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Application of Portable X-Ray Fluorescence (PXRF) for compositional analysis of metallic heritages of Ethiopia and implications

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Abstract

In this study data generated with Portable X-Ray Fluorescence (PXRF) through community service in one of the Ethiopian Orthodox Church (EOTC) museum is used. The PXRF was applied to determine the type, mineral content and quality of gold (karat) of heritages along with visual observations. Measurements of elemental compositions on more than 331 contemporary and antique museum items helped to know the proportions of major and minor trace elements. The hand and processional crosses in the museum indicated two or three elemental compositions of major elements (Gold (Au), Silver (Ag) and Copper (Cu); Gold and Copper; Silver and Copper; Silver and Nickel (Ni)). Minor elements include Chromium (Cr), Tungsten (W) and Titanium (Ti) and particularly observed on memorials and souvenirs (e.g., medals, pendants and watches). Minor amounts of Tungsten which can tolerate high temperatures are added as part of a jewelry practice to increase durability and toughness. The presence of Chromium indicated to avoid tarnishes on Silver made items. Some heritages are decorated with unidentified colored stones. Similar ones are seen in other Ethiopian museums. Documentation of the colored stones and associated metals in terms of (e.g. carat, color, cut, benefits) are not available. These gaps along with destructive goldsmith practices for identification of gold karats and the lack of modern visiting applications would expose the heritages for covert theft. The FDRE Mines proclamation to regulate transactions of minerals does not include specific articles about treatments and required declarations. The absence of national labs for identification, certification and proofing standards further exacerbates the challenge by making the regulatory process inept. The application PXRF is very crucial for quick feedbacks about the compositions of the heritages without damaging the physical appearance and protection of heritages in all Ethiopian museums.

1. Introduction

X-Ray Florescence (XRF) is one of the non-destructive analytical tools for measurement, analysis and determination of elemental compositions of metallic and metal alloyed objects. The Portable X-Ray Fluorescence (PXRF) and Hand-Held X-Ray Fluorescence instruments have been in regular application to determine the type, mineral content and quality of gold, quick frontier exploration in the assessment of green field and industrial application of alloys such as [1, 2, 3,4] and determination of gold fineness in karats (on 1 to 24 scale) has been in the practice for long period of time. The PXRF both hand held and table top with shield were gradually introduced for the application in museums, archaeological artifacts for elemental compositions determinations and metallic artifacts such as copper alloyed archaeological studies [5, 6]; ancient coins of Roman [7], Japanese coins [8], metal purity and verifying origin of ancient artifacts and artworks [9,10]. Applications for custodian ship of the museum objects [2, 11] could be extended for quick inventory purposes and content data and information in museums. The museum object should be described by features and benefits as customarily done in the jewellery industry for a number of purposes. There are various models and types of PXRF in the market that can be used for such purposes. The term PXRF is preferred and used here instead of the Hand-Held X-ray Fluorescence (HH-XRF). The application of PXRF's includes the less common ones in archaeology, to trace back origins of antic materials of historical objects as well certifications and authentications of art objects, contemporary human history among others [5, 9]. Other studies executed using PXRF devices in the measurement of the elemental composition of bulk and corrosion layers of copper-alloyed artifacts are reported in [6, 12]. The potential of PXRFs to provide accurate and quick results in a non-destructive sense both in field and laboratory brought forward the intention of using for periodic check and inventory in many museums. With the advent of new state of the art of PXRF as a non-destructive technologies and the purpose of having a consistent and detailed data for the catalogues on various historical, cultural, religious (sacred) artifacts, jewellery objects, antique watches, Medals and Badges among others becomes important globally.

Nevertheless, the scientific and modern method of analysing the type, quantity, quality, and composition of the minerals that make up the valuable's museum items, etc., without affecting their physical appearance, is not a common practice in Ethiopia [13]. This study is therefore using the data generated from the voluntary professional service rendered to assist the rapid identification and delivery of the mineral content of gold- and silver-plated enumerated artifacts and others in one of the EOTC museums [13]. The PXRF measurement gave particular focus for various sacred and other metallic and metal-alloyed (composed using precious and base metals) artifacts archived in the museum mainly used for religious processional (sacramental) purposes. Some of the sacred items used for religious services include, stands, podiums, lecterns; various sizes and designs of hand, processional or blessing crosses. When these objects retained in the museum for different reasons or decisions, they will carry national, indigenous, cultural, historical values as heritages other than the religious and monetary values.

The traditional practice of gold and silver smith is subject to periodic nicking of particles from the sacred parts or museum artifacts to confirm the quality of gold in Karats using aqua- rage (a mixture of nitric acid and hydrochloric acid). The results are often rounded to basic Karat readings 14, 16, 18, 21, 22 in the 24 Karat system and are considered as representative of the entire body of the artifact (summed for all parts) although taken from a single spot. The readings are not indicated using the complete 24 Karat system accurately at least with two significant digits and this has compromised the actual Karat (gold content). The karats imprinted for jewelry products customarily indicated with the decimal points ignored, which is not applicable for heritages having significant values. In addition, the appearance and beauty of the heritages will be damaged by repeated inspections carried out periodically for documentation and custody. The non-destructive techniques to analyse the content and quality of these precious heritages made of gold and other metallic minerals and nationally important artifacts should be organized and systematically installed in all museums. In particular, the lessons and practices gained in the museum on sacred objects and other artifacts assist efforts for proper protection from various types of covert thefts and replacement with replicas or fake (synthetic and imitation) products. This procedure allows sacred objects to be organized without disrupting the religious sanctification practice according to the canon. Installing visitors' application by new technologies and or documentation of each object characteristics metallic composition, origin, application and design type and of features and benefits in accordance to the jewellery industry procedures is crucial [13].

2. Methods and Instruments in the museum

2.1. PXRF instrument, measurement procedures and principles

A portable hand-held XRF (PXRF) with the necessary X-ray shielding is arranged table top for safe and convenient operation in the museum (Figures 1 and 2). Verification of the code and weight of the item is measured and recorded for more than 331 metallic museum items. The measurements of the elemental compositions were made using precious mode of the PXRF to increase the level of reliability to ±3 times the standard deviation [14]. At the inventory scale the purpose is to know only the elemental compositions of other heritages (major and trace elements) and the gold karat values without advanced processing and analysis.

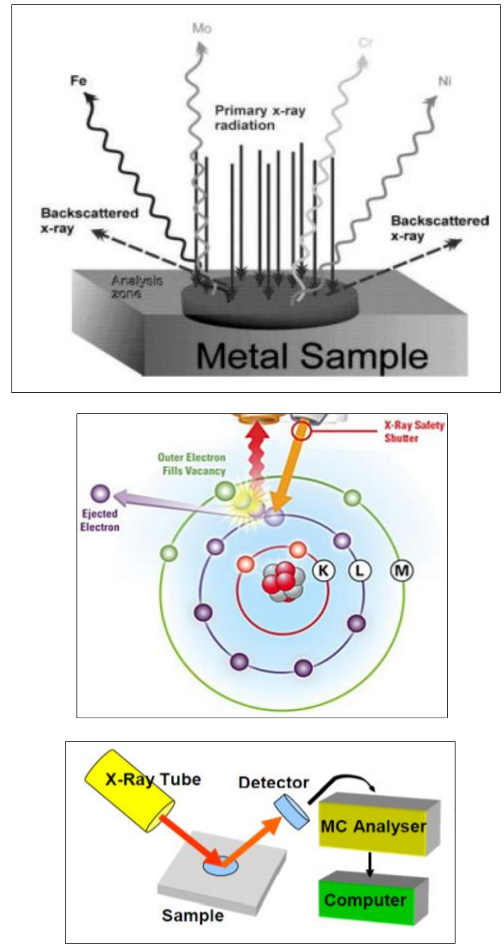
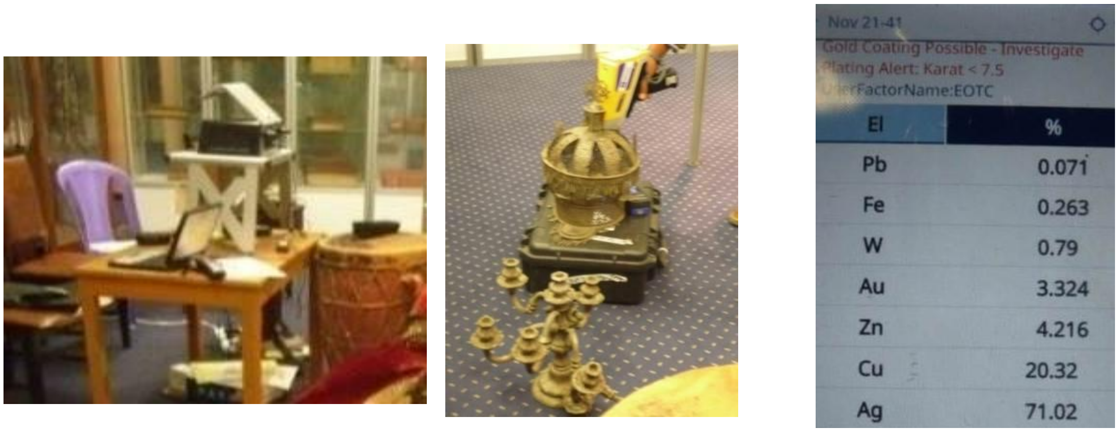


Fig. 1: PXRF detector working principle starts from the part that generates. X-rays and impact the sample (material) surface (upper part) and the impact and excite the electrons revolving on the different atomic orbitals (K, L, and M) and record the energy of the electrons that change their orbits due to the wave are counted and related to the types of elements listed in the periodic table and works above atomic number 12 for magnesium only. The detection is sensed by the main detector and transferred to Mc Analyzer and completed to be displayed at the front panel screen of the XRF gun or displayed on the computer attached to it (Figures 1, and 2). (Courtesy for the pictures [14]).

Weighing of each object/artifact is made using a highly reliable weighing balance (e.g., Precis Digital, Model HT1500) for small sizes. Large and heavy museum items were dismantled and separated whenever possible. To increase the accuracy a suitably flat surface is located for maximum penetration of X-rays (Figure 1). Measurements are recorded and listed separately as part or added to complete the measurement for the object under consideration. This was particularly important to validate the quality of the gold and the variation of compositional elements.



(a) (b) (c)

Fig. 2: (a) Top left, setup for measurements performed by inserting samples into the X-ray shield; on the right (b) When flat surface is not available and not suitable to insert the heritage on the shield holder the X-Ray gun was used on various curved parts of for better accuracy. The result is entered into the database after validation on the screen as depicted in (c).

Heritage objects having greater dimensions in size and were not convenient to dismantle, the measurements were affected at the different parts and sections of the heritage using the X-Ray gun (Figure 2). For example, if a processional cross is considered the karat contents and elemental compositions are measured at the different parts of the cross (e.g. Side wings, central parts, handle and lower part and top part of the cross) to have as many flat sections [13]. Similarly, this was done for cultural heritages like on a saddle and its parts and ornamentations to investigate any variations of elemental compositions in terms of gold karats (quality).

Registered and archived data such as submission/discovery date, details on the compositions, model types, manufacturer and originator were not available in the museum. Missed data and information also include about gemstone-minerals (natural, artificial/imitation, synthetic, treated, faceted, brilliant cuts, un-calibrated cuts, beads, cabochon, double cabochons, riveting pinning etc.) in the designs to conduct additional analysis [13]. In this inventory details such as trace elements found with negligible amounts were not analyzed completely. The physical aspects of some of the sacred objects that arise from the natural and or artificial surface properties or expressions of the minerals, such as rust (tarnish) and other issues are not discussed. Gemstones specific gravity and content, natural vs. imitations, origin and other gemological characteristics are not described or analyzed as measurements of gemological properties require at least basic instruments. In general, detailed issues and advanced holistic measurements as stipulated in the foregoing and studies including like type of design (version); age (period); geological source/origin of the minerals and historical background or sourcing methods etc., are not done because of the requirement of advanced scientific-gemological tools and instrumentations including analysis and interpretations. The PXRF instrument and accessories with the X-Ray shield and computer was installed bench top as shown in Figure 2. Measurements were conducted by mounting and facing the flat surface of the object in the X-Ray shield for maximum penetration of X-Rays (Figure 2a). When the heritage is not suitable and or lacking flat surface for measurements the X-Ray gun is utilized (Figure 2b). Results after inspection and validation are accepted and organized in a spread sheet. The measurements were further analysed for the most abundant major and minor trace elements and gold content in karats using two significant digits. The measurements and analysis of minor (trace) elements are particularly important in determining the colour of the heritage. The PXRF used for this measurement is Olympus–Vanta hand Held XRF analyzer VMR model measuring elements as low as single parts per million (ppm) up to 100%. The Limits of detection (LOD) calculated for three times the standard deviation (99.7%) confidence level. The LOD for each element is a function of the testing time.

2.2. Basics from applied Jewelry and implications to museum heritages

Based on the physical characteristics of the materials and the resulting potential of tangible and intangible features and benefits (e.g., historical, cultural, religious, emotional, social and economic) are briefly defined as part of promotional standards in the Jewellery industry. In similar contexts the sacred objects of material content (metallic elemental compositions, gemological and other physical characteristics) values could be reiterated as features and benefits of the jewellery industry without losing the religious (devotional) context.

a) Features of Jewelry objects

Physical characteristics are mostly related to the materials' physical, chemical, crystal structure, petrographic and gemological characteristics and formation conditions. As for example diamonds rarity, its top hardness on the Moho scale, brilliance and reflection when exposed to different light and special properties (e.g. phenomena, fire, phosphorescence etc. in gemological context), carat weight, karat values of gold, cut type, origin and along with contents of metal composition and standard characteristics are some required by professionals and customers and briefly described as features.

b) Benefits of Jewelry objects

The features of notably physical and special gemological characteristics and the potential implications and specific qualities as for example spiritual and religious, historical and cultural or social values and significance of intangible nature are considered as benefits. Each profile feature describes the potential benefits it provides to the user in concise and clear language. As for example because diamond is rare, it confers high value, prestige and honor to the owner; being the hardest material not scratched easily, everlasting and having non-vanishing makes it to be adorned by many. These intangible qualities, spiritual and emotional, historical or legendary and social values and manifestations of the jewellery effect are expressed in combination with features of (gemological, physical chemical).

2.3. Cultural and sacred artifacts produced by gemstones and metallic minerals

The common metallic minerals, such as gold and silver and base metal and alloys and various gemstones (opal, Ruby, Sapphire, Emeralds and diamonds, pearls) both natural and synthetic and imitations widely used in jewelry making are similarly used also for sacred objects with a purposeful design. Through time, the natural or native forms of metals of gold and silver and platinum become expensive and scarce and as a result the contemporary designs witnessed replacement by gold or silver paints (coatings) and widely available metals such as copper, lead and metals-alloys like bronze. Natural coloured stones with bright colours and brilliant cuts (sapphires, emeralds and diamond looking) might have been combined as decorations in most of the antique museum objects along with ornamental colours of honorary customs for kings and queens and in that successive hierarchies. Although the study is limited to metallic and metal alloyed, there are no standard gemological practices in Ethiopia to determine the coloured stones are natural or synthetic.

Gold and silver, are among the most commonly used precious metals for design and manufacturing of jewellery products. These precious metals in the jewellery industry are used based on the specific design and standard, fused and combined in different ways, either separately or in combination with others. In addition, Copper, Nickel, Zinc, Tin, lead, Iron, Chrome, Tungsten and Titanium are used extensively in various combinations with the precious metals. The resulting new characteristics and appealing qualities are derived from the unique and specific characteristics of each metal. Metals are combined for increasing strength, durability and aesthetics with different proportions and gemstones are used as beads and or different cuts and styles either supplementing the Jewelry design or as a major component. In sacred and sacramental objects (for example crosses) gold and silver are combined with different proportions and quality (Karat) along with gemstones (natural/synthetic or imitations) as beads or ornaments of customized shapes. The gold content (quality) is measured using karat and the difference and the various compositions and making alloys is indicated in Table 1.

Colour on metallic objects and gemstone is the first entity to comprehend and conjecture the object easily. However, color alone cannot be used to identify the object. The presence of major (primary) and minor (secondary) minerals are important in the content and appearance of the mineral. The major minerals in the analytics of PXRF correspond to the formation (crystal structure) while the minor or trace elements are often determining the colour.

3. Results and Discussions

In this study the average karat for gold was recorded to be 16.77 Karats, minimum value 10.49 and a maximum of 21.82 karats. This is agreeable to the common karat contents used by the gold smiths for jewelry purposes in combination (by fusion) with other base metals for increasing strength and durability, for example engagement rings. The measurements registered for gold karats could further be disaggregated into categories of religious, historical and of cultural heritages and valuated to demonstrate the wealth and treasures (Table 2). This will help to emphasize the requirement of technology assisted appropriate safe guarding, protection and a nondestructive tool for periodic inventory. More importantly, preparing illustrative photos and short descriptions of features and benefits according to applied jewelry principles for visitors and researchers is highly recommended.

Many of the artifacts are made from metals commonly recognized (gold, silver, copper and nickel). As summarized in Figure 4 and Table 2 hand crosses have the most numbered, followed by prayer and blessing crosses. This is because the hand crosses are used per person, smaller in size, often pocketed and produced in different designs and decors. In most cases a combination of three and two metals are used in cross works having variations in weight. It is necessary to work out the standard of the method of design and production for various types of crosses at different levels accordingly. The value chain of the major resource material based on the result of each heritage could be reconstructed by making a backward mapping for linkage and materials required sustainably. For example,

Table 1. Summary examples of compostions of gold with other metals and fineness in parts per thousand and purity of gold out of 24 karats (Pure gold with maximum malaeability).

	Parts of Gold (Au) in Karat and Gold fineness. Accepted minium Gold Karat standards varies by country (**)			Major other metals			
				Silver	Copper	Zinc	Palladium
Color of Gold	Gold out of 24 Kt	Gold grains out of 1000	Purity/quality of Gold %	%	%	%	%
Yellow Gold	10	416	41.7	52	6.30	----	----
White Gold	10	417	41.7	47.4		0.9	10
Yellow Gold	14	583	58.3	30	11.7	----	----
White Gold	14	583	58.30	32.20			9.50
Yellow Gold	18	750	75	15	10	-----	-----
White Gold Yellow Gold	18 22	750	75 91.70	----- 5	----- 2	---- 1.30	25% (or Pt) *)
Green Gold	-----	------	---------	Gold, Copper, Silver increased silver content			
Rose Gold	10K, 14K, 18K, 22K			Gold, Copper, Silver and increased Copper content with low purity of Gold or Gold content			

*	Variable
**	Minium value in most countries is 14K , US (10k), France, UK, Austria, Iraland (9K), Denmark , Greeec (8K): source: https://www.gold.org/about-gold-jewelery

taking the cross as an industrial product, it is crucial to think about how it can be manufactured (reproduced) at industrial scale with specific material selection and standard. This is strictly done on one hand preserving the spiritual connotations and religious doctrine that governs and set the standard, and on the other hand based on jewellery market trends and cross-cultural fusions for different purposes of public consumptions. The major and minor chemical elements applied to manufacture, for adding special strength, or color, glamour and durability could be assessed for different applications. For example, those combined for color/harmony and magnificence are Chromium (Cr), Tungsten (W) and Titanium (Ti). Mostly these elements are observed in small amounts in icons, crosses, and heritages originated from overseas and require advanced design and manufacturing methods (Figure 5, and Table 2).

Elements such as Tungsten have a special characteristic of resisting high temperatures (over 3400◦ C), and applied in certain quantities to increase the strength of the jewelry, others, such as chrome, are widely used in the jewelry industry to prevent rust or tarnish and also for aesthetics. A variety of mostly undisclosed and unknown, probably of synthetic or imitation-like beads and pinning were seen in some of the sacred heritages designs. market for a long-time imitating diamond. According to [15] it was first marketed in 1976 and became the dominant diamond imitation, with production of approximately more than 60 million carats per year. This has continued until recently replaced by moissanite. Therefore, it is only possible to rule out qualitatively whether it is cubic zirconia or moissanite product or natural (bead) by comparing the age of the artifact/heritage with the first market year, and the result might be deceptive. However, specialized gemological test is required to exactly differentiate (identify) natural from synthetic gemstone (ruby or sapphire emerald or diamond).

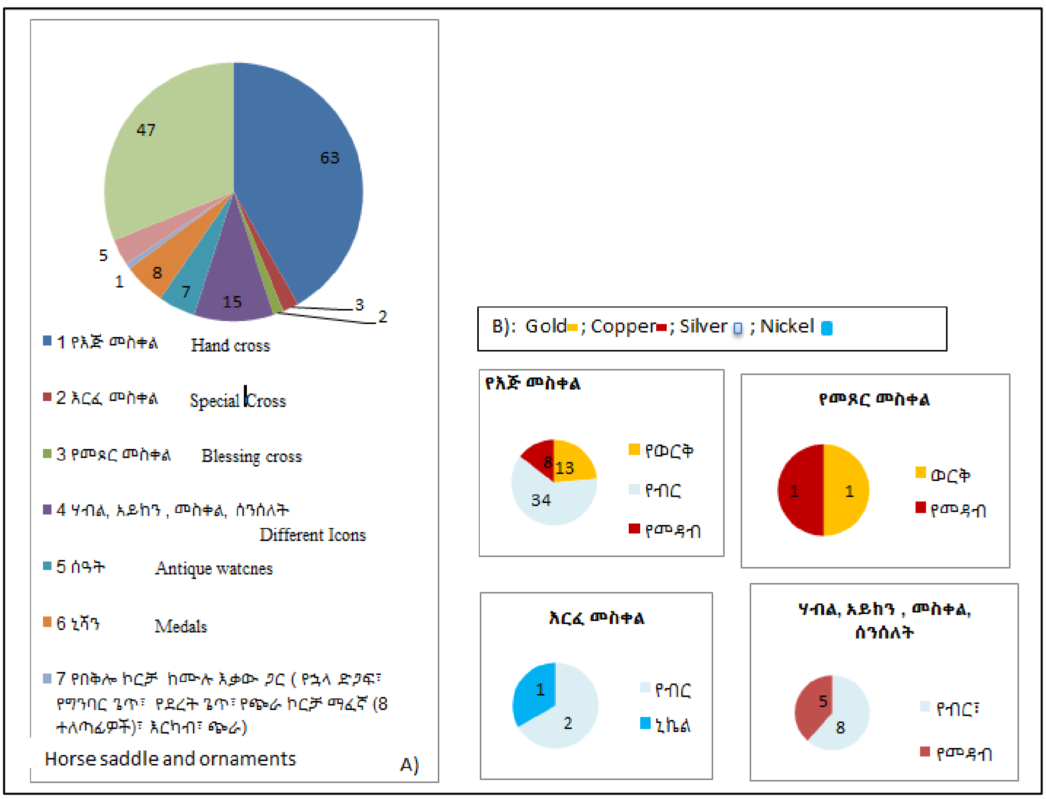


Fig. 4: Different genres and abundances of major elemental compositions. For example, as shown in Figure A), there are large numbers of hand crosses. It shows the major types of metals they are made of by classifying the sacred heritages and artifacts into different groups (hand cross, clocks (processional or prayer stuff mounted cross, blessing cross, icons, chains, mule/horse saddles and associated ornaments). Most are made using gold and silver and in some cases combination of Copper, Nickel and Tin (Figure B upper panels from left to right hand crosses and prayer/blessing crosses; lower panel from left to right special crosses and Icons and chains [13].

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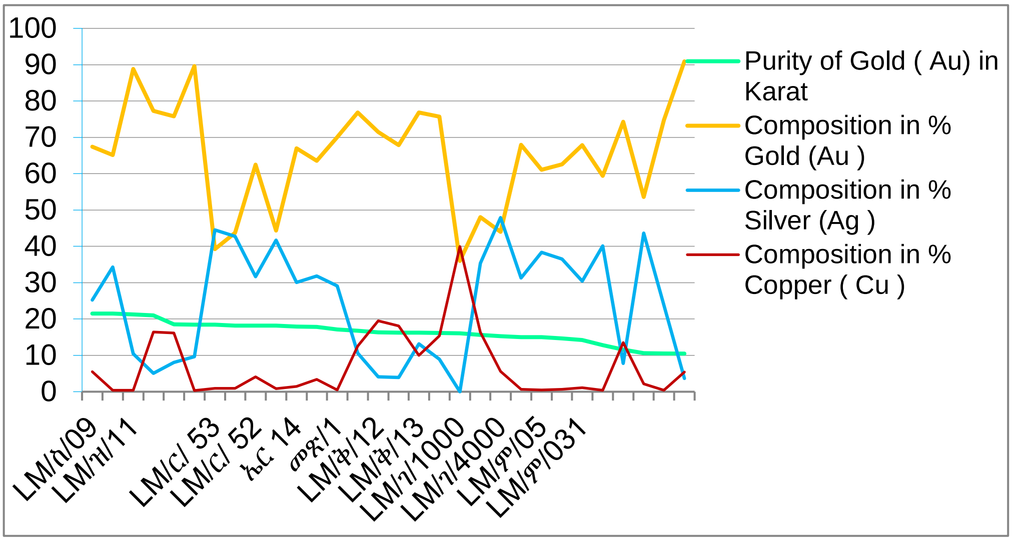

Fig. 5: Gold karat amount found in various gold made heritages and artifacts (green line): amount of gold in the artifact (yellow line %); Other metals added for crafting are the silver blue line; and copper in red line.

The amount of gold in each heritage is related to particle size (or quality). For example, the amount of copper added to heritage LM/ስ/09 is significantly less than the amount of silver added. The amount of gold present is less than that of artifact LM/ዝ/11 (Table 2) because artifact (LM/ስ/09) a hand cross is mostly made of gold except for small amounts of silver and copper added to harden the gold. The quality of gold is above 21K (87.5%) (Figures 6 and 7). The combinations of various precious metals and base metals and resulting colors and standards are shown in Table 1. In all hand crosses different types of combinations are indicated showing lack of country wide standard (Table2).

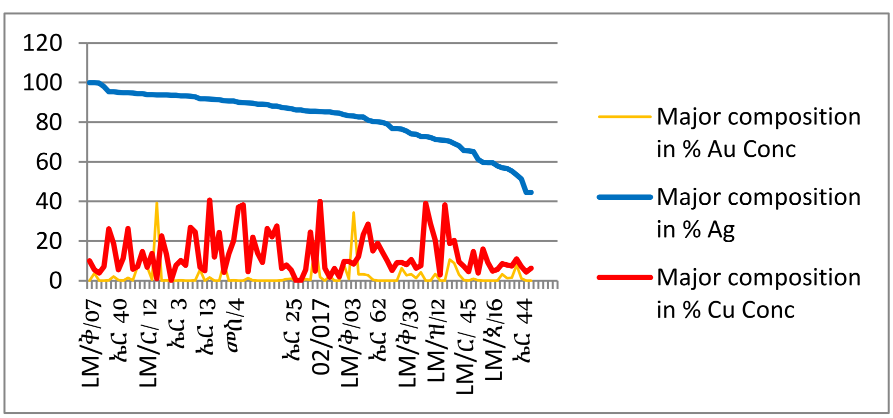

Fig. 6: Amount of silver (dark blue line) found in various silver heritages and artifacts; Less than 40 percent copper (shown in red) is mostly used for hardening; Gold (yellow) is nothing more than plating except for few ones. Additional information about each metal and metal alloyed heritage is detailed in the database other than in this illustration.

The artifacts from the past and now considered heritage, by and large are made of precious metals decorated with natural-colored stones. More recently the trend of using precious metal (gold and silver) coatings of very much reduced gold and associated colored stones of synthetics or imitations variants become common in the contemporary designs. This is notably related to the introduction and availability of new technologies in powder coating, enameling, rubber technology, growing diamonds in labs and increased production of various imitations and synthetics of colored stones. Other contributing pushing factors could be finite and limited natural resources of metals and colored stones, scarcity and market prices volatility and high demands of affordable jewelry products. Above all jewelry is the culture of human beings since time immemorial although there are variations and intercultural mixings and several changes and modifications in the arts, designs and material usage through time. This has stimulated the industry to remain vibrant all the time. Similarly, it is reverberated in the religious and cultural rituals of various forms with constant changes and modifications, customizations in the designs and the use of materials for manufacturing the products. In most of the cases genuine heritages especially antique, rare and exotic ones are made of natural materials unless otherwise swapped with fake products by covert thefts. There is no modern scientific, and technology assisted practice of proofing to protect them from covert replacements using coated material of reduced Karat, imitations and synthetics of colored stones. Such malpractice will continue and very much affect the industry and also museums as the prices of the major three big (sapphire, Ruby and Emeralds) are always on the upside. The scale of the change in the value for the big three of colored gemstones occurred only in the year (2020–2021) alone compared to 10 years ago is unprecedented [16]. Dwindling supply particularly on the high-end markets is due to the depletion of premium quality resources from the mines. These trends will make the management of museum objects very challenging particularly with respect to safe guarding and protection. The recent practice of custodianship in the museums using traditional methods with dearth of data based technological controls to avoid replacements is a futile exercise. The problems of natural stones are not only the huge volumes of synthetics and imitations; it is also the different types of treatments of natural-colored stones and the lack of compulsory declarations. This makes the challenge with respect to colored stones more interacted and complicated. It often becomes impossible to differentiate synthetic and imitations products from natural ones visually. Therefore, the application of scientific and technology assisted systems is a requirement at different levels for identification process, certifications and periodic checks in the museums and certified and skilled personnel handling this task. On the other hand, the absence of clear detailed directives about treatments and the declarations of colored stones opens up for weak regulatory practices, associated with ill-posed and non-genuine trading an obstruction for healthy, competitive and ethical growth and development of the fledgling jewelry industry. The recent Mines proclamation No. 1144/2019 issued to regulate transactions of minerals does not include binding articles towards allowed treatments and obligations for compulsory declaration for the treatments applied. It does not also list at least the major or common types of treatments and associated practices. In most countries for allowed treatments (bleaching, dying, surface modification, irradiation etc.) a proper declaration is compulsory in all transactions.

4. Conclusions and Recommendations

The measurement of elemental compositions of the museum metallic and metal-alloyed heritages using PXRF brought a new dimension in the customary inventory process i.e., against the goldsmith destructive practice that gives only gold karat values. The application of PXRF is proved to be a quick and non-destructive process with a consistent and reproducible data of major and trace elemental compositions and gold content and quality readings of increased accuracy. It has helped to avoid permanent physical damage on the heritages that diminishes aesthetic beauty and dimension and weight reduction with repeated sampling by hewing. The work has indicated the major issues that will be done in the future for similar heritage management and preservation, protection and integrated services in Ethiopian museums. The data and resulting analysis showed the need to set national metal and metal alloy standards with maximum and minimum compositions for all sacred and cultural heritage items for industrial scale manufacturing. The designs of Ethiopian crosses are the list studied and categorized and this requires a holistic integrated study from the Jewellery aspect. Revisiting the regulatory process for marketing and transactions of heritages made of metallic and metal alloyed and gemstones including treatments of gemstones and associated declaration are crucial. This is also a concern about quality and standard inspection on the trade and transaction of value added or raw natural gemstones and requirements of genuine declarations of surface and internal treatments (e.g., physical modification using chemicals, dying and bleaching) other than physical polishing and cutting in the course of installing responsible sourcing and trading. In short period of time documenting using photographic catalogue with full description (e.g., origin, any background history, design type etc.) for each museum artifacts are important until contact less technology-enabled visitor's application is installed. Building systemic tools and database of the mineral content from PXRF measurements as a standard inventory procedure will safeguard and protect heritages from possible thefts and non-original replacement using replicas, imitations and synthetics.

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