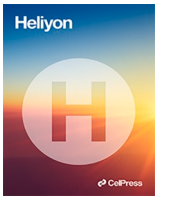
Heliyon 10 (2024) e34623

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon



Research article

A two-way analytical investigation of ancient gold coins: Elemental and colorimetric description of precious materials

Roberto Sáez-Hernández [a,*], María Josefa Luque [b], Adela R. Mauri-Aucejo [a], Ángel Morales-Rubio [a], M. Luisa Cervera [a]

[a] Department of Analytical Chemistry, Faculty of Chemistry, University of Valencia, C/ Dr. Moliner, 50, Burjassot, 46100, Spain
[b] Department of Optics and Optometry and Vision Sciences, Faculty of Physics, University of Valencia, C/ Dr. Moliner, 50, Burjassot, 46100, Spain

ARTICLE INFO

Keywords:
Gold coins
Elemental composition
pXRF
Smartphone
Color
Non-destructive analysis

ABSTRACT

The investigation of ancient artifacts is often constrained by their scarce availability and high protection and custody protocols. Among these, coinage represents an especially valuable kind-of-samples given their uniqueness and the subjacent information that is hidden behind their composition. Their analysis are often carried out using non-destructive techniques in order to avoid any alteration of the samples. In the field of Cultural Heritage analysis, smartphone-based methodologies have experienced a significant increase during the last few years, given their wide availability and ability to yield fast results. However, their analytical application demands a thorough and careful tuning during the methodology optimization. In this work, 21 historical gold and golden coins spanning a historical period of more than 2000 years have been analytically investigated. To that end, a two-fold approach has been implemented: first, the elemental composition has been analysed using portable X-ray fluorescence; and second, an innovative smartphone-based imaging method has been applied to measure their colour. Results allowed to describe the coins from their elemental profile, identifying some potentially debased ones, as well as some others not containing any gold. When possible, the results have been compared to previously reported cases, but our samples include some previously unreported cases representing new insights. All in all, this article provides new analytical data on unanalysed unique historical samples, in terms of their elemental profile and colorimetric properties, making use of an innovative, non-invasive nor destructive, fast and affordable colorimetric smartphone-based method to characterise historical coins.

1. Introduction

Coinage is a characteristic of complex societies, since it implies the manufacturing of exchange pieces that are acknowledged by all the members of the community who trust them as a medium of keeping and transferring value. During thousands of years, different civilizations have minted coins both for economical and commemorative purposes, often using cheap and affordable metals (like copper, zinc or tin), but also more expensive and valued ones. This is the case of metals like silver and gold.

Ancient coins are objects of interest to the analysts' community. From the elemental composition to the state of conservation, the

* Corresponding author.
E-mail addresses: roberto.saez@uv.es (R. Sáez-Hernández), maria.j.luque@uv.es (M.J. Luque), adela.mauri@uv.es (A.R. Mauri-Aucejo), angel.morales@uv.es (Á. Morales-Rubio), m.luisa.cervera@uv.es (M.L. Cervera).

https://doi.org/10.1016/j.heliyon.2024.e34623
Received 14 February 2024; Received in revised form 10 July 2024; Accepted 12 July 2024
Available online 14 July 2024

Abbreviations

BCE	Before common era
CE	Common era
CRM	Certified Reference Materials
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
μXES	Muonic X-ray emission spectroscopy
PCA	Principal Component Analysis
p-ED-XRF	Portable Energy Dispersive X-Ray Fluorescence
ROI	Region of Interest

application of analytical techniques to these samples allows to better understand the past. For example, the gradual compositional change in the precious element over time might be correlated to economical constraints in a particular society. The elemental composition of ancient coins must be studied by non-destructive and non-invasive techniques. Among these, X-Ray Fluorescence (XRF) is of particular importance and common use [1–3], because it provides affordable, fast and reliable results about the samples, turning it into the first and most commonly used tool in this field. However, some constrains and limitations must be considered when applying this technique: first, the fact that results are only representative for the outermost part of the coin, and second, that the limits of detection (LOD) are relatively high for some elements, not allowing to determine trace elements. For these cases, more sophisticated and expensive techniques, such as muonic X-ray emission spectroscopy (μXES), would deal with the first problem [4], while employing Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) could tackle with the second [5,6]. While μXES is non-destructive, LA-ICP-MS can be considered as invasive given the fact that a powerful laser is directly applied to the surface of the sample.

The different metallic composition of the coin, as well as their conservation and corrosion state generate differences that reflect on the appearance of the coin. This means that the colour of the samples, evaluated either by their reflectance spectra or by their chromaticity coordinates, is dependent on the metal proportions and nature of the elements present on the surface of the coins. Hence, the investigation of the colour of these historical and cultural samples emerges as a potential analytical tool to characterise these samples. Considering that colour arises as a physical interaction between an incident radiation and the object, the experimental conditions (angle, light source, geometry …) and the properties of the sample influence the final result and hence must be considered when developing analytical methods.

Smartphone applications to Cultural Heritage samples are still scarce, although some examples are already starting to appear [7–9]. Using smartphones as analytical devices gives rise to many different advantages, such as the general availability of the devices, which ensures that analytical information can be obtained in any context. Ease-of-use is also interesting, since they are devices which are well known by the public and this facilitates their incorporation to multidisciplinary fields like Cultural Heritage studies. Analysis based on smartphone images are fast and non-invasive, making them suitable for the study of valuable historical items. However, given the fact that they are not originally intended to be used as analytical tools, some important concerns must be addressed additionally to those previously mentioned.

1) *Lighting conditions*: Smartphone cameras work by capturing the continuous light spectrum that gets to the sensor, and transforming it into a three-channel system (RGB). This means that the recorded analytical signal depends on the lighting conditions. Since colour is the result of the interaction between incident light and the object under investigation, the final result will depend upon the incident light. This means that all the surface of the sample should be illuminated by a homogenic light, with the same intensity, and the same angle, to avoid differences caused by the lighting.
2) *Internal transformations and image enhancements*: As the original aim of the smartphone cameras is to capture and store images, manufacturers tend to implement some automatic image processing techniques to enhance colour contrast and make the images more arresting. These processes take into account the lighting and colour environments of the scenes, so that each image will suffer slightly different transformations. These modifications are often ignored by the analyst, meaning that analytical signals are often used without correcting these changes.
3) *Glare*: Given the metallic composition of the samples, these are generally shinny and present some parts which appear almost as white. These are artifacts caused by the lighting/capture geometry, and lighting environment which should be taken into account when assessing the real colour of the coins.

For problems 1 and 2, a colorimetric characterisation of the camera is needed. This means that a calibration must be done by the means of a set of colour chips which cover the chromatic range of the samples, under the same or similar lighting conditions. This set of chips needs to be measured also by a reference device, which provides the real colours of the calibration points, or to be retrieved from the manufacturer of the colour chips. With this data, a calibration model which correlates the real value of the chips (obtained by the reference device) with the colour observed by the smartphone under those conditions is created. Then, that same model can be applied to the samples (as long as they have been measured under the same conditions) in order to transform them to a corrected value. This

value is now corrected by the lighting environment and internal transformations of the smartphone. When it comes to problem 3, it can be sorted during the segmentation step, by selecting the appropriate Regions of Interest (ROI) based on the adequate colour parameters.

Some prior research has demonstrated that the application of smartphones as imaging tools for the analysis of historical coins allows for a fast and quantitative estimation of their colour. In this way, more subjective methods, often based on the naked eye can be potentially superseded [10]. Thus, in this work a two-way analytical approach for the investigation of a set of historical coins is presented. On the one hand, a non-invasive elemental analysis using portable energy dispersive X-ray fluorescence (p-ED-XRF); and on the other hand, a colorimetric investigation of these coins using smartphone-based colorimetry. To this end, the previously reported method has been tested using a more diverse and complex dataset, including samples with very different origins. Overall, this work presents new analytical data about 21 historical artifacts that had not been previously investigated, both in compositional and colorimetric terms.

2. Materials and methods

2.1. Samples

This work focuses on the analysis of 21 gold and golden coins of the Historical Library of University of Valencia. Historical and physical characteristics (mass and size) are summarized in Table S1. When possible, the coins have been identified in numismatic catalogues.

Samples cover a wide time span, ranging from the year 200 before common era (BCE), represented by an *octadrachm*, to the independence of the Spanish colonies in America. Coins from the Roman Empire and the Almoravids are represented, as well as two coins belonging to two different Visigoth kings. Also, commemorative coins from the United Kingdom and America are present. Finally, two coins with Prussian origin are also found within the collection. Given the historical and cultural interest and value of the coins, analysis were restricted to *in situ* and non-destructive ones.

2.2. Portable X-ray fluorescence (pXRF)

The elemental profile of the samples was obtained by the means of a portable energy dispersive X-ray fluorescence (p-ED-XRF) spectrometer S1 from Bruker (Ettlingen, Germany). The application for metals within the "Restricted materials" program was used. Two different measurements per side of the coin were done, targeting different regions in each measurement. To that end, the coin was placed on the device, measured, turned on the same plane 180^{o}, and measured again. The procedure was repeated with the other side of the coin, given a total of 4 measurements per coin, with an additional measurement if extreme values for some elements were observed. For coins with significantly bigger diameter, up to three different measurements per side were done. The final elemental composition of the coins was obtained as the mean value of the measurements.

2.2.1. Quality control and assurance

In total, 9 reference items were considered, three certified reference materials (CRM) and six jewellery items with different compositions. The elemental profile of the three CRM was provided by the manufacturer, while the other six reference items were measured by a reference benchtop XRF instrument at the Spanish "*Instituto Tecnológico Metalmecánico, Mueble, Madera, Embalaje y Afines*". These six elements were selected so as to create a correction model as the coins could not leave the controlled environment and custody under which they are stored. Then, all these items were subsequently measured using the p-ED-XRF to cross-reference the response of both instruments (see the results in Table S2). As the statistical comparison (*t*-test, paired samples, Table S3) demonstrated that a correction was needed for the main constituents (Au, Ag and Cu), a linear correction model was applied.

The limits of detection (LOD) for the three main elements (Au, Ag and Cu) were calculated as 3 times the square root of the noise divided by the slope for each element [11,12]. In order to compute the slope, the counts for the main peaks of Au, Ag and Cu (9.70, 22.16 and 8.02 keV, respectively) were cross-referenced with the concentrations output by the instrument. The limits of quantification (LOQ) were calculated as 10/3 times the LOD.

2.3. Colorimetric analysis

2.3.1. Smartphone-based procedure

The method implemented has been based on the work previously reported on smartphone applications for coin analysis [10]. Briefly, samples were introduced within a white foam closed sphere, whose external surface was painted in black to avoid any external influence of the ambient light. Inside the sphere, around the perimeter of the internal surface and parallel to the ground, a strip of white LED lights was stuck to provide homogeneous lighting. The smartphone device was a Samsung Galaxy Edge S7 model SM-G93F, equipped with a 12.2 MP camera sensor, and images were taken with the native camera app, in automatic mode. The coins were placed on top of a white surface that served two purposes: first, to simplify the image segmentation process, and second to be a reference white for the computation of CIELAB values. Focus was made on the coin, and each side was photographed. Image files in *.jpg* format were transferred to Matlab to carry out image segmentation and treatment using the COLORLAB toolbox [13]. The coins were also measured by a reference spectrocolorimeter (SpectraScan PR650) in the same experimental set-up to check the suitability of the smartphone-based results.

2.3.2. Image treatment: segmentation and camera characterisation

Colour segmentation was used to separate the pixels of the coin from those of the background. To that end, the sRGB values of each pixel were converted into CIELAB descriptors using the standard sRGB transform [14]. K-means segmentation was carried out ($k = 2$) to separate the white background from the coin according on their lightness, L*, and chroma, C* (the modulus of the (a*, b*) vector). The procedure was subsequently repeated in the regions occupied by the coin to exclude the degraded or dirty parts. In Fig. S1, an example of the results of the different segmentation steps on one of the coins is presented.

To colorimetrically characterise the response of the camera, a set of Munsell chips (covering sheets from 1.25G to 10 YR of the Munsell Book of Colour, Glossy Finish Collection, 1976, Macbeth, Kollmorgen Corporation, Baltimore, Maryland) was selected as it covered the chromatic range of the coins. These chips were photographed with the camera, and their reflectance spectra were retrieved from the COLORLAB Munsell database [13] and used to calculate their CIELAB values. At this point, a 5th degree polynomial model was created through least squares minimization using the image RGB values and the computed CIELAB descriptors of the chips. It must be considered that each photograph is taken with the automatic mode of the camera, so slight illumination changes are expected. To tackle this potential interference, the CIELAB descriptors of the segmented coin and the white background are computed and subsequently converted to CIEXYZ colour space, using a reference illuminant (D65). Next, the CIEXYZ of the samples are converted back to CIELAB values by using the CIEXYZ of the white background.

Overall, with this protocol, the image-based RGB values can be inputted, and converted to corrected CIELAB descriptors that take into account both the experimental (lighting) and the internal conditions (colour enhancement procedures).

2.4. Statistical treatment

R [15] was used for data treatment and visualization, employing the *ggplot2* [16], *missMDA* [17] and *corrplot* [18] packages. The Pearson correlation coefficients between elemental and colorimetric descriptors were calculated using the *cor* function, selecting the non-zero pairs of values (*pairwise complete observations* option in the function). Consequently, observations with values below LOD for some of the elements were not considered for the calculations.

3. Results and discussion

In this section, the analytical results obtained by both non-destructive approaches are presented. First, the elemental composition of the samples is assessed by the means of the XRF analysis; subsequently, a colorimetric analysis of the samples is carried out using non-invasive smartphone-imaging. The results regarding the performance of the camera characterisation are also presented.

3.1. Elemental composition analysis

3.1.1. Quality control of the elemental data

A paired comparison of the concentrations yielded by the *p*-XRF and the reference values for the nine items demonstrated that the quantification of the three main constituents (Au, Ag and Cu) was not statistically comparable (Table S3). Thus, a linear correction model was implemented for Au, Ag and Cu using cross-referencing the contents values obtained by the *p*-XRF and the reference values.

Table 1
Elemental composition of the different samples as obtained through p-ED-XRF. Results were linearly corrected for Au, Ag and Cu.

Sample	Mass percentage														
	Au			Ag			Cu			Zn			Hg		
B1M01	97.5	±	0.3	1.9	±	0.1	0.21	±	0.02	<LOD			<LOD		
B1M02	99.32	±	0.06	0.40	±	0.07	0.17	±	0.02	<LOD			<LOD		
B1M04	94.10	±	0.09	6.05	±	0.09	0.112	±	0.008	<LOD			<LOD		
B1M05	98.5	±	0.3	1.17	±	0.02	0.16	±	0.02	<LOD			<LOD		
B1M06	66.1	±	0.5	19.9	±	0.8	0.43	±	0.06	<LOD			13.31	±	0.06
B1M07	66.5	±	0.7	32.7	±	0.4	1.94	±	0.08	<LOD			<LOD		
B1M08	62.1	±	0.3	38.4	±	0.2	1.2	±	0.1	<LOD			<LOD		
B1M09	98.1	±	0.1	1.84	±	0.04	0.13	±	0.02	<LOD			<LOD		
B1M10	96.43	±	0.03	3.4	±	0.1	0.24	±	0.03	<LOD			<LOD		
B1M11	98.0	±	0.1	1.58	±	0.04	0.15	±	0.01	<LOD			<LOD		
B1M12	94.75	±	0.06	5.3	±	0.1	0.31	±	0.01	<LOD			<LOD		
B1M13	96.44	±	0.08	3.16	±	0.02	0.200	±	0.009	<LOD			<LOD		
B1M14	90.0	±	0.5	8.54	±	0.09	1.57	±	0.02	<LOD			<LOD		
B1M15	91.3	±	0.1	8.47	±	0.03	0.173	±	0.008	<LOD			<LOD		
B1M16	74.6	±	0.3	13.26	±	0.1	13.3	±	0.2	<LOD			<LOD		
B1M17.1	90.0	±	0.1	4.37	±	0.03	5.76	±	0.04	<LOD			<LOD		
B1M17.2	89.6	±	0.2	7.1	±	0.1	3.5	±	0.4	<LOD			<LOD		
B1M18.1	<LOD			0.220	±	0.002	70.3	±	0.4	22.8	±	0.2	<LOD		
B1M18.2	<LOD			0.212	±	0.005	70.3	±	0.4	23.1	±	0.4	<LOD		
B1M19	<LOD			0.28	±	0.008	85.1	±	0.6	9.7	±	0.3	<LOD		
B1M20	59	±	4	0.49	±	0.04	36	±	4	0.06	±	0.03	3.5	±	0.4

3.1.2. Elemental description of the samples

Based on the analysis carried out with p-ED-XRF, the five main elements found (Au, Ag, Cu, Zn and Hg) are presented for every sample in Table 1. Fig. S2 shows some of the spectra.

The *octodrachm*, B1M01, contains a high quantity of Au (97.5 ± 0.3 %), with a small amount of Ag (1.9 ± 0.1 %). These type of coins were minted by the Ptolemy dynasty [19], but their elemental analysis had not been published previously in the literature. The Roman coins (B1M02 – B1M06) include two examples of *aureus* (B1M02 and B1M04) and two of *solidus* (B1M05 and B1M06). Samples B1M02 – B1M05 present similar compositions with Au contents around 90 %, and small contents of Ag, with values between 0.5 and 5 %. These samples present slightly lower Au contents than the values reported for coins of the same type [20]. However, the results presented in this work agree with the ones presented for Roman gold coinage from a similar period [4], around 300 of the common era, pointing to an average gold content of 95 %. Coin B1M06, however, dating from the year 400, contains only around 60 % gold, while the rest of the coin is made of Ag and Hg. Based on bibliographic research on coin collections, this sample can be traced back to the Imperial period [21,22].

The presence of Hg alerts for potential surface gilding [23], and its presence in roman coins has been previously reported in silver coins, given the fact that amalgam silvering process was used in order to apply a paste of Ag – Hg to the surface of the coin, and then the Hg would be partially evaporated by a heating process [24]. This process has also been described for golden-like coins [25,26], as a way of implementing an Au layer on the surface of the coin. It is referenced that this process was sometimes used for counterfeiting coins [24,25], which could be carried out by simpler processes (like folding a thin layer of the precious metal around the coin), or by means of more sophisticated procedures like the one explained previously [27]. Some mentions in the literature related with the gold-enrichment of silver coins are also found [4].

Regarding the case under investigation, it must be considered that the measurements were made on the surface of the coin, so the elemental composition is only representative of the thin layer that X-ray energy is interacting with. As seen in Table S1, the width of the coin is around 1.1 mm, and previous works on XRF application to metallic roman coins have demonstrated that only a few microns are analysed by this approach [28]. This means that the results obtained by this work are circumscribed to the surface of the coin. Also, a debasement of the value of the Roman Coinage was suffered during the 3rd century of the common era [25]. Hence, overall, it can be concluded that Hg presence in such high concentrations in this sample could either be linked to the amalgamation process used to obtain the raw materials [29] or to the result of applying a mixture of Ag and Au to the surface of the coin. More sophisticated analysis, like muonic X-ray emission spectroscopy [4] would be needed to know the exact composition of the internal regions of the coin.

B1M07 and B1M08, both coins from Visigoth kings, are composed of around 60 % Au and 30 % Ag. It needs to be taken into account that Visigoth gold coins present varying gold percentages, depending on the period and region [30]. Still, the values obtained in this work are within the normal ranges presented in the literature for coins [30] and gold Visigoth objects [23]. Compared with previous and ulterior periods, like the Romans and the Muslims, Visigoth coins are characterized by their lower Au and higher Ag concentrations generated by sequential debasements due to the lack of gold [31] and economic constraints. The weights, around 1.3 and 1.4 g, are consistent with the weights of *tremisses* of the time [32].

Samples B1M09 to B1M12 are dinars from Almoravid origin, with very stable and reproducible Au concentrations around 96 %, and Ag ranging from 1.5 to 5.3 %. Given the elemental results observed for these coins, it could well be thought that they were minted from "Sudanese gold". This ore was famed all around the world and valued as a very stable and precious content [33,34], and a recent analysis of gold from this region proved that concentrations around 92 % of Au are found [35]. Hence, the results presented in this work could indicate that these four Islamic coins could have been produced using this ore during the Almoravid presence in the North of Africa and Mediterranean area of the Iberian Peninsula.

Sample B1M13 consists of a very small and light piece of gold without any inscription or symbol, but with a relatively high Au percentage. Samples B1M14 to B1M17.2 represent different Spanish kings from different periods: B1M16 is florin coined in the Aragon Crown, based on the *fiorino d'oro*, but with the addition of the wording "ARAGO.REX" as a distinctive sign which is observed in B1M16. B1M14 is an *escudo* from the last Habsburg king, Carlos II (1661–1700). Samples B1M15 and B1M17.1 are *escudos* from the first Bourbon king who succeeded Carlos II: Felipe V (1683–1746). Finally, sample B1M17.2 is another *escudo* from Fernando VII (1784–1833) from year 1808.

All these coins, except for the Aragon florin (B1M16) present similar gold percentages around 85 %, with Ag values generally at 7–8 %. B1M17.1 (*escudo* from Felipe V) has half this Ag amount, which is substituted by a higher Cu content. In the composition of B1M16, on the other hand, Au represents 74.6 %, while the rest of the coin is split in halves between Ag and Cu.

The next pair of samples (B1M18.1 and 2) are two Prussian coins which, despite looking alike to the rest of the gold coins, are basically made out of brass in a 70-25 proportion (Cu–Zn).

Finally, two commemorative medals/coins are included in this collection (B1M19 and B1M20). B1M19, a commemorative coin celebrating Queen Victoria, is composed of brass in an 85-10 proportion (Cu–Zn). B1M20 is a very heavy (35 g) medal composed of 59 % Au, with a 36 % of Cu and commemorates the independence of Guatemala.

When it comes to the LOD and LOQ, they were estimated to be 0.03 %, 0.016 % and 0.008 % for Au, Ag and Cu, respectively.

3.2. Colorimetric investigations

In this section, the analysis of the colour of the coins is presented and discussed. First, the colour results as obtained by the smartphone method are checked in order to ensure that the obtained results are in good accordance with the reference method. Next, once the validity of the procedure has been demonstrated, the CIELAB descriptors of the different samples are presented to better describe the dataset.

3.2.1. Validation of the smartphone-based colorimetry method

To check the colour reproduction, the CIELAB descriptors of the samples computed with the colorimetrically characterized smartphone camera are compared with the reference device, using the CIEDE2000 colour difference formulae [36]. This approach allows to compare two different sets of colours based on the differences between L* (lightness), C* (chroma, the modulus of the vector (a*, b*), and H* (hue, the arctangent of b*/a*)). Hence, ΔE* can be calculated for each coin (n = 21), being the interpretation as follows: the closer to 0, the more similar both colours, to further from 0, the more different. Hence, in this specific case, a result close to 0 is interpreted as a high similarity between the reference CIELAB values and the descriptors as obtained by the proposed method. Overall, the results for the CIEDE2000 difference, ΔE*, and partial differences in lightness, ΔL*, chroma, ΔC*, and hue, ΔH*, are shown in Fig. 1, while Table S4 shows the numerical values.

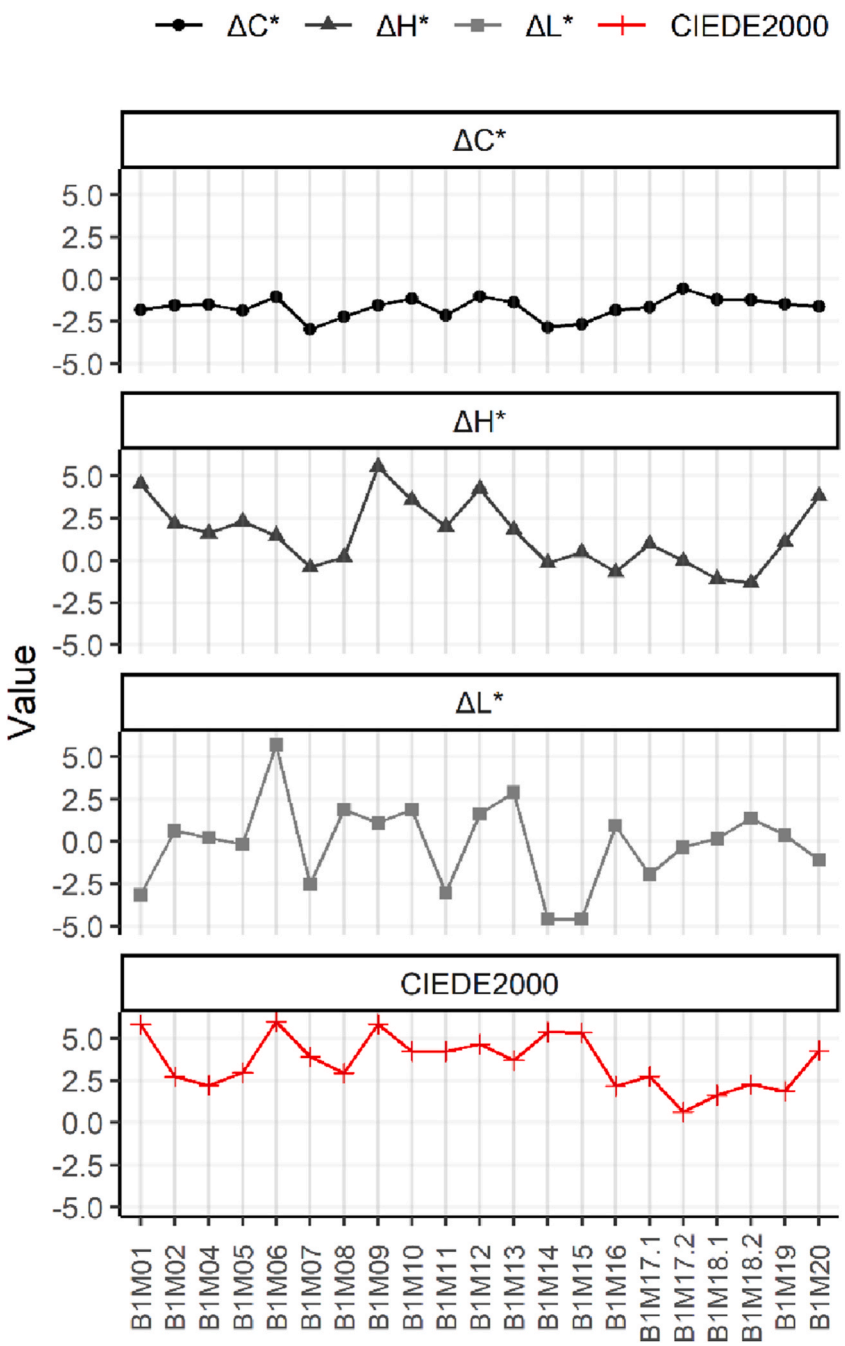


Fig. 1. ΔC*, ΔH*, ΔL* and ΔE*values obtained for the samples (n = 21) under investigation. Results compare the computed CIELAB descriptors as obtained through smartphone imaging with the reference ones obtained through the spectrocolorimeter.

The results plotted in Fig. 1 show that the average value of ΔE* is 3.6 ± 1.6 Lab units, while ΔL*, ΔC* and ΔH* present mean values of (−0.1 ± 2.5), (−1.7 ± 0.6) and (1.5 ± 1.9) Lab units, respectively. These demonstrate that the proposed image-based analytical method works acceptably [36] when capturing the colour of historical metallic coins under the proposed procedure, given that the colour differences are within the [2.8–4] CIEDE2000 units tolerance proposed by the ISO 12647–2:2013 specification [37]. Also, the trend observed in the figure suggests that there is no specific bias of the image method to incorrectly capture neither L*, C* or H*, as the coins that have higher overall error (this is, higher ΔE*) are driven by higher ΔL*, ΔC* or ΔH* indistinctively.

3.2.2. Colour description of the samples

Once having justified the necessity of cropping and characterising the smartphone camera, the obtained CIELAB descriptors of the samples will be described. Fig. 2 plots the CIELAB descriptors of the coins under investigation.

A qualitative description of the samples allows to draw some first conclusions: for example, all the coins are light, with lightness L* values between 55 and 80 CIELAB units. Also, as expected for gold-like coins, all the samples have b*>0 and a*>0, as corresponds to reddish-yellow colours.

When assessing the relationship between Au content and CIELAB descriptors, it is observed that samples with higher Au content appear on the positive and higher end of b* axis (which represents yellowness), while those samples that do not contain any gold (like the Prussian or the Queen Victoria ones) appear lower on this component. Thus, it can be concluded that the effect of the amount of gold is colorimetrically reflected on the b* component, and that this can be objectively observed through smartphone-imaging. Additionally, the effect of Au content does also play a role in the L* component, as samples with decreasing Au proportion do appear lower on the L* axis, meaning that they are darker.

A quantitative analysis of the Pearson correlation between elemental composition and colour descriptors did not yield any significant correlation (Table S5). This result means that, based on the dataset we present here, it is not feasible to predict the Au, Ag or Cu exclusively based on its appearance.

3.2.3. Practical implications of the image-based methodology

The description of these samples is generally limited to qualitative indications about the aspect of the coins, without quantitative description of the colour. Thus, the ability to objectively quantify the colour of samples in a fast and non-invasive way may help the researchers to spot similarities and differences among coins before running more sophisticated analyses on them. With the proposal presented here, a very important feature of these historical artifacts, which is colour, can be objectively described using affordable and easy-to-use technology based on smartphone colorimetry. This approach allows to have an analytical method at the disposal of conservators and cultural heritage scientists without the need of expensive and sophisticate instrumentation, like a spectrocolorimeter.

The work presented here delves into the application of a previously reported image-treatment method [10] to investigate a more sophisticated data set. Results have demonstrated that the different experimental and image-treatment steps allow for a correct quantification of the colour even in a more diverse and heterogeneous data set, with coins from very different origins. However, it must be considered that these results do not allow to draw definitive conclusions about the composition of the samples, as the correlation between colour parameters and gold content is not perfect.

This methodology needs to be implemented with caution, as there are some potential drawbacks. First, the fact that this is a surface investigation. This means that it is only yielding information about the very first microns of the coins. Nevertheless, as the objective of this methodology is to improve the workflow that has been carried out so far when describing the coins in a subjective eye-based way, this issue does not bring major concerns.

Second, it must be considered that potential surface-related events might interfere with the final colour. In this instance, despite the degradation of pure gold being negligible in normal conditions [38], prior research has demonstrated that some impurities like Cu and

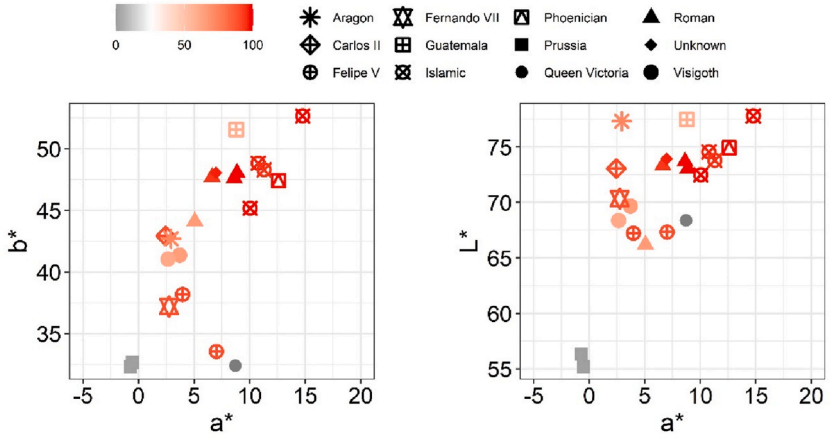


Fig. 2. CIELAB biplots for the coins under investigation, as obtained through the image-based procedure. Colour represents the Au percentage measured in the samples, and the shape is based on the "Origin" as appears in Table S1.

Ag are able to generate darkened spots ranging from dark red-brown to black [39–41]. These could then modify the final result in terms of colour parameters, as they differ from the colour of gold and gold-like coins. To sort this problem out, the proposed image treatment method implements an image pre-treatment step (as described in 2.3.2) that is based on colour parameters to remove the regions of the coins that significantly differ from the major fraction of pixels. In this way, as these potentially darkened spots would have greatly different CIELCh values, they would be not considered. Lastly, in the case that a few pixels of these spots still make it to the final result, it needs to be considered that the final CIELAB value assigned to each coin stems from the mean value of all the pixels of both faces, so the importance of these few pixels over the total amount of pixels would be negligible.

4. Conclusions

In this work, a two-way non-invasive analytical approach is implemented on a unique sample set consisting of 21 historical gold and gold-like coins ranging from a time span of more than 2000 years. On the one hand, the elemental profile for major elements has been assessed using energy-dispersive portable X-ray fluorescence. These results allowed to detect some samples with high gold contents (>90 %), while some others presented lower to no gold in their composition. Also, some interesting cases in which mercury has been found might be attributable to either an intended debasement of the coin or to manufacturing processes' leftovers. This is a rare phenomenon not very commonly reported in the literature, emphasising the singularity of the investigated samples.

On the other hand, a novel colorimetric approach has been implemented in order to measure the colour of historical coins. This proposal allows for an objective and quantitative approach to obtain a colorimetric description of ancient coinage, as the results demonstrate. This procedure improves the general approach carried out so far that is generally based on an eye-based subjective and qualitative description of the samples. The procedure has been validated by comparison to a reference device, confirming that the obtained colour descriptors are comparable to the ones obtained by the reference colorimeter. Apart from the methodological proposal, which has demonstrated to work efficiently also in this diverse dataset, this quantitative colorimetric information has been described for the first time for these particular Cultural Heritage items, contributing to the knowledge of these peculiar artifacts.

Data availability

Has data associated with your study been deposited into a publicly available repository? Yes. Zenodo: 10.5281/zenodo.10631002.

CRediT authorship contribution statement

Roberto Sáez-Hernández: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **María Josefa Luque:** Writing – review & editing, Validation, Software, Methodology, Formal analysis, Data curation, Conceptualization. **Adela R. Mauri-Aucejo:** Writing – review & editing, Validation, Supervision, Investigation, Conceptualization. **Ángel Morales-Rubio:** Writing – review & editing, Methodology, Investigation, Conceptualization. **M. Luisa Cervera:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

M. Luisa Cervera reports financial support was provided by Conselleria d'Innovació, Universitats, Ciència i Societat Digital - Generalitat Valenciana. Roberto Saez-Hernandez reports financial support was provided by Government of Spain Ministry of Universities. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Authors thank the Valencian Regional Government (Conselleria d'Innovació, Universitats, Ciència i Societat Digital) for the funding (PROMETEO/2019/056). Roberto Sáez-Hernández thanks the Ministry of Universities of Spain for a predoctoral position (FPU19/02304) and Cesar Albert Alcañiz for his contribution in the identification of the samples. Authors thank the help from Marisa Hernández for her help in the analysis of the reference materials, and Francisco Montes Suay for his collaboration in the data analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e34623.

References

[1] C. Arias, S. Bani, F. Catalli, G. Lorenzetti, E. Grifoni, S. Legnaioli, S. Pagnotta, V. Palleschi, X-ray fluorescence analysis and self-organizing maps classification of the etruscan gold coin collection at the monetiere of florence, Appl. Spectrosc. 71 (2017) 817–822, https://doi.org/10.1177/0003702816641421.

[2] M. Baldassarri, G. de H. Cavalcanti, M. Ferretti, A. Gorghinian, E. Grifoni, S. Legnaioli, G. Lorenzetti, S. Pagnotta, L. Marras, E. Violano, M. Lezzerini, V. Palleschi, X-ray fluorescence analysis of XII–XIV century Italian gold coins, J. Archaeol. 2014 (2014) 1–6, https://doi.org/10.1155/2014/519218.

[3] A. Gorghinian, A. Esposito, M. Ferretti, F. Catalli, XRF analysis of Roman Imperial coins, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 309 (2013) 268–271, https://doi.org/10.1016/j.nimb.2013.02.022.

[4] G.A. Green, K. Ishida, B.V. Hampshire, K. Butcher, A.M. Pollard, A.D. Hillier, Understanding roman gold coinage inside out, J. Archaeol. Sci. 134 (2021) 105470, https://doi.org/10.1016/j.jas.2021.105470.

[5] S.A. Junk, Ancient artefacts and modern analytical techniques – usefulness of laser ablation ICP-MS demonstrated with ancient gold coins, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 181 (2001) 723–727, https://doi.org/10.1016/S0168-583X(01)00366-4.

[6] M.F. Guerra, C. Roux, L'or de la Péninsule ibérique des invasions à la Reconquista. Circulation monétaire des Wisigoths aux rois chrétiens, ArchéoSciences Rev. Archéom. 26 (2002) 219–232, https://doi.org/10.3406/arsci.2002.1035.

[7] M. Ramacciotti, G. Gallello, M. Lezzerini, S. Pagnotta, A. Aquino, L. Alapont, J.A. Martín Ruiz, A. Pérez-Malumbres Landa, R. Hiraldo Aguilera, D. Godoy Ruiz, A. Morales-Rubio, M.L. Cervera, A. Pastor, Smartphone application for ancient mortars identification developed by a multi-analytical approach, J. Archaeol. Sci. Rep 43 (2022) 103433, https://doi.org/10.1016/J.JASREP.2022.103433.

[8] R. Sáez-Hernández, K.U. Antela, G. Gallello, M.L. Cervera, A.R. Mauri-Aucejo, A smartphone-based innovative approach to discriminate red pigments in roman frescoes mock-ups, J. Cult. Herit. 58 (2022) 156–166, https://doi.org/10.1016/j.culher.2022.10.003.

[9] M. Ramacciotti, G. Gallello, S. Columbu, D. Fancello, A. Diez-Castillo, O. García-Puchol, A. Pastor, M.L. Cervera, Smartphone photos as a non-destructive approach to characterise siliceous artefacts, STAR Sci. Technol. Archaeol. Res. 9 (2023) e2240175, https://doi.org/10.1080/20548923.2023.2240175.

[10] R. Sáez-Hernández, M.J. Luque, A.R. Mauri-Aucejo, Á. Morales-Rubio, M.L. Cervera, Unveiling origins, composition, and appearance of ancient Islamic gold coins through elemental and smartphone-based colorimetric studies, Sci. Rep. 14 (2024) 3652, https://doi.org/10.1038/s41598-024-53981-6.

[11] D. Guimarães, M.L. Praamsma, P.J. Parsons, Evaluation of a new optic-enabled portable X-ray fluorescence spectrometry instrument for measuring toxic metals/metalloids in consumer goods and cultural products, Spectrochim. Acta Part B At. Spectrosc. 122 (2016) 192–202, https://doi.org/10.1016/j.sab.2016.03.010.

[12] R. Dalipi, E. Marguí, L. Borgese, L.E. Depero, Multi-element analysis of vegetal foodstuff by means of low power total reflection X-ray fluorescence (TXRF) spectrometry, Food Chem. 218 (2017) 348–355, https://doi.org/10.1016/j.foodchem.2016.09.022.

[13] J. Malo, M.J. Luque, ColorLab: the Matlab toolbox for colorimetry and color vision. http://isp.uv.es/code/visioncolor/colorlab.html, 2002.

[14] M. Anderson, R. Motta, S. Chandrasekar, M. Stokes, Proposal for a standard default color space for the internet: sRGB, in: Color Imaging Conf. Color Sci. Syst., Appl., Arizona, USA, 1997, pp. 198–205.

[15] R-Core-Team, R, A Language and Environment for Statistical Computing, 2021. https://www.r-project.org/.

[16] H. Wickham, ggplot2: Elegant Graphics for Data Analysis, 2016, https://doi.org/10.1007/978-3-319-24277-4.

[17] J. Josse, F. Husson, missMDA: a package for handling missing values in multivariate data analysis, J. Stat. Software 70 (2016) 1–31, https://doi.org/10.18637/jss.v070.i01.

[18] T. Wei, S. Viliam, R package "corrplot": visualization of a correlation matrix. https://github.com/taiyun/corrplot, 2023. (Accessed 1 February 2023).

[19] C.G. Johnson, The divinization of the ptolemies and the gold octadrachms honoring Ptolemy III, Phoenix 53 (1999) 50–56, https://doi.org/10.2307/1088122.

[20] M. Hall, F. Kovacs, EDXRF analyses of roman gold coinage, Bull. Met. Mus. 30 (n.d.) 52–64.

[21] Roman imperial constantine III, Acsearch.Info. https://www.acsearch.info/search.html?id=7452361, 2020. (Accessed 1 February 2024).

[22] Roman imperial constantius III, Acsearch.Info. https://www.acsearch.info/search.html?id=7452362, 2020. (Accessed 1 February 2024).

[23] A. Perea, A. Climent-Font, M. Fernández-Jiménez, O. Enguita, P.C. Gutiérrez, S. Calusi, A. Migliori, I. Montero, The visigothic treasure of Torredonjimeno (Jaén, Spain): a study with IBA techniques, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 249 (2006) 638–641, https://doi.org/10.1016/j.nimb.2006.03.071.

[24] K. Manukyan, C. Fasano, A. Majumdar, G.F. Peaslee, M. Raddell, E. Stech, M. Wiescher, Surface manipulation techniques of Roman denarii, Appl. Surf. Sci. 493 (2019) 818–828, https://doi.org/10.1016/j.apsusc.2019.06.296.

[25] C. Vlachou, J.G. McDonnell, R.C. Janaway, Experimental investigation of silvering in late Roman coinage, MRS Online Proc. Libr. OPL 712 (2002) II9.2, https://doi.org/10.1557/PROC-712-II9.2.

[26] G.M. Ingo, E. Angelini, T. de Caro, G. Bultrini, Combined use of surface and micro-analytical techniques for the study of ancient coins, Appl. Phys. A 79 (2004) 171–176, https://doi.org/10.1007/s00339-004-2510-8.

[27] G.M. Ingo, C. Riccucci, F. Faraldi, M. Pascucci, E. Messina, G. Fierro, G. Di Carlo, Roman sophisticated surface modification methods to manufacture silver counterfeited coins, Appl. Surf. Sci. 421 (2017) 109–119, https://doi.org/10.1016/j.apsusc.2017.01.101.

[28] F. Caridi, L. Torrisi, M. Cutroneo, F. Barreca, C. Gentile, T. Serafino, D. Castrizio, XPS and XRF depth patina profiles of ancient silver coins, Appl. Surf. Sci. 272 (2013) 82–87, https://doi.org/10.1016/j.apsusc.2012.02.071.

[29] V. Cojocaru, C. Beşliu, C.A. Manea, Nuclear analyses of the Pietroasa gold hoard, J. Radioanal. Nucl. Chem. 240 (1999) 897–908, https://doi.org/10.1007/BF02349869.

[30] M.F. Guerra, T. Calligaro, A. Perea, The treasure of guarrazar: tracing the gold supplies in the visigothic iberian Peninsula, Archaeometry 49 (2007) 53–74, https://doi.org/10.1111/j.1475-4754.2007.00287.x.

[31] M.F. Guerra, On gold recycling. A physicochemical point of view, Archaeometry 64 (2022) 134–149, https://doi.org/10.1111/arcm.12710.

[32] P. Bartlett, D. Yoon, R. Pliego, Weight, fineness, and debasement in visigothic tremisses from theudis to leovigild: new evidence from the hoards of seville and reccopolis, Am. J. Numismatics 1989– 29 (2017) 149–212. https://www.jstor.org/stable/26932647.

[33] R. Corinee, M.F. Guerra, A moeda almoravida: Estudo do titulo e caracterização do metal, in: Actas IV Congr. Nac. Numismática, Lisboa, Portugal, 1998, pp. 145–168.

[34] R.J. Hébert, The coinage of islamic Spain, Islam Stud. 30 (1991) 113–128. https://www.jstor.org/stable/20840029.

[35] R.A. Messier, The Almoravids, J. Econ. Soc. Hist. Orient 17 (1974) 31–42, https://doi.org/10.1163/156852074X00020.

[36] M.R. Luo, G. Cui, B. Rigg, The development of the CIE 2000 colour-difference formula: CIEDE2000, Color Res. Appl. 26 (2001) 340–350, https://doi.org/10.1002/col.1049.

[37] International Organization for Standardization, ISO 12647-1:2013 - graphic technology - process control for the production of half-tone colour separations, proof and production prints. https://www.iso.org/standard/57816.html, 2013 (accessed January 7, 2024).

[38] G. Gusmano, R. Montanari, S. Kaciulis, G. Montesperelli, R. Denk, "Gold corrosion": red stains on a gold Austrian Ducat, Appl. Phys. A 79 (2004) 205–211, https://doi.org/10.1007/s00339-004-2534-0.

[39] G. Gusmano, R. Montanari, S. Kaciulis, A. Mezzi, G. Montesperelli, L. Rupprecht, Surface defects on collection coins of precious metals, Surf. Interface Anal. 36 (2004) 921–924, https://doi.org/10.1002/sia.1800.

[40] C. Liang, C. Yang, N. Huang, Investigating the tarnish and corrosion mechanisms of Chinese gold coins, Surf. Interface Anal. 43 (2011) 763–769, https://doi.org/10.1002/sia.3597.

[41] K.E. Mayerhofer, K. Piplits, R. Traum, M. Griesser, H. Hutter, Investigations of corrosion phenomena on gold coins with SIMS, Appl. Surf. Sci. 252 (2005) 133–138, https://doi.org/10.1016/j.apsusc.2005.01.111.