gave information about the variety of elements needed to produce a pigment. It is important to note that elements interact in various ways with each other that is the reason a different amount is needed in each pigment. Although copper is found in all three pigments, the amount and the other elements, such as cobalt, iron, lead etc., can cause a different reaction depending on the firing conditions (reduction or oxidation), (Singer 1963; Rhodes 1959).

The conservation was a complicated process, because of the multitude of construction materials in every metallic book cover. The objects of copper and zinc create special needs for their conservation. But the material causing more difficulties was nickel, which was used as a coating. The silver objects were certainly easier to cope with, except the peculiarity of the surface of the object AM7, which had an embossed form due to the fire from that the objects were rescued. The collection of metallic covers of ecclesiastical books was a unique sample of difficulty in order to choose the conservation materials, and in brass cleaning effort, the primary goal was to completely prevent the weakening of nickel plating. The conservation methodology used in the collection, remained conservative when it comes to oxidations and deposits (mainly glue residues) in order to maintain the nickel surface.

The metals used in the 19th century, are in a transitional state, from classic metalwork to new techniques influenced by the West, for categorizing objects, physicochemical documentation contributed. The construction with brass, and the use of nickel, makes the collection unique technologically and aesthetically, without giving them any other kind of value, with the exception of silver items of the collection.

The most common metals used by metal workers were primarily gold, silver, and bronze and rarely lead. The metals that were detected in the collection, agree with the metals used in classical metallurgy, brass and silver. The peculiarity of the collection is the use of nickel as coating, which might be element of transitivity of the manufacturing technology in a more modern form.

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REFERENCES

Anderson J.C., Leaver K. D., Rawlings R. D., Alexander J. M., (2003) *Materials Science*, Chapman and Hall, 5th Edition, United Kingdom

Ashton J., Hallam D., (2004) *Metal 04 Proceedings of the International Conference on Metals Conservation* (Canberra Australia, 4-8 October 2004), National Museum of Australia

Beckhoff B., Kanngießer B., Langhoff N. , Wedell R., Wolff H., (2006) *Handbook of Practical X-Ray Fluorescence Analysis*, Springer Verlag Berlin Heilderbeg, Germany

Callister W. D. JR, (2000) *Materials Science and Engineering, An Introduction*, John Wiley & Sons Inc, U.S.A.

Chatterjee U.K., Bose S.K., Roy S.K., (2001) *Environmental Degradation of Metals: Corrosion Technology Series/14*, Marcel Dekker Inc., U.S.A.

Creese R.C, (1999) *Introduction to manufacturing processes and materials*, Marcel Dekker Inc., New York.

Cronyn J. M., (1990) *The elements of archaeological conservation*, Routledge, New York.

Copper Development Association, (2016) http://copperalliance.org.uk/ (accessed in 8/3/2016)

Diehl E., (1980) *Bookbinding: Its Background and Technique*, Dover Publications Inc., U.S.A

Hamilton D. L., (1999) *Methods of Conserving Archaeological Material from Underwater Sites*, Conservation Research Laboratory Center for Maritime Archaeology and Conservation Texas A&M University.

Hatchfield P.B., (2002) *Pollutants in the Museum Environment. Practical Strategies for problem solving in design, exhibition and storage,* Archetype Publications, Glasgow

Hodges E. R. S., Guild of Natural Science Illustrators (U.S.), (2003) *The Guild Handbook of Scientific Illustration*, Published by John Wiley and Sons, Inc., Hoboken, New Jersey

Ikonomaki-Papadopoulos Y., (1990) "*Church Metalwork*", Manafis K.A. (ed.), *Sinai. Treasures of the Monastery of Saint Catherine*, Ekdotike Athenon, Athens (in Greek)

Ikonomaki-Papadopoulos Y., (1991) "*Church Silver*", In: *Simonopetra, Mount Athos*, Hellenic Industrial Development Bank, Athens (in Greek)

King S., Pearson C., (1992) *Environmental Control for Cultural Institutions, Appropriate Design and the Use of Alternative Technologies,* La Conservation Preventive, Paris 8-9 et Octobre 1992. Paris: ARAAFU

Kirk J., Ruiz J., Chesley J., Titley S., (2003) *The Origin Of Gold in South Africa*, The American Scientist, Volume 91 http://www.sas.rochester.edu/ees/ees119/reading2.pdf (accessed in 6/3/2016)

Kousouni C. K., Panagopoulou A., (2017) *The evolution of metalworking in the 19th century: case studies of metal covers of ecclesiastical books in Ionian islands (Zakynthos) in Greece,* e-Journal of Science & Technology, (e-JST), Issue 5, Volume 12, http://e-jst.teiath.gr/issues/issue_53/Kousouni_53.pdf

Lasseter – Clare T., Lins A., (2008) *Finishing Techniques in Metalwork: An introduction to the History and Methods of Decorating Metal,* Published by Philadelphia Museum of Art, U.S.A

Lide D. R., (2004) *CRC Handbook of Chemistry and Physics*, 85th Edition, CRC Press, New York.

Liritzis I., (2001) The contribution of archaeometry to the development (cultural, economic) of the Mediterranean islands, *Journal of Mediterranean Studies*, vol.10, 225-235

(https://www.researchgate.net/profile/Ioannis_Liritzis/publication/284188443_MESOGEIOS_ARCHAIOMETRIA/links/564f675308aeafc2aab3d4be.pdf (accessed in 15/4/2018)

Liritzis I., Zacharias N., (2011) Portable XRF of Archaeological Artifacts: Current Research, Potentials and Limitations, In: Shackley M. S., 2011, *X-Ray Spectometry (XRF) in Geoarchaeology*, Published by Springer Science + Business Media, LLC, U.S.A (accessed in 23/1/2018)

Mantler M., Schreiner M., (2000) *X-Ray Fluorescence Spectrometry in Art And Archaeology* http://trajan.numizmat.netnwww.trajan.numizmat.net/papers/num8.pdf (accessed in 5/8/2015)

Map of the Balkan States *1899 Map from "Stanford's Compendium of Geography and Travel: Europe"* Volume 1, 1899. https://legacy.lib.utexas.edu/maps/historical/history_balkans.html (accessed in 10/4/2018)

McNeil, M. B., and B. J. Little, (1992) Corrosion mechanisms for copper and silver objects in near-surface environments, *Journal of the American Institute for Conservation*, http://www.conservation-us.org, (accessed in 8/3/2016)

NPCS Board of Consultants & Engineers, (2016) *The Complete Book on Adhesives, Glues & Resins Technology (with Process and Formulation),* 2nd Revised Edition, Pacific Business Press Inc., India

Porter F. C., (1991) Zinc Handbook: Properties, Processing and Use in Design, Marcel Dekker, New York.

Reedy C. L, Corbett R. A., Long D. L., Tatnall R. E., Krantz B. D., (1999) *Evaluation of three protective coatings for indoor silver objects*, Objects Specialty Group Postprints, Volume Six, The American Institute for Conservation of Historic & Artistic Works, Washington, DC. http://resources.conservation-us.org/osg-postprints/wp-content/uploads/sites/8/2015/02/osg006-04.pdf, (accessed in 13/5/2015)

Rhodes D., (1959) *Clay and Glazes for the Potter*, Krause, U. S. A.

Rosenberg S. J., (1968) *Nickel and Its Alloys*, Institute for Materials Research, National Bureau of Standards, Washington D.C.

Scott D.A., (2002) *Copper and Bronze in Art: Corrosion, Colorants, Conservation*, The Getty Conservation Institute, Los Angeles

Singer F., Singer S., (1963) *Industrial Ceramics*, Chapman and Hall Ltd, New York

Stolow N., (1987) *Conservation and Exhibitions, Packing, Transport, storage and environmental consideration,* Butterworths, London

Treister M. Y., (1996) *The Role of Metals in Ancient Greek History*, Published by E.J. Brill, Leiden, The Netherlands

Tolcin A. C., (2008) *Zinc*, U. S. Geological Survey, Mineral Commodity Summaries

Watkinson D., (2010) *Preservation of metallic cultural heritage*, In: Cottis, R. A. ed. Shreir's, *Corrosion*, 4th ed., Vol. 4., Elsevier, London

Young L. S., (1995) *Bookbinding & Conservation by Hand: A Working Guide*, Published by Jerilyn Glenn Davis, U. S. A

Zora P., (1980) *Greek Art, Folk Art,* Publisher L. Braggiotti, Athens (in Greek).