An Approach to Microanalysis and Conservation of Silver - Copper Object in Agriculture Museum, Cairo, Egypt

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This research dealt examining, analysis and treatment of a silver - copper belt, it exhibited in Agriculture Museum in Cairo. This research aims to study the ancient silver alloy; because of the successful examination and analysis helps in the treatment of old metal objects and then maintain them.

The analysis of archaeological objects requires simultaneously non-destructive (the objects are unique and precious), versatile (samples with different geometry), sensitive (trace elements are often important) and multi-elemental methods.

In this paper, scanning electron microscopy (SEM) employed to diagnose the characteristic morphology and environmental effects of the silver-copper object. X- Ray diffraction (XRD) used to identify the mineralogical composition of samples, inductively coupled plasma optical emission spectrometer (ICP) used to determine the accurate elemental composition of the silver-copper object.

The results obtained by this research showed that the alloy containing about 22% silver, 65% copper, and it covered with copper corrosion products, these results represent the correct diagnosis, which will help us to understand the fabrication of ancient silver-copper alloy, which is still needed more studies.

KEY WORDS: Ancient silver alloys, ICP-OES, treatment silver – copper object.

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1. INTRODUCTION

Silver is a very noble metal and often found in a native state combined with gold, tin, copper, and platinum. It is completely stable in aqueous solutions of any pH as long as oxidizing or complexion substances are not present. In addition, silver did not appreciably affect by dry or moist air that is free from ozone, halogens, ammonia, and sulfur compounds. [(1)]

The corrosion products of silver are stable, the treatment accorded silver artifacts is less critical than for other metal objects, when treating base silver with a significant amount of copper, it is the copper and its corrosion products that can create problems; in these case, the artifact should treat as copper. [(2)]

Analytical investigations of archaeological objects bring us much information on the development and propagation of technologies on cultures. To conserve and restore these valuable and scarce objects, it is indispensable to understand their chemical constituents and crystal structures. [(3)]

1.1 object description and technology

The silver-copper belt exhibited in the agriculture museum; under no. (SH1996); which undated and weighs about 500:600 gm. Figure no. (1A) shows that the metal belt decorated with metal wire, there is a ring in the top of the belt with a long chain with pendants, the lower part of the metal belt relates to its six rings, and there are three chains out of each ring, and there is a coin in the end of chain. It was also noted that the second ring in the right hand has two coins; and lost the third coin.

These inscriptions are difficult to describe because they hide under corrosion products. Figure (1B) Describes the behind face of the

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metal belt; and there is a black webbing used to connect the belt during wear.

Fig.1 (A, B) show the metal belt before treatment

This research studies objects represents techniques used by artisans in metal smelting, where they found in silver and copper alloy proportion of silver from about 25: 30%, sometimes up to 80%, as alloy containing small amounts of tin, arsenic, lead. The presence of lead in the alloy index extraction and smelting silver by cupellation process, which requires the study of alloy belt consisting of silver-copper alloy, and study the possibility of identifying the technology used by the manufacturer in melting and extraction the alloy.(4)

2. METHODS OF INVESTIGATION AND ANALYSIS

Scanning electron microscopy (SEM) attached with an energy dispersive X-ray spectrometer (EDX) used to diagnose the structure and morphological texture of the samples. For the analytical and metallurgical study, X-ray diffraction (XRD) used to identify the mineralogical composition of the samples. The elements determined by an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), furthermore,

4- Gordon R, Knopf R. Late horizon silver, copper and tin from Machu Picchu, Peru, Journal of Archaeological Science2007; 34: 38 -47.

For SEM examination, very small samples required, the samples were coated with amorphous carbon, and SEM operated in secondary electron mode, which suitable for examining the surface morphology of sample material, magnification 10 X up to 400,000 X and resolution for 3.5 nm. For XRD, the samples were cleaned and finely powdered to avoid any imbrications in the obtained results. For ICP, samples were prepared as solutions with standard.[(5)]

2.1 Scanning Electron Microscope Equipped With Energy Dispersive X-Ray Analysis (SEM)

SEM allows the observation and surface characterization of inorganic and organic materials at a higher resolution and depth of field that the conventional optical microscope. In the SEM analysis, a thermo-ionic emission of an electron beam directed over the sample to produce characteristic signals that provide information on crystalline array, chemical composition, and magnetic structure and even on the electric potential of the specimen under observation. SEM offers a high resolution (approximately 100A˚) and high field depth giving a 3D effect to the images. [(6)]

Samples investigated and analyzed by [JEOL – JXA840A Electron probe Microscopy], equipped with EDX micro analytical system to obtain the total element content qualitatively and quantitatively by EDX unit in the samples. It was useful for semi quantitative elemental analysis to make up for the deficiencies of XRD. [(7)]

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6- Loaned, E., Loaned, A., Rusu, D., Doroftei, F., Surface investigation of some medieval silver coins cleaned in high – frequency cold plasma, Journal of cultural Heritage, 2011: 12, 220 226.

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2.2 X- Ray Diffraction Analysis

XRD is a convenient and useful tool for the identification of crystalline compounds as well as for assessing the structure of complex natural compounds. The theoretical basis of this method is the fact that X-ray diffraction patterns are unique for each crystalline structure. When the X-ray beam passes through the material, a large number of the particles can expect to align in such directions that they can fulfill the Bragg relationship for reflection for each possible inter- planar spacing. (8)

X-ray diffraction analysis carried out with X-ray diffraction equipment model XPERT-PRO-P Analytical, Cu radiation 1.54056A° at 40 KV, 25mA, 0.05 /sec. High-resolution graphite monochromatic, rotating sample holder and a proportional detector. Measurements carried out on powders of the samples, in the range $0° < 2\theta < 70°$ with a step of 0.02°.

2.3 Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES)

The elements determined by used inductively coupled plasma – optical emission spectrometer (ICP-OES) PERKIN ELMER OPTIMA 2000 DV. The samples prepared as solutions with standard. In general, HNO_3, HCL, H_2SO_4, H_3PO_4, $HCLO_4$, HF and H_2O_2 used for alloys and minerals samples. (9)

3. RESULTS:

It is indispensable to understand the chemical constituents and crystal structures. The technology of the materials used in the fabrication of ancient Egyptian metal object is still not fully investigated. (10)

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10- Daniels, V., Analyses of copper – and bees wax – containing green paint on Egyptian antiquities, studies in conservation, 2007, 52, pp.13 -18.

A study of the techniques used by craftsmen in the smelting and extraction of metals, and identify on rates of minerals for silver - copper alloy helps to reach to successful treatment. [11]

3.1 Scanning Electron Microscopy (SEM) coupled with EDX

the surface of the metal belt has a lot of corrosion products as showed in figure (2) with a magnification of 2000x, EDS of the sample points out that it consists of 42.02% oxygen, 2.34% silicon, 0.82% sulfur, and 0.54% chlorine, they represent the corrosion products, also EDS contains 17.2% copper, and 37.09% silver, they represent the composition of the object alloy.

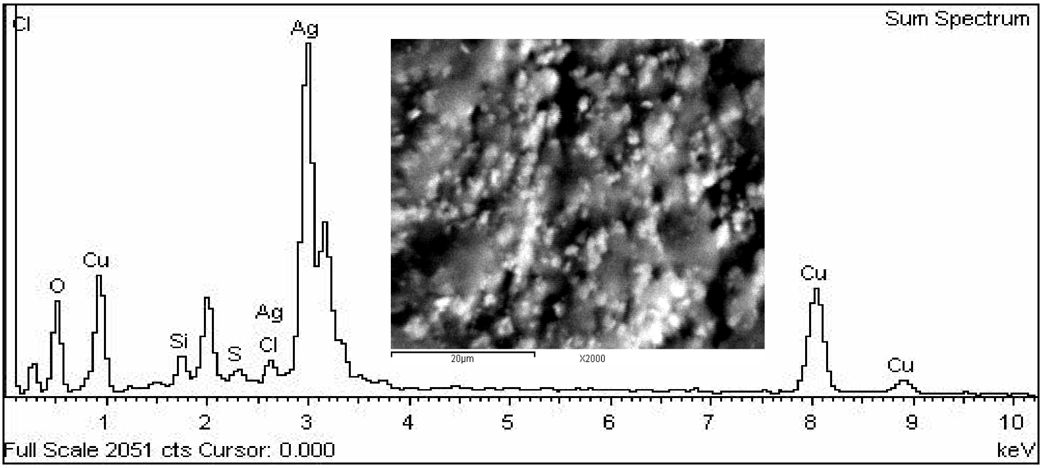

Figure (2) SEM image at magnification2000x of silver and copper alloy shows the metal surface pitted and porous; SEM-EDX pattern shows the alloy consists of 42.02% oxygen, 2.34% silicon, 0.82% sulfur, and 0.54% chlorine, 17.2% copper, and 37.09% silver.

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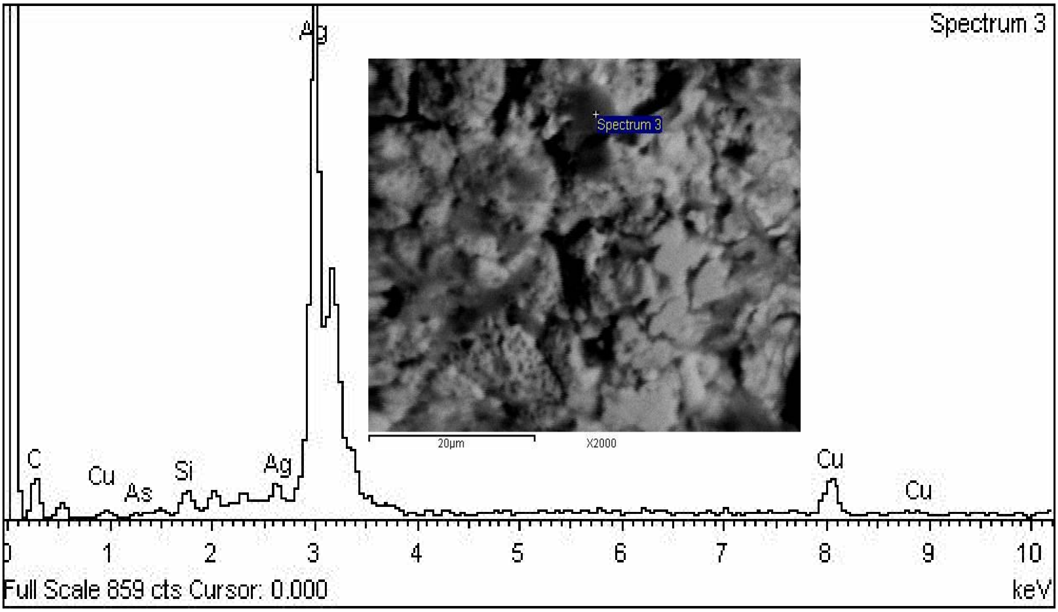

Figure (3) SEM image at magnification2000x of silver and copper alloy shows the metal surface etched and porous; SEM-EDX pattern shows the alloy consists of 21.81% carbon, 1.92% silicon, 8.12% copper, 0.19% arsenic, and 67.96% silver.

Figure (3) with a magnification of 2000x shows another area of the object surface, EDS of the sample reveals that it consists of 21.81% carbon, which represents the adhesive agent used to adhere the sample to the device holder, 1.92% silicon, which represents one of the corrosion products, and 8.12% copper, 0.19% arsenic, and 67.96% silver, they represent the composition of the object alloy.

3.2 X-ray diffraction (XRD)

Figure (4) shows the X-ray diffraction pattern of the sample, the major is silver, the minor is copper, and they represent the components of the object alloy, corrosion products represented in minerals Cuprite Cu_2O, silver oxide Ag_2O and Paratacamite $Cu_2CL (OH)_3$.

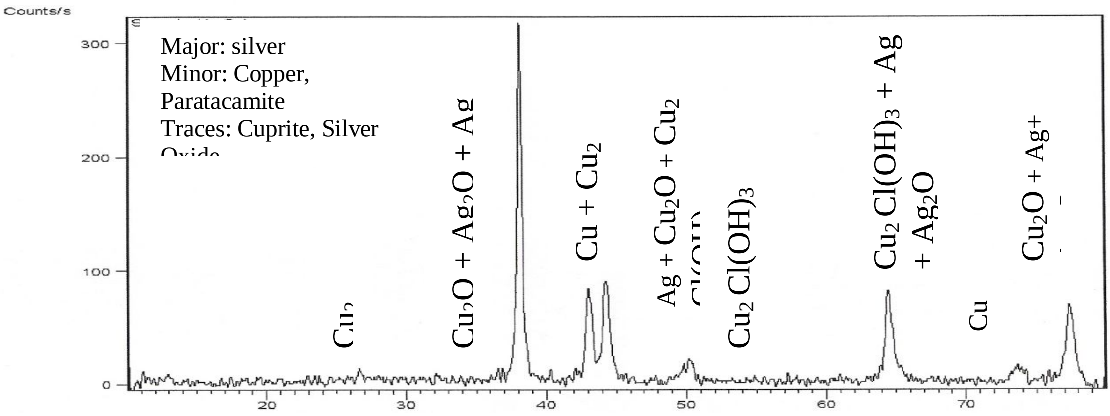

Figure (4) shows the X-ray diffraction pattern of the sample, the corrosion products represented in minerals Silver Ag, Copper Cu, Paratacamite $Cu_2Cl(OH)_3$, Cuprite Cu_2O, and silver oxide Ag_2O.

3.3 Analysis by Using ICP

The study and analysis by use ICP enables us to identify the components of the object alloy, and the techniques used in the smelting the metals. Table (1) shows the alloy consists of silver and copper. The percentage of the minerals are 21.9% silver, 64.7% copper, 2.64% Arsenic, 1.85% tin, 0.16% lead, and 0.0% antimony.

Table no.1 shows the elements ratio% by ICP-OES.

Element%	Ag %	Cu %	As %	Sn %	Pb %	Sb %
Ratio	**21.9**	**64.7**	**2.64**	**1.85**	**0.16**	**0.00**

The variation ratio between silver and copper in the samples that examined by using SEM and analysis by using ICP; due to the portion of the sample which examined by using SEM is a part of surface object, which content a high percentage of corrosion products and silver, while the part which analyzed by using ICP represents part of the object alloy, which represents the true proportion of minerals in the alloy.

4. TREATMENT PROCESSES

Different cleaning strategies considered, with special regard for mechanical and chemical methods; these should be suitable to remove the thick layers of corrosion products which hide most of the surfaces, thus preventing their readability.

After removing a webbing; and jaw for easy cleaning without damaging the webbing, it can study the metal belt through the examination and analysis, we can identify corrosion products and metal alloy, so it is easy to clean and treatment.

Mechanical cleaning was used due to the possibility of better controlling the cleaning level. Optical aids for the magnification of the concerned areas extensively used. A mechanical and chemical combined cleaning was used for those areas with alternate stratification of corrosion products, which particularly delicate due to the small dimensions and thin lamina. (12)

The majority of silver objects recovered from archaeological contexts require only limited treatment. In most instances, the various corrosion products can remove with simple chemical solutions. (13) For base silver with copper corrosion compounds (as the metallic object), concentrated ammonia effectively cleans all copper compounds from the silver. Care must take, however, because ammonia dissolves silver chloride and will substantially weak badly corroded silver.

Metallic copper films can be removed with a silver nitrate solution, (14) and then we removed the products residues by rinsing in distilled water and ethanol; drying with infra-red lamps; final

12- Olsoufieff, A., Alessandri, O., an approach to the conservation of deeply corroded archaeological silver: the polos from crucinia, proceeding of metal, national museum of Australia Canberra ACT, 4 – 8 October, 2004, P. 263.

13- Plenderleith, H., Werner, A., the conservation of antiquities and works of art, University press, Oxford, 1971, P. 239.

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protection of object surfaces with 4 percent Paraloid B 72 in acetone. [15]

After treatment and maintenance procedures, the writings and inscriptions hide under the corrosion products became clear, fig. 5(A_1, A_2, B_1, B_2, C_1, C_2) show three coins.

The first coin in the front surface was written (hit in Constantinople 1255), and in the behind surface engraved seal of Sultan Mohamed Abed al Hammed Khan.

The second coin in the front surface was written (Sultan Mohamed Abed Al Hammed Khan of the Emirate of Egypt in Constantinople 1223), and in the behind surface wrote (Sultan Al Din and Hakim Bahrain Sultan bin Sultan).

The third coin in the front surface was written (hit in Constantinople 1223), and in the behind surface engraved seal of Sultan Mohamed Abed Al Hammed Khan. These inscriptions repeated on the coins. Figure 6A, B shows the metal belt after treatment.

Sultan Mohamed Abed Al Hammed appointed in 1223 AH, he is a Thirty-Sultan in the order of the Ottoman state, and the country became progress of civilization, he died in 1255AH-1839AD[16] [17][18]

15- Olsoufieff, A., Alessandri, O., Ferretti, M., an approach to the conservation of deeply corroded archaeological silver: the polos from crucinia, proceeding of metal, national museum of Australia Canberra ACT, 4 – 8 October, 2004, P. 263.

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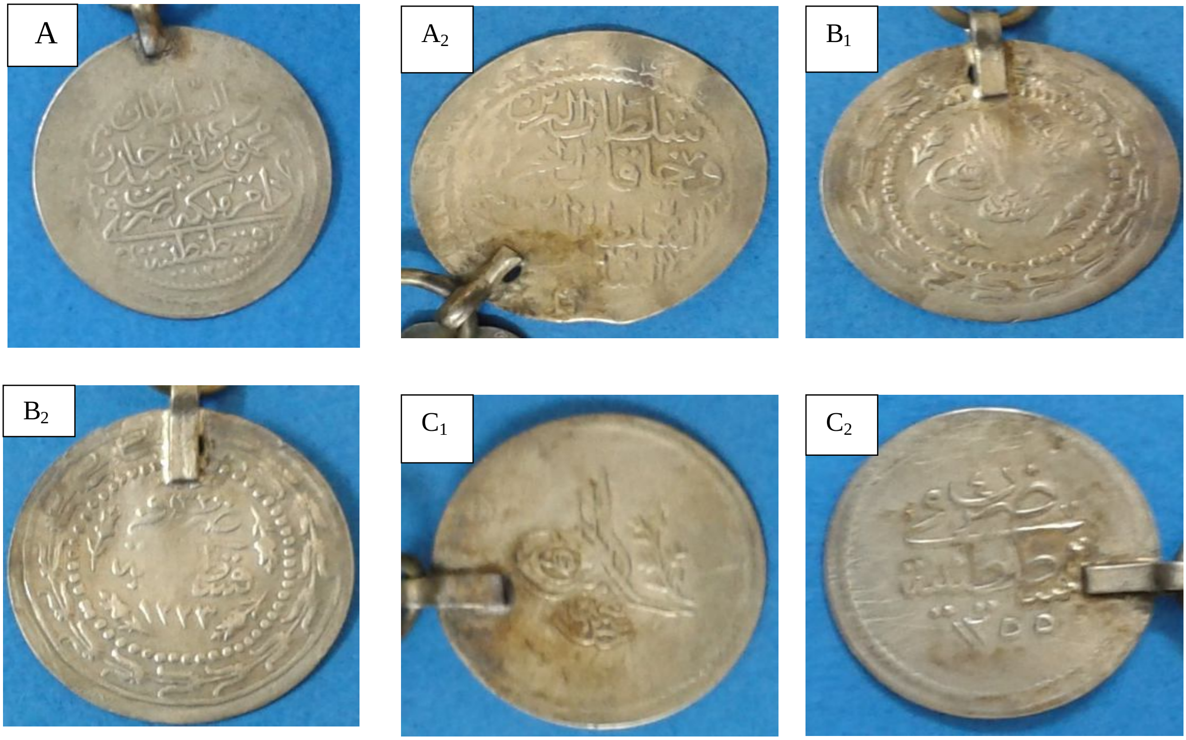

Figure 5 (A_1, B_1, C_1) show the front faces of three coins, and (A_2, B_2, C_2) show the behind faces of the same coins after treatment.

5. DISCUSSIONS:

Alloys of silver with copper have impurities; the principal impurities in the silver-copper alloys are tin, arsenic and lead. ICP results revealed the alloy contained about 1.85% tin, 2.64% Arsenic, 0.16% lead, and 0% antimony.

Ancient artisans could make copper- silver alloys directly by smelting the copper ores containing silver minerals. The resulting alloys would expect to contain less than 20% silver along with the antimony that commonly accompanies the silver minerals. However, the higher silver content and the absence of antimony in the objects against direct alloy production. Instead ancient artisans

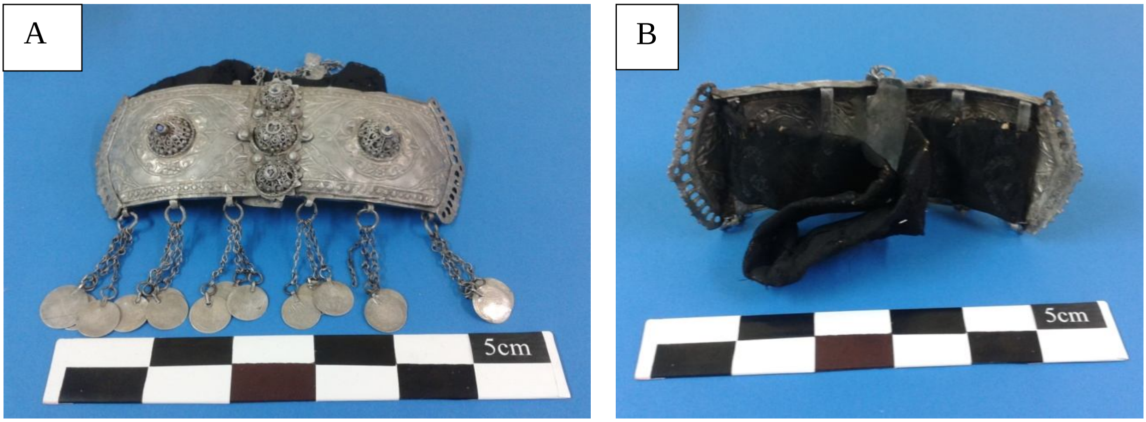

Figure 6 (A, B) shows the metal belt after treatment.

probably melted silver and copper metal stock together in the desired proportions to make their alloys. [19]

The silver used by the ancient metal workers could smelt from silver ores containing minerals such as silver chloride (AgCl) and argentite (Ag_2S). If these ores were free of lead the resulting silver would have a lead content less than 0.05%. The lead content in the artifacts analyzed is as high as 0.9%. Lead used as a solvent in silver smelting. [20] Additionally, silver may have smelt from silver-rich lead ores composed of minerals such as of cerussite ($PbCO_2$) or galena (PbS).

Cupellation to recover the silver from the lead would result in a residual lead content of 0.2% or more in the product. [21] We can interpret this as evidence that artisans smelted lead silver or lead ores, and refined the resulting silver by cupellation. It would expect to have a much lower tin content than it does since cupellation

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reduces the tin content to well below 0.2%. It is likely, then, that the tin and arsenic found in the artifacts entered the alloy with the copper used rather than the silver. (22)

CONCLUSION:

Alloys of 25% to about 30% silver with copper are the most common among the artifacts, but objects containing 80% or more silver are also found. The principal impurities in the silver- copper alloys are tin, arsenic, and lead. The absence of antimony indicated that probably melted silver and copper metal stock together in the desired proportions to make their alloy. The lead content of the silver-rich constituent indicates that the silver in the alloys made by cupellation.

When silver smelting from ores free from lead, such as argentite and cerargyrite, the ratio of lead is less than 0.05%, but if there is more 0.2% lead as the topic of the research, the silver extracted from ores of lead, such as cerussite or galena.

When treating base silver with a significant amount of copper, it is the copper and its corrosion products that can create problems; in these cases, the artifact should be treated as copper.

ACKNOWLEDGEMENTS

The author is grateful acknowledges the help of Mohamed Allay Al Din the general manger of Agricultural Museum and all the assistants, also, the central metallurgical research and development institute for facilitate analysis by using ICP.

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