The sampling of archaeological metals for lead isotope analysis using EDTA
A "minimally destructive" alternative

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Introduction

A new sampling method has been investigated using ethylenediaminetetraacetic acid (EDTA) to extract lead (Pb) directly from metal artifacts for Pb isotope analysis without the need for taking a solid sample, a common sampling method which is destructive and damaging to the object. EDTA extraction of lead has been used with reported success in the sourcing of lead and silver objects from Pakistan[1] and the sourcing of lead glazed Majolica in the American Southwest[2]. Where metal artifacts have been soaked in low concentration solutions of EDTA using this technique, no macroscopic changes to the surface of the metal objects have been reported.

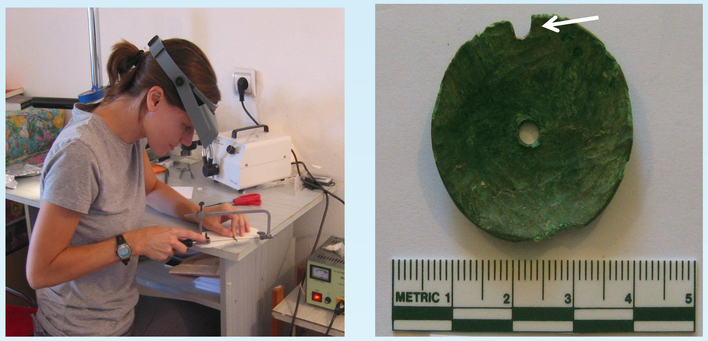

Figure 1. Sampling a bronze disc from the site of Lofkënd using a jeweler's saw (left). Sampling required a small piece from the edge of the disc to be taken (right).

Objectives

- To determine whether the EDTA extraction technique can be used to source lead, silver and bronze objects from the sites of Kerkenes Dağ (Turkey) and Lofkënd (Albania)
- To establish a methodology for this type of analysis using inductively coupled-time of flight - mass spectrometry (ICP-TOF-MS)
- To determine whether the EDTA extraction damages or alters the surface of the metal object

EDTA extraction of Pb

Objects were immersed in solutions of 0.05% EDTA (pH=5) in deionized water for 5 minutes, with the solution agitated every 20 seconds. For small objects, the entire object was placed in the EDTA solution. For larger objects, only a portion of the object was immersed. After immersion, the objects were rinsed in several baths of deionized water (for at least 5 minutes) to remove any EDTA. Both objects in good condition and those heavily corroded were used for the extraction.

Figure 2a. Bronze ring from Lofkënd in 0.05% EDTA solution

Figure 2b. Sample vials containing EDTA extractions of Kerkenes Dağ metals

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Examination of artifacts after extraction

Objects were examined using a stereomicroscope (5-45x) before and after soaking in the EDTA solution to determine whether there were any changes to the surface, such as etching or pitting. The solution was also examined for any color changes.

No changes in color or surface texture (pitting or etching) were observed on any of the objects immersed in EDTA. For larger objects, where only a portion was placed in the solution due to their size, no differences were noted in color or surface texture between the immersed areas and those not immersed in the solution.

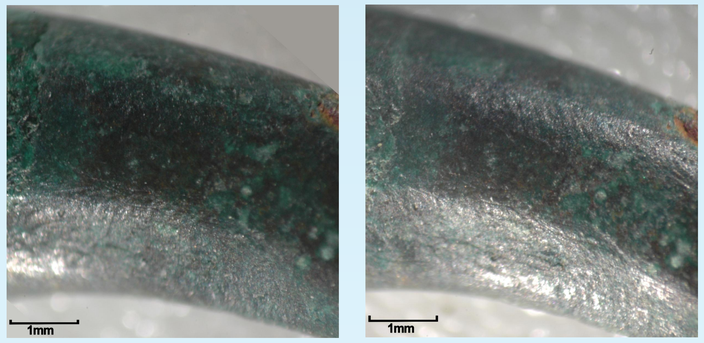
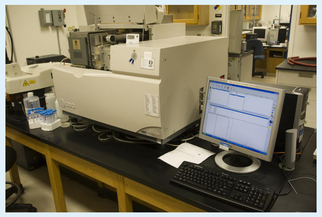


Figure 3. Photomicrograph of a ring from Lofkënd before (left) and after (right) extraction. No changes to the surface were noted.

Figure 4. Though no surface changes were observed, the EDTA solution did change color (from clear to blue or green) during immersion of some of the bronze objects, such as with these metals from Kerkenes Dağ. This indicates that other components, in addition to lead, have been extracted and gone into solution.

ICP-TOF-MS Methods

An Optimass 8000 ICP-MS with a time-of-flight (TOF) mass analyzer setup with a liquid nebulizer was used to determine Pb isotope ratios.



NIST standard reference material (SRM) 981, a lead wire standard, was used 1.) as an external calibration for unknown archaeological samples, and 2.) to test the efficacy and validity of EDTA extractions. Two separate series of standard solutions of SRM 981 were prepared for comparison. The first was prepared by soaking 0.05 g of SRM 981 in 20 ml of 2.0% EDTA solution for 30 mins., which was then transferred to a series of vials and diluted to 1:5, 1:10, 1:20, 1:40, and 1:80 so as to create a concentration ramp. The same was completed with a 5.0% ultra pure nitric acid solution. EDTA extractions of archaeological samples were diluted with 1-3 ml of ultra pure water so as to regulate their lead concentrations.

Ten replicates of 10 second measurements were collected for two runs of EDTA and one run of nitric acid extractions. Mass bias was corrected for by subtracting a calculated correction value from the measured value.

ICP-TOF-MS Results

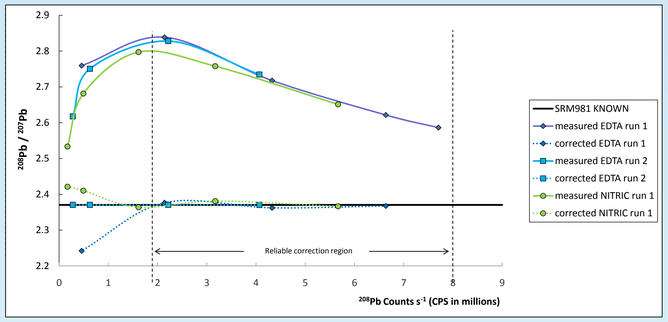


Figure 5. As the concentration increases around 2 million CPS, the mass bias curve reaches a point of inflection from where a systematic linear regression continues. This allows for a fairly accurate correction value to be computed within a reliable correction region of 2-8 million CPS.

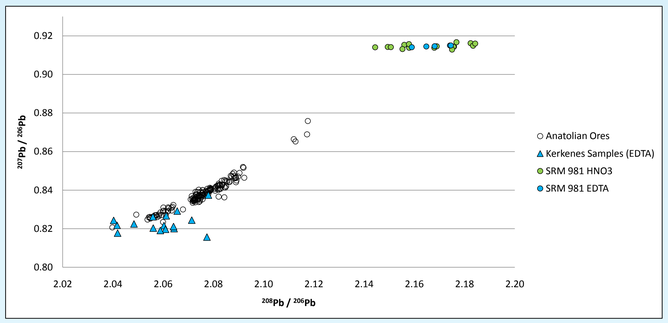


Figure 6.. This bivariate plot presents the analytical results comparing ^{207}Pb / ^{206}Pb and ^{208}Pb / ^{206}Pb isotope ratios of SRM 981, archaeological sample solutions and previously measured known ore sources from Turkey [3,4]

	Pb207/Pb206	Pb208/Pb206	Pb206/Pb204
SRM 981	0.9146	2.1681	16.9371
Mean EDTA	0.9146	2.1681	16.9407
1 StDev	0.0003	0.0050	0.2807
Mean HNO3	0.9146	2.1664	17.0492
1 StDev	0.0011	0.0132	0.9464

Table 1. This table indicates the degree to which measured SRM 981 compares to its known ratios.

Conclusions

- Results demonstrate that low concentration EDTA extractions representatively solubilize lead for its accurate measurement by ICP-MS.
- No changes were observed to the surface of the objects up to 45x magnification after immersion in EDTA. However, further studies should be undertaken at higher magnifications to identify any surface changes occurring during the extraction. These studies should also look into determining whether the extraction and solubilization of metallic components may alter the surface or composition of the object posing possible future condition issues.

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References

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