A practical treatment and conservation study for a group of silver coins from Dhamar regional museum

by Mohamed M. Megahed

Yemen's earliest history, dating from the stone and bronze ages, has only recently been studied. Islam came to Yemen during the time of prophet Mohamed. The period of the first three orthodox caliphs was one of stability and steady growth of Islam in the Yemen, with the assumption of the caliphate by Ali ibn Abi-Talib in 656 A.D (35 A.H). A civil war broke out between his followers and those of Muawiyah, and Sana'a adhered to the Ali side. Muawiyah had to conquer Sana'a by force in order to establish Umayyad authority there. From there after Sana'a continued to be ruled by governors appointed by the caliph, first Umayyad (41- 132 A.H) and then, after transfer of the caliphate to Baghdad, Abbasid.

The Arab region, Levant and Egypt remained using gold and silver coins, which were prevalent before Islam as approved by the prophet (peace be upon him), and since El-caliph Omar ibn El-Khattab reign (20 A.H) appeared on the face of currency same Arabic inscriptions in Kufic script [1], especially on the face of silver dirhams, such as phrases of thankfull, No God but Allah, Mohamed is the messenger of Allah. After him, El-caliph Othman ibn Affan added song magnification (God is great) [2]. In fact the fundamental changes that have occurred for Islamic currency, occurred in the reign of the Umayyad caliph Abd al-Malik ibn Marwan (65- 86 A.H)(685-705A.D) [3], who caused a great revolution in the currency. He transferred the currency completely into Arabic, after it was written in Greek, Coptic and Pahlavi, and this happened after dispute erupted between him and the Roman emperor. So the currencies became a purely Islamic and didn't have any pictures carved, as it was before, but it became phrases of Unification and Mohamedan's message and Al-baslma [4].

The mission of Yemeni Antiquities Authority acting active archaeological excavations in the site of El-Banawa, Jahran District, Dhamar governorate, was active for three weeks (from 3/7/2002 to 1/8/2002). This site located south of Sana'a (capital of Yemen) about 70 Km, and to the north of Dhamar governorate about 30 Km, this site dated back to the Bronze age (1800 B.C), and the beginning of Sabaean period in Yemen. In the northern west part of the site appeared a new settlement during the Islamic period. The mission discovered the ruins of these settlement besides a lot of antiquities such as pottery, glass and metallic objects, specially the silver coins, which date back to Umayyad period (41- 132 A.H), as well as a range of other currencies due to a period of Al-imam Nasser bin Al- imam Al-Hady Yaha bin Al- Hussein from the beginning of the fourth century A.H, and others date back to the reign of king Al-Kamal Ayoub (640 A.H). All these silver coins were handed to Dhamar regional museum in August 2002.

Three groups of these coins (A, B,C) include thirty five coins, date back to Umayyad period (41- 132 A.H9 were selected for study.

Precious noble metal objects are high value objects for their intrinsic nature and for the great and sophisticated skill used to produce them . In many cases these artifacts were used not only as Jewels or precious artistic items but also as currency, a medium of exchange and a form of saving there by a acquiring an historical, artistic and economic value [5]. The precious metal artifacts are characterized by a wide compositional nature and have been produced via different complex manufacturing techniques that have greatly influenced their chemical and metallurgical stability[6].

Metal corrosion is a process of chemical dissolution, cations migrate from the metal substrate and react with available anions to form the metal salts that constitute tarnish layers and corrosion crusts. The character and chemical makeup of the corrosion products depend on the nature of the substrate and environment to which it is exposed [7].

Tarnishing is due to the reaction between silver and hydrogen sulfide (H_2S), carbonyl sulfide (OCS), or various other sulfur-containing organic compounds in the atmosphere to form silver sulfide according to the following simplified overall reactions:

$$2Ag + H_2S + \frac{1}{2} O_2 \rightarrow Ag_2S + H_2O$$

$$2Ag + OCS \rightarrow Ag_2S + CO$$

The rates of these reactions are strongly dependent on temperature, concentration, and relative humidity. In the case of sterling silver, the tarnish layer contains cuprous sulfide (Cu_2S), which may be distributed in homogeneously depending upon the composition and distribution of the silver-copper phases in the alloy [8]. Furthermore, the Ag or Au based alloys can be characterized by different amount of impurities coming from the extractive or refining processes, which can influence the long-term mechanical and chemical properties [9]. The contact between silver and copper in the silver copper alloy coins has enhanced the corrosion phenomenon whose main agent is the chloride anion coming from the soil, this induces the formation of silver and Cu [I] chlorides that could give rise to the copper cyclic reaction that continues to corrode copper when exposed to oxygen and humidity, where there are two detected basic copper chlorides Atacamite and Paratacamite that are identical in chemical composition but differing in crystal form the second one is found as a powdery, light green secondary corrosion layer on the patina surface, while the first one Atacamite occurs as a sugary-looking coating of dark green glistering crystals [10]. Often this dark green crystalline Atacamite is altered to a paler green powdery product of paratacamite [11 ,12]. The soluble chlorides in the presence of copper or its salts in contact with silver as silver plated copper objects or as an alloy of the two metals will corrode silver severely resulting in occurrence of insoluble thick layer of silver chloride [13] .
This study aims to:

- Identified the metallic composition of the coins, and explain its relation with the economic situation of that period.
- Investigate the nature of corrosion grown during the long-term burial and identify its products that will help us to understand the corrosive factors and the degradation mechanisms.
- Cleaning the group of coins from the superficial dirt and the corrosion products in order to discover as much as possible the surface topography, and to reveal the surfaces details .
- Establish them against further deterioration .
- Know the history of coins and place of mint.

To achieve that the selected groups of silver coins have been studied by using of Metallographic Microscopy, Scanning Electron Microscopy, X-Ray Diffraction and X-Ray Fluorescence.

MATERIALS AND METHODS - Description and condition
A big group of silver coins (35 coins) was discovered in Banawa excavation, season 2002, and now it is situated in Dhamar Regional Museum. These coins dates back to Umayyad period, exactly the reign of caliph Abd al-Malik ibn Marwan (65- 86 A.H) and his descendants till 106 A.H. It is purely Islamic currency, written in Arabic inscriptions such as phrases of Unification, Mohamedan's message and Al-baslma. All these coins were minted in Waist, the coins are classified in three groups as the fallowing:

- Group A, consists of 17 coins (6 coins date back to 95 A.H, 10 coins date back to 96 A.H and 1 coin dates back to 100 A.H, the diameter of the coins ranges from 2.5 - 2.6 cm and 1mm thick).
- Group B consists of 8 coins (2 coins date back to 90 A.H, 2 coins date back to 94 A.H and 4 coins date back to 104 A.H, the diameter of the coins ranges from 2.6 - 2.8 cm and 1mm thick).
- Group C consists of 10 coins (3 coins date back to 85 A.H, 2 coins date back to 95 A.H, 2 coins date back to 97 A.H, 1 coin dates back to 99 A.H and 2 coins date back to 100 A.H, the diameter of the coins ranges from 2.5 - 2.8 cm and 1mm thick).

The deterioration's aspects that these coins suffer from can be restricted in the following points:

- Some coins suffer from a thin corrosion layer black and grey that partially disfigured them, as it is shown in figs. 1, 6.
- Some coins miss parts and others lost their circular edges, as it is shown in Figs no, 1- 6 .
- Same coins suffer from micro cracks , as it shown in Fig. 2.
- Iron stains on some coins surfaces, as it is shown in Fig. 1.

Fig. 1 - The obverse of the group A (17 coins) before treatment.


Fig. 2 - The reverse of the group A (17 coins) before treatment.

Fig. 3 - The obverse of the group B (8 coins) before treatment.


Fig.4 - The reverse of the group B (8 coins) before treatment.

Fig. 5 - The obverse of the group C (10 coins) before treatment.

Fig. 6 - The reverse of the group C (10 coins) before treatment.

EXAMINATION AND ANALYSIS

The visual appearance is not a dependable guide to tell us which metal or alloy this group of coins is made of, and because corrosion products are often the only available guide to the original elemental composition of an object, where metallic samples cannot be removed, and to its burial or corroding environments, so just analysis is the precise way to detect exactly the present corrosion products and to tell us from which metal or alloy these coins made of. The examination and analysis were carried out as the following.

METALLOGRAPHIC MICROSCOPE EXAMINATION (ME)

Metallographic examination for samples of the three groups of coins (A, B, C) were performed, as it is shown in (Figs. 7, 8, 9 ,10).

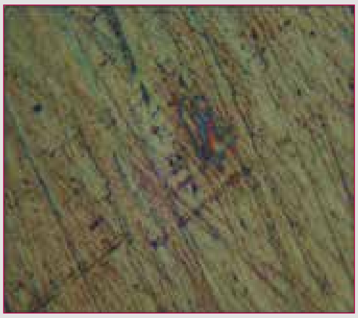

Fig.7 - ME for a sample from the group A, shows the micro crocks (50X).

Fig.8 - ME for a sample from the group B, micro cracks & pitting corrosion (150 X).

Fig.9 - ME for a sample from the group C, shows layers of lead in silver (150 X).

Fig.10 - ME for cross- section of silver coins shows the islands of lead in silver (150 X).

SCANNING ELECTRON MICROSCOPE EXAMINATION (SEM)

Scanning Electron Microscope images (Figs 11, 12,13) showed that the more external uncovered spots.

Fig.11 - SEM examination for a sample from the group A, suffers from micro cracks & Crevice corrosion (500X).

Fig.12 - SEM examination for a sample from the group B, suffers from pitting corrosion (100X)

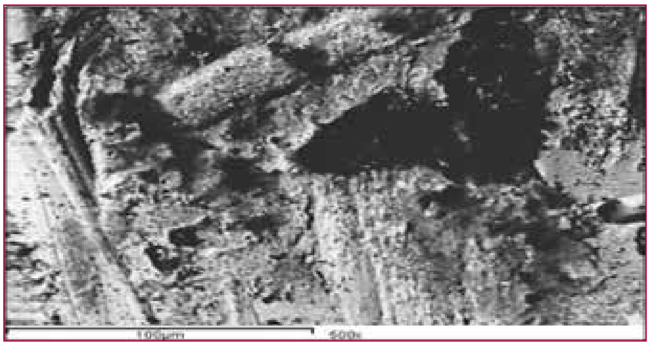

Fig.13 - SEM examination for a sample from the group no. C, suffers from pitting corrosion & distorted the surface (500X).

X-RAY DIFFRACTION ANALYSIS (XRD):

Three samples from the corrosion products of the three groups of coins (A, B ,C), and another sample from the soil were analyzed by using a Philips X-ray Diffractometer with Cu Kα radiation. The aim of this analysis is identification the corrosion compounds in order to decide whether it is authentic, stable, and suited to certain kinds of conservation treatment. also the sample of soil help us to know the natural and composition of the burial environment and explain the relation between it and the coins corrosion products. This information can assist in choosing the best environment for coins in storage or in show-cases. The obtained diffraction-scan given in figs 14,15, 16,17 and the identified compounds represented in table 1.

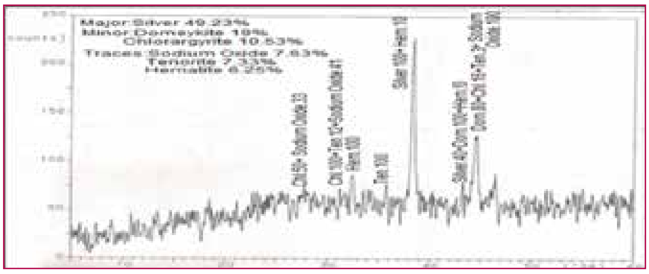

Fig.14 - XRD scan for the corrosion products of the first group (A).

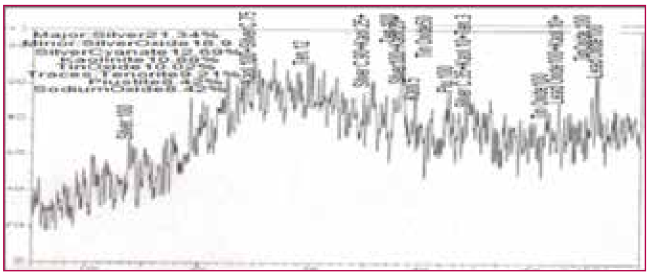

Fig. 15 - XRD scan for the corrosion products of the second group (B).

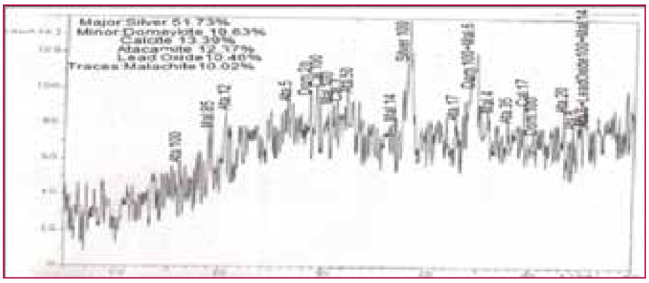

Fig. 16 - XRD scan for the corrosion products of the third group (C).

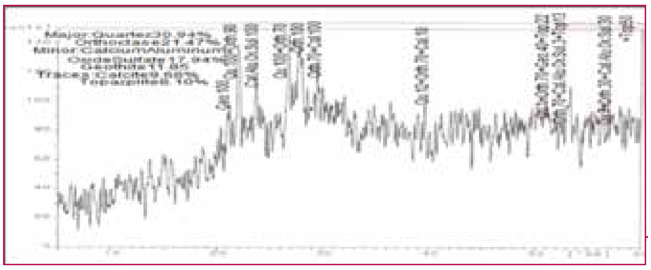

Fig. 17 - XRD scan for the corrosion products of the soil.

SAMPLES	COMPOUNDS		
Major	Minor	Traces	
-The group no. A	Silver Ag	Domeykite As Cu3 Chlorargyrite Ag Cl	Sodium Oxide Na2O Tenorite Cu O Hematite Fe2O3
-The group no .B	Silver Ag	Lead Oxide Pb2O Silver Cyanide AgOCn Kaolinite Al2Si2O5(OH)4 Tin Oxide SnO2	Tenorite Cu O Piustite Fe O Sodium Oxide Na2O
-The group no. C	Silver Ag	Domeykite As Cu3 Calcite CaCo3 Atacamite Cu2(OH)3Cl Lead Oxide Pb2O	Malachite Cu2Co3(OH)2
-The Soil	Quartz SiO2 Orthoclase KAlSi3O8	Calcium Aluminum Oxide Sulfate Ca4Al6O12So4 Geothite Fe O OH	Calcite CaCo3 Topazplite 3CaO.Fe2O3.3SiO2

Table 1 - XRD analysis results of corrosion products of the coins and the soil.

Elements Samples	Ag%	Cu%	S n%	P b%	Fe%	M n%	Total %
-The group {A}	86.72	1.23	1.86	8.47	1 .13	0.59	100
-The group {B}	87.75	1.44	1.53	7.61	1.17	0.50	100
-The group {C}	86.43	1.42	1.78	8.23			

Table 2 - XRF analysis results of the coins.

X-Ray Fluorescence is a non-destructive, powerful and easy-to-use technique for the elemental analysis of a wide variety of materials, three small samples from the groups of coins were analyzed by this technique to determine its composition, by using : NITON/XL8138 (USA), driven with software version 4.2E.The results are shown in the table 2.

TREATMENT AND CONSERVATION

The choice of method for cleaning depends on what is required from the object, what is made of, and what condition it is in. The mechanical cleaning of metals is preferred method for removing disfiguring corrosion, It allows more control and has less effect on the metal alloy. However, for coins where the main aim is to reveal as much detail as possible, treatments may be used that could not be justified for other metal objects. These include the judicious use of chemicals, the use of chemical treatments for coins is acceptable than the mechanical cleaning as these coins are often thin and brittle with surfaces that can be easily scratched or marked. Even very gentle pressure exerted during mechanical cleaning can damage them.
The chemical treatment was chosen assisted by skilled mechanical cleaning, this helped us to reveal and discover the original surface topography.
After searching in the previous studies (14,15), also tests were carried out to determine which chemical compound would be effective without damage the coins the least by varying the concentration and time of contact, it was found that aqueous 15% ammonium thiosulfate (NH4 S2O3) is the least damaging and fastest acting solution.
The treatment procedures included the following steps:

- The coins were treated locally by aqueous 15% ammonium thiosulfate for a short time, the corrosion products were removed mechanically with nylon soft brush.
- Rinsing with distilled water.
- Repeated washing in hot deionized water bathes with altering heating and cooling to ensure flushing capillaries to remove any chemical residues.
- Drying in repeated bathes of ether followed by drying in hot saw dust and mopped dry with soft , clean cloth
- The coins were coated with 3% paraloid B-72 solution, dissolved in acetone (figs 18, 19, 20, 21, 22, 23, 24).

Fig. 18 - The obverse of the group A (17 coins) after treatment.

Fig. 19 - The reverse of the group A (17 coins) after treatmen.

Fig. 20 - The obverse of the group B (8 coins) after treatment.

Fig. 21 - The reverse of the group B (8 coins) after treatment.

Fig. 22 - The obverse of the group C (10 coins) after treatment.

Fig. 23 - The reverse of the group C (10 coins) after treatment.

Fig. 24 - The obverse & reverse inscriptions of the coins after treatment.

RESULTS AND DISCUSSION

The Umayyad caliph Abd Al-Malik ibn Marwan minted purely Islamic dirhams 77 A.H, the pictures of sanctification fractional disappeared from it and transferred to Arabic literature, that was happened after dispute erupted between Al caliph Abd Al-Malik and the Roman emperor. We find on the face of dirham (Obverse), the message of unification in the center (No god but Allah alone with no partner, in the outer margin Al-baslma (name of god), then the place of mint(this dirham was minted in Waist or Damascus etc..), and the year of mint (year seventy seven). It is noticeable here that the direction of writings run counterclockwise. The back of dirham (Reverse) includes in center surat Al- sincerity (God is one, God Samad , didn't generate or wasn't born, into him wasn't one). On the outer margin Mohamedan's message (Mohamed is the messenger of Allah sent him with guidance and the religion of truth, even though the pagans may detest).
The importance of study these currencies is due to the following reasons:

- away for the exchange of trade and estimate the value of things in these distant time;
- of the prevailing economic conditions at that time; identification of the most important manifestations of Islamic state;
- tool to store purchasing power in these ages;
- the currencies consider an important historical documents: it tells us the names of caliphs, sultans, rulers and governors, also they describe the dependency or the secession of the regions from the center of Islamic caliphate;
- identification of the names of ancient cities and places of mint;

The chemical composition of the Silver coins is listed in table 2. Silver is the main component of all the coins, with a high amount of Lead ranges from (7.61% - 8.47%) and traces of Copper, Tin, Iron and Manganese. Lead whose occurrence is related to the silver extraction from Argenti ferrous lead ores.
By studying the structure and constitution of the grains and phases of these coins, an understanding not only of the properties of a particular metal but also the history of its manufacture may result. For instance, the metallographic investigation serves in revealing the nature of ancient technology of the objects, the manufacture process consisted of hammering between an immobile and a mobile die of a heated silver alloy blank to make its figures and inscriptions.
ME and SEM examinations (figs.7, 8, 11) show a lot of micro cracks disperse in the metal, as a result of this technique.
Metallographic examination of Silver coins shows the separation of Silver and Lead with the formation of Lead islands scattered in the Silver, it is a common feature of Silver or Copper alloys due to the non-solubility of Lead in Silver, also the structure appears elongated and flattened as a consequence of the mintage process (figs. 7, 9). As a consequence of the joining of different metals, the behavior and the rate of corrosion are remarkably influenced by the intimate contact between metals with different electrochemical potential , this contact induces the more reactive and less noble metal to become anodic in a couple

strongly conductive to corrosion. The amount of current which flows and therefore, the extent of corrosion depends on many variables, among which are the chemical-physical parameters of the burial context, the difference in potential of the two metals, the presence and nature of the electrolyte and the micro chemical structure of the alloy. As clearly shown by the above reported results, the contact between silver and lead in coins has enhanced the corrosion phenomenon whose main agent is the chloride anion coming from the soil.

Metallographic and Scanning Electron Microscope examinations on the damaged areas of the surface show the presence of chlorine as an aggressive agent as well as giving evidence of the some soil constituents Cl , Mg , Al , Si , Fe , Ca and degradation products. In addition ME , SEM and XRD results show the occurrence of selective localized or general chlorine corrosion phenomena are induced also by the separation of the coins constituents, which creates reactive electrochemical areas.

XRD analysis show that the composition of the coins corrosion product encrustations is Chlorargyrite and a small amount of Lead Oxide, Domeykite, Silver Cyanide, Kaolinite, Calcite Geothite and traces of Sodium Oxide, Tenorite, Piustite and Topazplite. Chlorargyrite is the most familiar alteration products of Silver during burial in salty archaeological soils, the presence of it in Corrosion products indicates that the soil where the coins were buried was an aerobic soil and has a high level of soluble salts especially chloride salts. We can thus deduce that Silver Chloride has been formed during the long-term archaeological burial and generating Chlorargyrite compound .

XRD analysis of a sample from the soil (fig. 17 & tab.1), where is the coins were discovered, show the presence of Quartz, Orthoclase, Geothite and traces of Calcite $CaCO_3$. The presence of Quartez as a major compound in the soil played an important role in their severe corrosion, this soil which is porous and changed from Sub-saturation to saturation with water, had different salt ions, specially the dangerous chlorine ion, this circulation of saline water in the soil had a serious effect on the coins. Calcite is an identified compound , which is most probably formed by the reaction of soluble calcium bicarbonate with hydroxide ions produced in the Cathodic reduction of Oxygen: thus the soil where these coins buried was a calcareous aerobic soil [16]. Such soil usually has high carbon dioxide and may be chemically very aggressive because the carbon dioxide may react with water to form carbonic acid, which may attack metals directly and prevent the formation of a protective film on the metal surface. A calcareous soil may also act in a quite benign, however, especially if carbon dioxide and water produce the soluble calcium bicarbonate [17], this may act to protect the objects from corrosion. Also Calcite ($CaCo_3$) is found as a minor compound in XRD results of the corrosion products from the group C (fig. 16 & tab.1), it is indicated the strong relationship between the corrosion compositions and the soil compositions.

XRD analysis for a corrosion products of the second group of coins (number B) declared the existence of silver cyanide (fig. 15 & tab. 1). It is an unusual corrosion product to be found , X-Ray diffraction analysis was generously performed for a sample from the soil to determine why the product developed on the object, also research was carried out on the previous studies to determine the true reasons for that [14], all the previous studies didn't give us a logical explain for the existence of cyanide match with our case , also XRD analysis results of the soil sample didn't show any trace for cyanide in that soil. So the reasonable explain for that , probably it came from the extraction of silver from Argenti ferrous lead ores or using Sodium or potassium Cyanide in extractive and refining processes.

CONCLUSION

As most studies rely on the most effective recovery of the surface topography of the coin, and other considerations such as composition, metallurgy, surface treatment and sometimes authenticity determination, treatments may be used that could not be justified for other metal objects, these include the judicious use of chemicals accompanying with gentle mechanical cleaning with caution.

It is difficult to define the ideal system for cleaning all silver objects. A more intricate or irregularly tarnished object may require a combination of techniques to remove the tarnish.

For health reasons close examination should give to all silver objects before any conservation treatments commence, particularly if the treatments involve acids.

Silver cyanide (Ag CN) is an extremely poisonous , any treatment involving acid in contact with silver cyanide could prove fatal. Therefore, any whitish-gray or black powdery wart shaped product found on historical silver objects should be handled with caution before conservation treatment is begun.

All treatments should be carried out wearing gloves in a fume hood, and any corrosion dust should be disposed of properly.

At the end, proper storage is recommended as it is important in preventing further corrosion. The coins should be stored in an area with as low a humidity as possible and packed in an airtight container with silica gel. And it is necessary to keep them away from possible sources of organic acids. Handling should also be kept to a minimum and preferably done with cotton gloves.

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Abstract

A big group of silver coins (35 coins) was discovered in Banawa excavation , Dhamar , season 2002, and now it is situated in Dhamar Regional Museum ,Yemen. They were covered with a thin grey and black corrosion layers that disfigured them and hid their figures and inscriptions , also Some coins miss parts and others lost their circular.The aims of this work are identified the metallic composition of the coins , investigate the nature of corrosion grown during the long-term burial and identify its products that will help us to understand the corrosive factors and the degradation mechanisms , cleaning the group of coins from the superficial dirt and the corrosion products in order to discover as much as possible the surface topography, and to reveal the surfaces details , finally to establish them against further deterioration .To achieve that samples from the coins were examined by Metallographic Microscope {ME} , Scanning Electron Microscope {SEM}, the corrosion products were analyzed by X-ray diffraction{XRD} , and X-ray fluorescence { XRF} was used to determine the coins metallic constituents. Chemical cleaning was chosen for treating the coins and they were isolated to preserve them against further attack. After treatment and conservation, the coins figures and inscriptions that could be identified showed that this group of coins dates back to Umayyad period , exactly the reign of caliph Abd al-Malik ibn Marwan{ 65- 86 A.H}{685-705A.D} and his descendants till 106 A.H.

Keywords

Umayyad caliphate; Islamic current ; Yemen; Silver coins; XRD analysis; SEM examination; XRF analysis; Treatment and Conservation

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