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A CHARACTERIZATION OF SELECTED PRECIOUS METALS ARTIFACTS FROM BENIN CITY

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Abstract

In the fabrication of artifacts, issues like the true components of produced materials, date of production and the provenance cannot be overlooked. Significantly, the foregoing has its close affinity with materials' forgery and faking. This brings to bear the pertinent question of the perceived materials employed in the production of an artifact, as against the true components. To examine the components of a material, there is a need for the application of an external technique to probe into the internal properties of the material, which is known as material characterization. The need for materials' scientific analysis, which has overtime provided failure-proof result, has increasingly become imperative even in the arts. To demonstrate this, nine precious metals artifacts from Benin City were studied using three different Ion Beam Accelerator techniques (IBA). These included Rutherford backscattering spectrometry (RBS), proton induced gamma-ray emission spectroscopy (PIGE) and proton induced X-ray emission spectroscopy (PIXE). The elemental analysis provided forensic evidence of faking of the studied silver alloy items and undercarating of the gold alloy items.

Keywords: *Characterization; True component materials (TCM); Perceived materials; Material analysis.*

Introduction

Materials' analysis is quite diverse and not restricted to a single classical technique. It is employed in materials science, art and art history, archaeology, archaeometry and sciences amongst others. Overtime, artists have come to derive more meaning in the production of artistic outcomes for sale as commodities. This makes the commodification of artifacts quite popular [1]. However, it is also expected that an artifact tagged as a commodity ought to be crafted with the material(s) so declared. This brings to bear the pertinent question of the perceived material employed in the production of an artifact as against the true component materials (TCM). Other issues such as the age, value, provenance, production technique, modification and restoration of an artifact amongst others are also significant at some point. An effective probe of the foregoing issues may require more than just physical examination. A critical scientific study in form and materials' analysis will, to a large extent, reveal beyond surface appearance. In other words, a characterization of materials entails the use of external testing techniques to probe into the internal structure and properties of a material, in this case, precious metals. Materials characterization entails materials profiling which is quite crucial in detecting the elemental composition of the materials. Thus, central to this paper is a scientific analysis of silver and gold alloys. Specifically, the focus is on some precious metals artifacts

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produced in Benin City. These will be studied scientifically so as to investigate their true component materials (TCM). Also, the elemental composition of the analyzed precious metals items will be examined against global standards.

Besides copper alloy casting for which Benin City is reputable for, gold and silver artifacts are also produced in Benin City. Gold and silver usually classified as precious metals are mostly used in the production of items of jewelry by jewelers. Characteristically, gold and silver in their pure forms, are too soft for jewelry production. This is one main reason why they are alloyed with other metals to increase their hardness [2]. Notably, in the course of alloying these precious metals, there are prescribed acceptable global standards with legal implications too. It is in this respect that the value of a precious metal artifact is determined by the precious metal component in the artifact [3, 4]. This forms the crux of this paper, where the aim of characterizing selected gold and silver artifacts from Benin City is primarily to determine their true component materials (TCM) so as to ensure that they stand the test of global standards. In this study, nine jewelry artifacts comprising of five silver alloys and four gold alloys were examined. All nine items of jewelry were procured in their polished state.

Experimental

For the purpose of this elemental analysis, 9 precious metals samples of artifacts were used. Specifically, these items were produced between 2000 and 2010, and acquired from different jewelers in Benin City metropolis. Out of the nine items sampled, five are of silver alloys and four are of gold alloys. Generally, jewelers in Benin City employ two types of silver in the production of artifacts. These are termed ‘high silver’ and ‘low silver’. For the purpose of this study, items coded Slv1 (Fig 1a), Slv2 (Fig 1b) and Slv3 (Fig 1c) are items made from the high silver, while items coded Slv4 (Fig 1d) and Slv5 (Fig 1e) are made from the low silver. For the gold alloy artifacts, one item representing the identified 4 gold alloy types used by jewelers in Benin City was sampled and analyzed. The gold items are coded thus: Gld1 (Fig 1f) is of 22 carat, Gld2 (Fig 1g) is of 18 carat, Gld3 (Fig 1h) is of 14 carat and Gld4 (Fig 1i) is of 9 carat.

All the 9 items as expressed in figures 1a-i, are small sized jewelry artifacts that fitted the size of the samples’ holder for the analysis and for this reason, there was no need for the items to be fragmented.

Three Ion Beam Accelerator (IBA) techniques; Rutherford backscattering spectrometry (RBS), proton induced gamma-ray emission spectroscopy (PIGE) and the proton induced X-ray emission spectroscopy (PIXE) were used simultaneously for the elemental analysis of the 9 sampled items. IBA techniques are analytical techniques originally dedicated to nuclear physics, but also attract the interest of solid state physicists and materials scientists as potential tools for both materials processing and micro-analytical analysis [5]. Specifically, IBA analytical techniques are favored for reliable elemental investigation of materials such as ceramics, stones, metals or pigments from paintings [6]. Ion Beam Accelerator (IBA) is an important family of modern analytical technique involving the use of MeV ion beams to probe the composition and obtain elemental depth profiles in the near surface layer of solids [7]. IBA analytical techniques were so employed because of their suitability to the items under study, essentially, these three IBA techniques produce both qualitative and quantitative analysis. They are also non-invasive, non-destructive and allow depth profiling of samples. These techniques are renowned for accuracy of the information obtained [8]. For this reasons, the IBA techniques of PIXE, PIGE and RBS are very often used simultaneously in art and archaeometry in the determination of the composition of objects [9]. Importantly too, any scientific technique for analysing valuable art and cultural objects should be: Non-destructive, fast, universal, versatile, sensitive and multi-elemental [10]. The IBA technique of materials’ analysis meets these criteria for analyzing objects of artistic, historic or archaeological.

Fig. 1. The jewelry: a - Silver alloy pendant, b - Silver alloy pendant, c - Silver alloy stud earring, d - Silver alloy neck chain, e - A pair of silver alloy wedding band, f - A pair of gold alloy wedding band, g - Gold alloy stud earring, h - Gold alloy pendant, i - Gold alloy stud earring

The Ion Beam Accelerator was used in the analysis of the sampled items. Precisely the Ion Beam Accelerator used in this study is situated in the Tandem Accelerator Laboratory of the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. The Tandem Accelerator is centered around a NEC 5SH 1.7 MV Pelletron Accelerator equipped with RF charge exchange ion source. The ion source is equipped to provide proton and helium ions.

Results and Discussion

A summary of the results of the elemental analysis of the nine jewelry artifacts are expressed in the table below.

Table 1. Summary of elemental composition of the nine precious metals items.

Item.	Elemental composition in Percentage (%).							
	%Ag	*% Au*	*%Al*	*% Ca*	*% Ti*	*%Fe*	*%Cu*	*%Zn*
Slv1	97.33	-	-	-	-	-	1.40	-
Slv2	97.91	-	-	-	-	-	2.2	-
Slv3	97.2	-	-	4.62	0.09	0.02	1.62	0.03
Slv4	-	-	90.95	0.13	-	0.32	-	-
Slv5	-	-	90.91	0.12	-	0.32	-	-
Gld1	2.23	58.35	-	-	-	0.04	0.51	-
Gld2	14.50	33.90	-	3.40	0.07	0.01	6.91	0.30
Gld3	15.73	24.92	0.6	19.1	0.04	0.05	12.5	0.25
Gld4	11.7	9.9	-	1.24	0.03	-	14.5	1.60

The 3 silver alloy items produced with ‘high silver’, recorded high values of silver in the range of 97.2% - 97.91%. For Slv1 and Slv2, copper was the only metal alloyed with the main constituent of silver and this recorded low values. In Slv3, five other elements; calcium, copper, titanium, iron and zinc were alloyed with silver. Of these five elements, calcium and copper recorded low values of 4.62% and 1.62% respectively, while titanium, iron and zinc recorded values less than 1% which could also be classified as trace elements. Calcium is a silvery white metal that bears a thin layer of oxide which protects the metal from attack by air. The presence of calcium in Slv3 may help prevent or slow the tarnishing of this item. The elemental composition for the two other silver items (Slv4 and Slv5) made of low silver is quite revealed. In both items, silver was not detected at all, rather aluminium that was detected in high values of 90.91% and 90.95% respectively as the major constituent. The other elements in Slv4 and Slv5 are traces of calcium and iron.

The detected analysis results of the silver content in Slv1, Slv2 and Slv3 meet the global standards, specifically in this regard, the elemental composition of Sterling silver prescribing silver with a value of 92.5% and copper as 7.5% [11], while for the Britannia silver alloy, the silver content is about 95.84% [12]. What can be deduced from this is that the silver content in items Slv1, Slv2 and Slv3 are even higher than those specified by Untracht [13] which are 925/1000 parts of silver for Sterling silver and 958.4/1000 parts of silver for Britannia. In the case of silver contents of the items made with high silver, the silver content is also higher than the German standard of 15 loth which is 93.75% of silver. But it is not quite comparable with German 16 loth which is 99.9% of silver content. For Slv4 and Slv5, there were no traces of silver. The implication being that jewelers may have termed the aluminium alloys ‘low silver’ in other to fake silver. Unfortunately, the unsuspecting consumer may not be aware of the fact that there is no trace of silver in this so-called low silver, yet will go ahead to pay for the worth of silver. It was also noted that the rate of oxidization in the two low sliver items is quite uncharacteristic of silver alloys. All the silver alloy items studied were polished to high lustre before purchase by the researchers and were wrapped up seperately with tissue paper. Significantly, it was only items Slv4 and Slv5 that were observered to show signs of discoloration after four months of procuring the items. The foregoing runs contrary to the belief that usually, silver alloys are quite resistant to corrosion and does not oxidize easily [14].

In the 22 carat gold alloy item coded Gld1, four elements were recorded. These are gold, silver, copper and iron. The value of gold detected in this item is 58.35% which is moderately high, silver was detected as 2.23%, while iron and copper were detected in trace amounts. For Gld2, the 18 carat gold alloy item, seven elements were detected. The gold content in this item recorded 33.90%, while silver, copper and calcium recorded low values that were 14.50%, 6.91% and 4.40% respectively. Titanium, iron and zinc were fingerprinted as trace elements. In the analysis of the 14 carat gold alloy pendant coded Gld3, eight elements were recorded. Gold, silver, copper and calcium recorded low values of 24.92%, 15.73%, 12.5% and 19.1% respectively. Other elements in this alloy include aluminium, titanium, iron and zinc that were recorded as trace elements. In the elemental composition of the gold alloy stud earring coded Gld4, six elements were detected; gold recorded a low value of 9.9%; while silver, copper, calcium and zinc recorded values of 11.7%, 14.5%, 1.24% and 1.60% respectively. Titanium was fingerprinted as a trace element in this item.

From the 9 precious metals items studied, some did not fully represent total elemental composition. In the case of silver alloy items (Slv4 and Slv5), one may not rule out statistical errors. But in the case of all four gold alloy items, what may seem evident is undercarting. This actually forms the bane of an investigation of this nature. The value of precious metals in precious metals alloys cannot be overemphasised. In the observation of Guerra and Dunwiddie, the quality of a precious metal alloy is its finesses in terms of the content of pure precious metals that the metallic alloy bears [15, 16]. It is in this context that global standards set for the purity of precious metals items cannot be compromised. Specifically, for gold alloys, the term carat gold which refers to the relative purity of gold is used. In this regard, pure gold is expressed as 24 carat, while gold alloys contain percentages of other alloying metals. However, there could be variances in standards. The gold purity standard in America is expressed in table 2.

Table 2: Percentage of gold in carat gold alloys [17].

Carat	% of Au	Carat	% of Au
24	100	12	50.00
23	95.83	11	45.83
22	91.6	10	41.67
21	87.50	9	37.50
20	83.33	8	33.33
19	76.17	7	29.17
18	75.00	6	25.00
17	70.83	5	20.83
16	66.67	4	16.67
15	62.50	3	12.50
14	58.33	2	8.33
13	54.17	1	4.17

Even at that, there are levels of alloying precious metals which is known as tolerance levels for precious metal purity. This may also differ slightly from country to country especially within the ambits of laws on precious metals. For example, in Britain, the specified Laws for a 14 carat gold should contain 58.5% of pure gold, while that of America is 58.3% [18].

Generally, when the items analyzed in this study, were compared against global standards of gold purity, the value of gold in the four gold alloys sampled tended to fall grievously short. Findings revealed that the gold content in Gld1 is 58.35% as against 91.67%, which is prescribed in the global standard. It is also same for Gld2, which revealed 33.90% as against 75.00%, Gld3 was 24.92% as compared to 58.33% and Gld4 which is 11.7% as against the prescribed 37.50% of the global standard. A further analysis in terms of the value of gold in the various cartages revealed that Gld1, a supposedly 22, is barely slightly higher than a true 14 carat. Gld2 of 18 carat actually falled in between 10 and 9 carats; Gld3, which is claimed 14 carat is between 5 and 6 carats, just like Gld4 that is claimed 9 carat actually falls between 2 and 3 carats. Evidently, all four tested and analyzed gold alloy items were grossly undercarated.

In the same vein, and in the case of the silver alloy items, two of the sampled items were actually aluminium alloys without traces of silver. The established cases of undercarating for the gold alloy items and faking in the case of two silver alloy items may not be peculiar to Nigeria. Its wide prevalence gave rise to the general insistence on the need for assaying and hallmarking of precious metals.

This growing prevalence of undercarating is fast becoming a global phenomenon. But it is more widespread in developing economies, especially countries without laws regulating the production and sale of items of precious metals. In Nigeria, precious metals dealings are still largely operated on 'trust'. That is, the trust between the smith or retailing outlet and the clients [19]. In an analysis of this concept of 'trust' as it relates to precious metals dealings, Girimaji holds the view that one can never fully trust a jeweler's assurances when it pertains to the purity of gold alloys [20]. According to Kloss, undercarating of jewelry whether done intentionally or by accident is a silent global crime that often goes unnoticed [21]. Painfully, the major result of this fraudulent misrepresentation of gold values in items of gold alloys is suffered by the consumers who end up paying more for a lesser worth of a precious metal item. This is in the sense that while gold alloys with pure gold in right proportion may not tarnish, those undercarated usually end up tarnishing [22].

The need to protect the investment of the consumers of articles of precious metals has led some countries to develop a process of testing and certifying articles of gold, silver and lately platinum and palladium before such items are allowed into the markets. This process of testing articles of precious metals is called Assaying, while the certification of the tested items is referred to as Hallmarking. Ordinarily, assaying is the qualitative chemical analysis of a material either for some specific elements or the sum total of its compositional elements. However, in terms of a gold alloy item, assaying simply means the determination of the content of gold in an alloy [23, 24]. On the other hand, hallmarking is a process marking or stamping articles made of precious metals. The emphasis in hallmarking a product especially as it pertains to consumer, amongst others, is stamping the year of the production of the article as well as the symbol of the maker on articles of precious metals as seen in figure 2. In so doing, there is a third party authentication of such items of precious metals. The third party in this case is the government of the day. Basically, assaying and hallmarking make the tracking of an article producer easy in the event of a confirmed sharp practice.

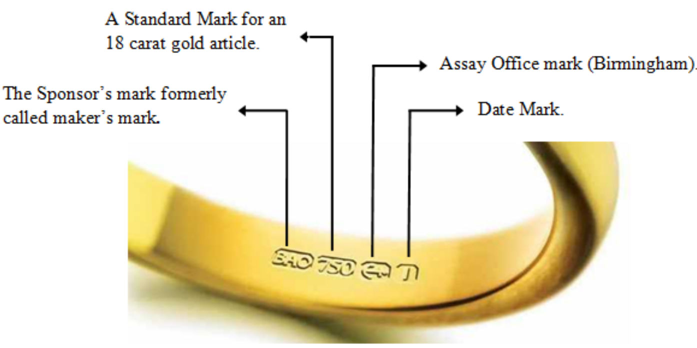

Fig. 2. Sample of Britain Hallmarks on an 18 carat gold alloy item [24].

Conclusions

The true chemical components of materials, date of production, provenance, undercarating and faking amongst others are quite crucial to the authenticity of an artifact. To clarify such issues, physical examination may not suffice, hence the need for materials analysis or materials characterization. Scientific materials study has been a veritable tool of materials analysis. The result from the study of nine items of silver and gold alloys indicated cases of faking in the silver alloy items and undercarating for the items of gold. In other words, IBA materials' analysis tool is useful in establishing forensic facts about the authenticity of the artifacts. This is also a necessary complement in the investigation, preservation and conservation of various types of artifacts.

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