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Archaeometric Contribution for Heritage Management
Compositional Analysis and dating of ceramics from a Portuguese collection

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Abstract

Different analytical methods comprising mineralogical and chemical analysis and thermoluminescence dating were used to assess the most appropriate techniques for the characterisation and dating of a ceramic collection. This study demonstrates the complementary nature of these techniques. The materials studied consist of ceramics from the collection of the Estrada Foundation, which will form part of a future museum in Abrantes Portugal.

Keywords: Ceramics, Heritage; Authenticity; Thermoluminescence dating; X-Ray Diffraction; Micro-X-Ray Fluorescence; Transform Fourier Infrared Spectroscopy; Instrumental Neutron Activation Analysis

Introduction

Archaeologists and physical scientists have been collaborating to learn more about the past than can be summarised using classical methods alone. A large proportion of archaeological and archaeometric investigations are oriented towards Heritage, having as their main objectives: identification, improved understanding, and preservation.

Artefacts and art work kept in museums originate in many cases from existing private collections, with a partial or total absence of historical information. Scientific investigations can help attribute artefacts to a corresponding culture, to develop their contextualisation and investigate their authenticity. The study of museum collections and their preservation requires the use of analytical techniques combined with examination techniques. In the present study, multiple analytical approaches are applied to better understand the composition and chronology of a group of ceramics.

The present study investigates a collection that will soon find its place in the future museum Museu Iberico de Arqueologia e Arte, in Abrantes Portugal. 10 selected ceramics were studied with the following objectives:

1. Establish the authenticity and absolute dates
2. Finding the mineralogical and elemental fingerprint of the samples to group the ceramics and indicate which of them may have the same source.
3. Evaluate the most appropriate and reliable method for the future study of the collection taking into consideration the integrity of the pieces and the conservation aspects.
4. Examine the complementary and compensating aspects of different methods.

Methods

The study was divided into 3 sections: 1. classical assessment of typology and style, which formed a basis to guide the application of instrumental analytical techniques; 2. compositional analysis; 3. absolute chronology. For sections 2 and 3, cores (c.500mg each) were drilled from selected portions of the artefacts using a hollow diamond tipped bit.

Assessment of typology and style

The ceramics' typologies and iconographies were compared with ceramics databases in published and online sources to find parallels, leading to a relative chronology and possible geographical distribution of the ceramics.

Compositional analysis

Compositional study including mineralogy and elemental analysis of the fabric was undertaken. X-Ray Diffraction (XRD) and Infrared Spectroscopy (IRTF) were used to define the mineral composition. Instrumental Neutron Activation Analysis (INAA) and Energy Dispersive Micro X-Ray Fluorescence (μEDXRF) were carried out to determine the chemical composition of the paste and surface coating respectively. One destructive and one non-destructive or minimum invasive method have been chosen for both the analyses.

Mineralogical. XRD is one of the most important characterization tools used in solid state chemistry and materials science and allow the identification of crystalline phases. Powder XRD was used in the present work and samples' powder were scanned from 2°-70° of 2θ, under a speed of 0.5steps/min with a Tension 45 KV and Current 40 for 2 hours with a PANalytical X'Pert PRO powder after being mounted on a glass sample holder.

IRTF is one of the ideal methods applied to archaeological and heritage materials to identified molecular components, first due to the minimum amount of material required, about 2 mg and the exhaustive nature of the analysis (Hachi *et al.*, 2002) and also has speed advantage. Sample was grinded below 2 μm, mixed with KBr and transparent pellets of diameter 13mm were prepared to be scanned in the IRTF spectrometer by transmission technique under the resolution of 2cm-1; 32 scans.

Chemical. Two techniques: INAA and μEDXRF Spectroscopy were applied to identify the chemical fingerprints.

INAA is one of the most used analytical techniques for the determination of trace element concentrations in pottery and clay materials, due to its high precision, accuracy and sensitivity for many elements but it is destructive.

The samples were dried in an oven at 110 °Cand bundled together with standards and irradiated at a thermal flux of. 3.96×10^{12} $cm^{-2}s^{-1}$ $\phi_{epi}/\phi_{th} = 1.03\%$; $\phi_{th}/\phi_{fast} = 29.77$ for 6 hours. Standard reference materials GSD-9 and GSS-1 were used to calibrate. Iron (Fe) flux monitors were irradiated with the samples to allow corrections due to variation in neutron flux.

Methods, based on multivariate statistical analysis were used to treat the data. Pattern recognition methods such as cluster analysis, plots of the original data in two and/or three dimensions, and principal components analysis (PCA) are customary approaches to data handling (Glascock *et al.*, 2004). Presently the data was first treated as absolute values building histograms of each element to compare the composition of an element in each sample. The absolute values were also used to plot Bivariate plots, where the relationship between the variables is plotted to examine the correlations between variables and within the samples. To further group and perceive the outliers, the tree-clustering method, was employed on standardised values of the chemical elements by using the Statistica Program 8. Coefficient correlation of Pearson to define groups with similar chemical composition and Euclidean distances allowing separating outliers were also used and represented as dendograms showing the order and levels of specimen clustering. The Rare Earth Elements (REE) were also normalised to the Haskin et al 1968, Chondrite values to give equal weight to the largely varying concentration values of the elements.

μEDXRF is a portable, non-invasive and non-destructive method which permits the analysis of a whole ceramic including its fabrics, paintings, glaze and varnish without sample preparation. However, it has its own limitations; in theory it may not detect the elements which are present in less than ½ % hence may not identify the trace elements.

The μEDXRF spectrometer 'Oxford instruments X-Ray Technology', comprising of a fluorescence rays producing tube and Beryllium exit window was used under maximum voltage 30 kv, max current 0.1 mA, max power 3 W and max temperature 45 degrees. A Si x-ray detector detects the emitted x-rays from the sample (XR – 100 CR) and transmits the x-rays to an Elemental Analysor (PO-2 with max 30 kv). Hence outputting the chemical elements present at the scanned point.

Besides, the chemical characterisation, this application would also indicate how far, obtained data is reliable and accurate to characterise this collection being favoured compared to INAA due to its non-invasive character. Simultaneously pigment and varnish identification would also be possible.

Absolute chronology

Thermoluminescence dating is an appropriate method to date ceramic as the latter contains mineral crystals that have absorbed energy during exposure to radiation. The basic principle is that clay and its temper of pottery lose their accumulated geological dose when the pot is fired during its manufacture thus setting the thermoluminescence to zero. The newly formed pot is now subjected to natural radiation from its surroundings and the pottery accumulates an absorbed dose which is a function of its archaeological age.

In its simplest form:

Age (years) = Palaeodose (Gy)/Dose rate (Gy/year)

In the present study the Palaeodose- was measured using aliquots of 4-11 µm polymineral grains settled onto aluminium disks in acetone. The palaeodose was evaluated using 3 different techniques.

The Regenerative Technique, which applies laboratory irradiations to aliquots that have first been measured for their natural signal and thus zeroed. This procedure 'regenerates' the sample's response from zero and the Palaeodose is calculated by interpolation. The Regenerative technique was used as an initial test: 1 disc of each sample was measured using a single regenerative dose.

The 2nd technique used consisted of the Multiple Aliquot Additive Dose Technique. Incremental irradiations are given to different aliquots that still retain their natural dose which results in enhancement of the luminescence signal and a growth curve is constructed plotting irradiation against luminescence signal. The natural signal forms the lowest point on this curve, which is then extrapolated back to zero signal to estimate the Palaeodose.

The 3rd technique employed was the pre-dose technique. Here, the archaeological age of the specimen is related not to the natural thermoluminescence intensity, but to its sensitivity. The sensitivity of the 110 °C TL peak in Quartz is found to be dependent upon the amount of radiation previously received which, in the case of an archaeological specimen, is the archaeological dose (Hachi *et al.*, 2002). Importantly, while the regenerative and additive TL signals generally used for dating are reset by brief heating to 400 °C or less, the Pre-dose sensitivity is more thermally resistant: it requires prolonged heating at temperatures in excess of 500 °C to be reset. In the present study a simplified Pre-dose technique proposed by Galli *et al.* (2006) was adopted, which is a method adapted for samples yielding low signal levels.

All measurements were conducted in a Risø DA-15 automatic reader with a ^{90}Sr/^{90}Y irradiator (Bøtter-Jensen *et al.*, 2000) giving 0.065±0.001 Gy/s to these aliquots (Richter *et al.*, 2003). Signals were detected using either BG25 and HA3 filters (blue emission region), or a U340 filter (near UV). However, for the MAAD technique, lab doses were given in a Daybreak Beta irradiator calibrated to 0.145 Gy/s before being measured in the Risø. All the steps of measurement and data processing is summarised in Table 1.

The alpha, beta and gamma dose rates from potassium, thorium and uranium in the samples were calculated from elemental concentrations determined by INAA. To finalize the Gamma dose it is important to consider the Gamma dose rate of the sample's surroundings. As there is a lack of information on the context of the samples, the Gamma dose was calculated using the 'Local hypothesis' (Zink & Porto, 2005). Assuming that the pot was buried in Portuguese soil or similar soil, an average Gamma dose of the Portuguese soil was calculated based on the gamma doses in a selection of Portuguese soils and sediments. The effectiveness of alpha radiation in producing luminescence signals was assumed, based on measured values for similar samples. Water of the pottery or in the soil where the pottery was, absorbs part of the radiation before reaching the thermoluminescence grains; that is water decreases the radioactivity per unit mass compared to dry situation (Aitken, 1985). Once again water content from both the sample and the sediment was a limitation in our measurement due to lack of context and the water content had to be estimated based on expected values from Aitken (1985), and the experience of the GeoLuC group in dating ceramics (a mass fraction of 0.1 was chosen).

Steps	**Reg. Technique**	**MAAD Technique**	**Predose Technique**
	1 disc	**8 discs**	**3 – 6 discs**
1	PH 160°C	β Dose, Daybreak: 2 discs 9.86 Gys; 2 discs 19.72 Gys; 2 discs 39.44 Gys; 2 discs 78.8 Gys	Dose 0.65 Gy
2	TL -500°C at 5° C/s	Rest for 3 weeks	TL -450°C @ 5°C/s – S0
3	3.25 Gys	PH 140°C for 16 hrs in oven	Repeat steps 1 & 2 x 30 - Sn
4	PH 160°C	Slow cooling	TL-450°C at 5°C/s x 2 (background)
5	TL- 500°C at 5° C/s	TL - 450°C @ 5° C/s, Risø	Plot data: Temperature against TL
6	Plot data: Temperature against TL	Plot data: Temperature against TL	2 Integrals: 60-119° C (110° C peak); 120-159° C (base line)
7	Signal = Integral 351-450°C	Signal = Integral 200-399°C	Plot Integrals against Cumulative Predose
8	Palaeodose = Regen. Dose x (Natural Signal/Regen Signal)	Linear fit to Integral vs Added Dose, Palaeodose = - Intercept with 0 signal	Calculate SN/S0 of both Integrals and plot vs. cumulative predose
9			Linear fits to linear sections of growth in SN/S0, compare Palaeodose from intercept of fits and intercept with SN/S0 = 1

Tab.1. Summarised the steps of each technique.

Results

Assessment of typology and style

The classical approach lead to an attribution and relative chronology for each ceramic summarised in Table 2.

Compositional Analyses

Mineralogical. Based on mineralogical analysis of XRD, 2 main groups were identified; one calcitic including A8/527, A8/589, A8/532 and A8/533 and the rests that is A8/588, A8/528, A8/530, A8/531, A8/526 and A8/529 do not have trace of calcite. IRTF Spectroscopy also illustrates that A8/527, A8/532 and A8/533 have calcite but at the same time CE 00012 also contains approximately the same amount of calcite as A8/527 which has not been identified by XRD. IRTF also pointed the presence of calcite in trace in A8/530 and A8/531 which XRD did not recognize most probably due to the absence of crystalline phases of the mineral.

At the same time comparing the spectra from IRTF the closeness of ceramics could be easily identified for instance A8/527 and A8/528 seem to be of exactly the same mineralogical composition and have gone through the same treatment, thus most probably from the same source.

Along with the mineral composition, mineralogical analysis also gives important information on the firing temperature. In our case a combination of data from both techniques proved highly compensating for this purpose for instance IRTF shows the presence of amorphous silicate in some ceramics indicating a firing temperature above 500° C. At the same time XRD shows clear presence of plagioclase feldspar indicating that the ceramic has been heated below 900° C. Hence A8/528 has most probably been fired around 900° C. A8/527 having plagioclase feldspar (XRD) and amorphous (IRTF), went through a temperature between 500 to 900° C not even reaching 900° C as there is calcite. A8/532 and A8/531 which have no plagioclase most probably went through a firing temperature of above 900° C. A8/588 and A8/526 were most probably fired at a temperature around 900°C due to the presence of both diopside and plagioclase. A8/589, A8/530, A8/533 and A8/529 were fired below 900° C but not very low.

Chemical. Based on the geochemical data obtained from INAA, specimen A8/530 is a principal outlier in this sample of 10 ceramics followed by A8/531 which is also different from others. The rest can be clustered in 4 different groups with A8/589 and A8/529 being close, A8/527 and A/528 form one perfect cluster as they are very close; A8/588 and A8/533 may have the same source and A8/532 and A8/526 form another group, as shown in figure 1.

Ceramic	Typology	Culture	Relative Chronology
CE 00008 A8/527	Impasto Asko	Villanovan	8th Cent. BC
CE 00012 A8/528	Crater	Villanovan	8th Cent BC
CE 00181 A8/532	Black Figure Amphora	Attic	6th Cent. BC
CE 00006 A8/588	Red Figure Kalathoid Psykter	Attic	Early 5th Cent. BC
CE 00185 A8/533	Red Figure Column Crater	Attic	5th Cent. BC
CE 02155 A8/526	Red Figure Rhyton	Attic	5th Cent BC
CE 00160 A8/530	Kalathos	Iberian	3rd-1st Cent BC
CE 00674 A8/531	Goddess Cybele Figurine	Iberian with Punic Influence	4-3rd Cent BC
CE 03939 A8/529	Black round pot	Mediterranean	4th-2nd Cent BC
CE 00069 A8/589	2 bottles joined at the handle	North African?	Ethnographic?

Tab.2. Cultural Affiliation and Relative Chronology

While according to µEDXRF, A8/589 is an outlier; A8/527 and A8/528 is of the same geochemical category; A8/533, A8/526 and A8/588 cluster together, A8/532 is completely apart and not even corresponding to the other similar looking ceramics and A8/530, A8/531 and A8/529 are also unique specimens. Thus, the geochemical similarity/dissimilarity of some elements points 6 sources of raw materials.

Dating

All the three techniques used along with different methods of data analysis gave very low or hardly any palaeodose for each of the ceramics. None of the aliquots gave natural signal during the Regenerative test measurement most of them leading to palaeodose below 0.5 Gys. The same resulted from the MAAD technique with even negative palaeodose for two of them. However due supralinearity and saturation several problems were encountered while applying MAAD. Although results from the Predose Technique were more variable, these indicate that the ceramics were not archaeological pieces recently affected by moderate heating (Fig. 2): one of the hypotheses being that they may have been heated to dry them. Overall the TL analyses, summarised in table 3, indicate that the ceramics were manufactured recently.

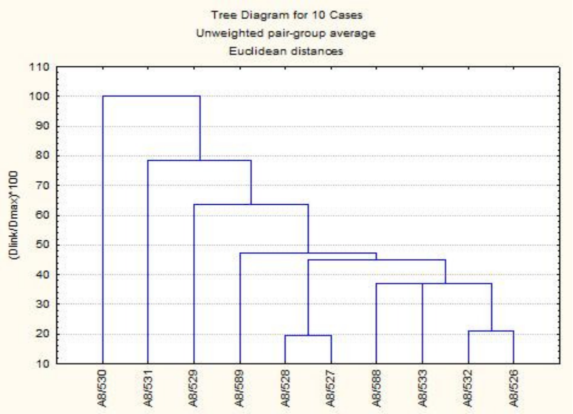

Fig.1. Tree Diagram showing outliers and groups.

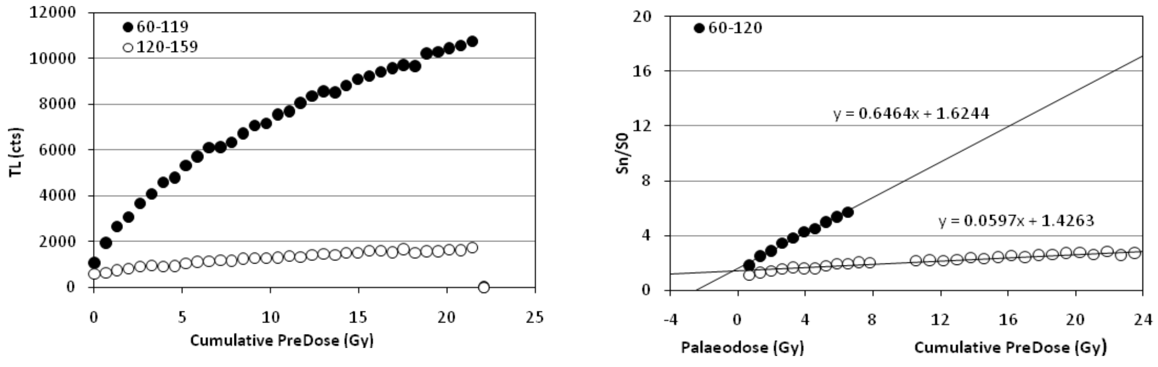

Fig.2. Integrals against Cum. Predose & Sn/S0 against Cum. predose with the linear equations.

Discussions and Conclusions

Both IRTF and XRD add up in the mineralogical understanding of the sample in their own way. IRTF is highly advantageous as it requires only 2.5 mg of powder for analysis and from a conservation point of view it is preferred. This method already gives an idea of the mineralogical composition and also about the firing temperature, depending on the presence of clay minerals or amorphous silicate or other mineral transformation phases. Moreover, along with non-crystalline minerals it can clearly identify the presence of organic materials. However, not all the minerals can be identified precisely for instance we can find the presence of feldspar but which one exactly cannot be said. XRD is quite accurate but is more invasive.

Ceramics	Predose Date AD ± yrs		Regenerative Date AD ± yrs		MAAD Date AD ± yrs	
A8/526 CE 02155	2229	98	1923	8	1964	11
A8/527 CE 00008	1989	47	2004	0	1929	9
A8/528 CE 00012	2167	54	2004	0	1948	8
A8/529 CE 03939	1912	16	1995	2	1974	8
A8/530 CE 00160	3236	226	1923	8	1995	3
A8/531 CE 00674	1609	132	1887	12	1958	5
A8/532 CE 00181	22	952	883	191	1991	5
A8/533 CE 00185	2176	44	1966	4	1936	22
A8/588 CE 00006	2237	75			2078	16
A8/589 CE 00069	2323	167			2149	37

Tab.3. TL dating results.

The two methods of chemical analyses compensate each other, for INAA analyses the paste and the µEDXRF looks at the surface. Nevertheless, for proper geochemical characterisation INAA is better as the latter analyses the paste and can identify trace elements. µEDXRF is efficient but not ideal for detailed chemical analysis especially if questions of Provenance are treated. Nevertheless, being a non-destructive method it is highly useful and can be the first step in chemical analysis.

The Mineralogical and chemical data of the ceramics were even useful in the Thermoluminescence Dating process of these ceramics. An obvious one is the use of data generated from INAA (for K, Th, and U) in calculating the Annual Dose. Moreover, the mineralogical data of the sediments (taken from inside the ceramics as proof of context) allowed us to reject the sediments to calculate the the external environment dose. Moreover, when amorphous silicate was identified in one of the sediments it was hypothesised that ceramics could have got accidently heated during its museological history. In this case the Regenerative and Multiple Aliquot technique would not give palaeodose. These observations lead to adoption of the Predose Technique. However, all TL applied techniques point out that most of the ceramics are 19th -20th Century A.D

at the most 14th-15th Century A.D production. The results are summarised in the and not 8th-5th cent BC production which the typology pointed
Finally, it can be said that along with the authenticity it has also been able to test different analytical methods on the 10 samples of the collection and test for several hypotheses. All the analysis conducted and the different methods used despite their limitations, are compensating and help to build up in the understanding of the ceramics and eventually the collection. As suspected, the collection does have some copies of artefacts.

It is normal to find copies in museums' collections as many museums have been buying artefacts from different sources to enrich their collection and often without authenticity test. However, it does not mean that the whole collection should be characterised as fake and ignored. On the contrary proper studies have to be undertaken for proper sorting and characterisation, thus achieving an important part in proper heritage management of the collection and the future museum.

Museum collections contain heteroclite items with unspecified archaeological context, origin and mode of acquisition. Some of these items have been submitted in the past to more or less ingenuous unspecified restorations, while others are mere copies, pastiches or fakes. Museum emerged from personal collection of noble families having particular attention for antiquities since the middle age. Artists tried to make objects as close in appearance as possible to the ancient originals: the Renaissance and the 19th century being the most prominent periods. Since the opening in 1888 of the Chemical Laboratory of the Royal Museums, Berlin, directed by Friedrich Rathgen, for the study, authentication and preservation of cultural heritage there has been huge progress in analytical techniques. To accomplish this work, science-based study, art history and conservation–restoration are carried out together. Nowadays, an increasing number of analytical techniques are applied to museum objects (Guerra, 2008)· Hence, analysing the collection of Estrada Foundation (collection under present study) add up in this global move.

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