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# First results on radiometric dating of metals by alpha spectrometry☆

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ABSTRACT

A new TSAC (Thick Source Alpha Particle Counting spectrometry) setup of high geometrical efficiency and low intrinsic background was built to measure the alpha particles coming from the $^{238}$U and $^{232}$Th decay chains radionuclides with concentrations down to the ppm level. It was designed to test the $^{226}$Ra/$^{230}$Th method, which is the only direct metal dating method proposed to date. Micro-PIXE, micro-RBS and SEM-EDS were used as complementary analytical techniques in order to search for heterogeneities and/or impurities that could bias the TSAC data. Ores, resulting slags and metallic prills from two recent smelting experiments that reproduced ancient techniques and two ancient coins were studied to determine how radionuclides fractionation occurs during smelting. With this TSAC setup the background signal was extremely low, but comparable to the signal from the measured metals. Preliminary results show no evidence of a preferential depletion of $^{226}$Ra in a melted metal with respect to the other radionuclides.



## 1. Introduction

Archaeometallurgical research focuses in the reconstruction of early trade routes in terms of location of metal sources (ore deposits) and in the study of metallic artifacts and metallurgical remains through various analytical and examination techniques. Important information can be derived from these studies, like ore provenance, contact between different ancient societies and their technological development.

It's not an overstatement to say that the Holy Grail of archaeometallurgists is to achieve a method that can directly give the date of the manufacture of a metallic artifact.

Until now, the dating of metallurgical processes is made indirectly, under favorable conditions, by [1]: a) thermoluminescence (TL) and optical stimulated luminescence (OSL) of burnt soil in kilns and crucibles, or of remaining core material in the metal artifact and slag products [2]; b) radiocarbon ($^{14}$C) applied on carbon found in trapped slag inclusions (mainly iron artifacts); c) association with other archeological artifacts found in the same archeological context; and d) some aging or degradation specificities that may differentiate an old from a new object (e.g. intergranular corrosion is a slower corrosion process).

In 2006 [1] I. Liritzis proposed a radiometric dating method for metals that are produced from ores (native metals excluded), based on the isotopic fractionation that may occur during ore smelting. This fractionation disrupts the secular equilibrium in the $^{238}$U series. In this sense, $^{226}$Ra, a radionuclide that occurs naturally in the decay chain of $^{238}$U with a half-life of 1602 years, tends to be withdrawn by slag products away of the melted metal, as a result of its low specific gravity, 5–6 g/cm$^3$, and its lower melting point (700 °C) when compared to some metals, as for example copper (8.9 g/cm$^3$; 1083 °C).

As a consequence, in a metal, $^{226}$Ra would appear from the decay of its parent, $^{230}$Th (half-life, $t_{1/2}$ = 80000 years). Assuming that initially in the metal $^{226}$Ra is not present, then at time t, the ratio between the activities of $^{226}$Ra and $^{230}$Th is given by Eq. (1) [1]

$$\frac{A_{226Ra}}{A_{230Th}} = \frac{\lambda_{226Ra}}{\lambda_{226Ra}-\lambda_{230Th}}\left[1-e^{-(\lambda_{226Ra}-\lambda_{230Th})t}\right], \quad (1)$$

where $\lambda_{226Ra}$ and $\lambda_{230Th}$ are the decay constants ($\lambda = \ln(2)/t_{1/2}$) of $^{226}$Ra and $^{230}$Th, respectively. As $\lambda_{226Ra} >> \lambda_{230Th}$ ($4.33 \times 10^{-4}$ yr$^{-1}$ >> $8.66 \times 10^{-6}$ yr$^{-1}$) the ratio of activities tend to the value $\lambda_{226Ra}$ / ($\lambda_{226Ra}$–$\lambda_{230Th}$) ≈ 1, and the secular equilibrium is attained after around 9000 years. This period is comparable to the elapsed time since the onset of metallurgy in some areas of the globe. Therefore, this growth of $^{226}$Ra back to secular equilibrium with its parent $^{230}$Th is the basis of this method. This model, known as the $^{226}$Ra/$^{230}$Th Liritzis method,

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can be considered theoretically consistent. However, its experimental validation still needs to be done. The key issues for this validation are:

- very low counting rate: ores contain traces of uranium ($^{238}$U and $^{235}$U, with natural abundances of 99.284% and 0.72%, respectively), thorium ($^{232}$Th, with 100% natural abundance) and their daughter products derived from their radioactive decay. $^{232}$Th series is taken into account in this study because it interferes with the measurements of $^{226}$Ra and $^{230}$Th. On average, uranium in copper ores is 2.4 ppm (1–3 ppm) and thorium is 0–1 ppm [1,3]. These concentration values are very low, so in order to get statistically relevant data, a high efficiency measurement system must be used together with a strict control and minimization of background sources;
- the efficient separation/fractionation of U and Th daughter products during smelting lacks in literature. In the geological field, primitive lavas present high $^{226}$Ra/$^{238}$U ratios that can be explained in a scenario of selective fractionation [1], but in the field of metallurgy, the fractioning efficiency is poorly understood because it depends on a variety of mechanisms operating in a smelting furnace, such as: a) sorting by density, b) sorting by melting point, c) sorting by chemical affinity (with strong influence on the thermodynamic conditions in the furnace) and d) differences in solubilities [4].
- radionuclide homogeneity in ores, metals and slags. In principle, it is expected homogeneity in ores since the uranium and thorium series are in equilibrium. For the metals and slags produced after ore smelting, it is expected that if there is no secular equilibrium a heterogeneous distribution of radionuclides can be present at a microstructural level, due to normal microstructural heterogeneities of the produced materials (as production of different phases in some alloys and the development of various mineralogical compounds in slags). However, this non-homogeneity is mostly expected at the microstructural level; the analysis of "macro-areas" should yield an average value.

According to Eq. (1), the $^{226}$Ra/$^{230}$Th (Liritzis) method implies the quantification of both radionuclides present in a sample. Considering that $^{226}$Ra and its progenitor, $^{230}$Th, decay by emitting alpha particles – $^{226}$Ra emits alpha particles with energies 4.784 MeV (94.45%) and 4.601 MeV (5.55%), while the alpha particles from the $^{230}$Th have energies of 4.687 MeV (76.3%) and 4.620 MeV (23.4%) – the TSAC (Thick Source Alpha Particle Counting spectrometry [5,6]) is a suitable technique to detect the presence of these radionuclides. Furthermore, the TSAC technique is accurate, sensitive to all alpha emitters from the uranium and thorium series, 15 in total (8 from the $^{238}$U series and 7 from the $^{232}$Th series), non-destructive (a fundamental point in the study of any rare and valuable metallic artifact), well suited to handle samples of several centimeters in size and masses of several grams, and it is a setup simple and easily portable to museum installations. The only constrain factors are that it is a technique sensitive to approximately only the first 10–20 μm of the sample, which is the range of alpha particles with energies between 4 and 8 MeV in a metal (thus can be considered as a superficial analysis); and the data acquisition period can be considered relatively long (several days are needed). Additionally, as the analyzed samples are thick, the alpha particles emitted in depth loose energy before they reach the sample surface producing a continuum energy distribution in a TSAC spectrum. This results in a more complex spectrum to analyze. However it will allow determining whether there is secular equilibrium or not and eventually where this disequilibrium occurs.

In this work the used experimental setup is described and preliminary results are presented and discussed, constituting the first step in testing the $^{226}$Ra/$^{230}$Th dating method, which may provide a secure basis for the application and development of the unique metal dating method proposed to date, and as such it will be especially important with respect to artifacts that have been found out of datable archaeological contexts, or where archaeological contexts have been lost, or even to detect forgeries.

## 2. Material and methods

### 2.1. Studied objects

The methodology followed in this work rests on measuring the TSAC spectra for two sets of samples:

1. copper and tin ores, resulting slags and metallic prills from two recent smelting experiments: a) smelting tin ores (cassiterite — $SnO_2$) by traditional and simple means (an ethnoarchaeographic approach); b) smelting tin (cassiterite) and copper ores (malachite — $Cu_2CO_3(OH)_2$) for the production of bronze, simulating ancient smelting techniques, namely those performed in open air fires (in crucibles) which have been used since Chalcolithic times to Iron Age in various regions of Europe. With the complete chain of materials involved in the smelting available, it is possible to study how radionuclide separation occurs during smelting. Here, the key issue is how efficient is the removal of $^{226}$Ra to the slags: once metal is separated from slag, ideally $^{226}$Ra will be associated with slag and metal will be free of radium. However, in practice traces may remain. If this happens the age obtained by the $^{226}$Ra/$^{230}$Th method will be higher than the real one, and the discrepancy increases with the amount of radium that remained in the metal;
2. coins from different centuries. The option for the study of coins comes from the fact that coins cover a wide period of metallurgy, their age is well known, they are made of different metals or alloys, they have similar shapes (which simplifies the experimental setup) and, frequently they are well preserved (absence or low level of surface corrosion). In this case, it must be considered the possibility of metal recycling, since it is well known that coins, as well as other metallic artifacts, were often obtained by re-melting previous objects. When metal is re-melted to make a new object, the equilibrium is disrupted because radon and polonium are removed, though soon after some days, equilibrium is set again; thus, the $^{226}$Ra and $^{230}$Th activities and their activity ratio are not affected by re-melting process. Consequently, in the case of measuring the age of a coin made by recycled metal the age refers to the smelting process and not to the later re-melting, meaning that the age obtained by the $^{226}$Ra/$^{230}$Th method will give an older date than the date of the object fabrication. The study of different coins from different epochs will allow verification of this. In this work, the results for two Portuguese coins are presented, a bullion coin named "dinheiro" from king Fernando I (ruler of Portugal between 1367 and 1383), and a "III Réis" copper coin minted in 1874 (under the reign of king Luís I).

All samples were cleaned with alcohol in an ultrasonic cleaning bath before the measurements and their surface was optically inspected with an Olympus SZX9 stereo microscope searching for some noticeable surface deposits.

### 2.2. Thick Source Alpha Particle Counting spectrometry (TSAC)

The alpha detector selected for this work is a specially designed PIPS detector (model A1200-32AM) from Canberra Industries (Meriden, U.S.A.) with a large surface area (1200 mm$^2$), energy resolution of 32 keV (FWHM) and a very low intrinsic background (nominal value below 0.67 counts/h in the energy range of 3 to 8 MeV) [7]. The pulses produced by the detector were processed and shaped by an ORTEC142 (not cooled) preamplifier and an ORTEC571 amplifier from ORTEC (Oak Ridge, U.S.A.) which are then digitized by a MCA-8000D Multichannel Analyzer from Amptek Inc. (Bedford, U.S.A.) to give a 4096 channels alpha particle energy spectrum up to ~10 MeV (2.5 keV/channel). In order to increase the number of counts per channel, the spectra were compressed to 1024 channels. Because of that the quantization error increased as we went from a 2.5 keV/channel to a 10 keV/channel configuration; nevertheless it is still suitable for this work.