Advancing Quaternary Geochronology: Impact of Sample Preparation and Analytical Techniques on Natural Radioactive Dose Assessment in Stream Sediments

Fernando Jimenez[1], Altug Hasozbek[1], Mathieu Duval[1], Josep M. Pares[1], M. Isabel Sarró-Moreno[1], Ana I. Barrado-Olmedo[2], Estefanía Conde-Vila[2], Marta Fernández-Díaz[2], José Manuel Cobo[2], Martin Perez-Estebanez[3], and Javier Alonso-Garcia[4]

[1] CENIEH, Uranium Series Laboratory, Burgos, Spain
[2] Centre for Energy, Environmental and Technological Research, CIEMAT, Madrid, Spain
[3] Department of Chemistry, Universidad de Burgos, Burgos, Spain
[4] Thermo Fisher Scientific, Madrid, Spain

fernando.jimenez@cenieh.es

ABSTRACT

In Quaternary geochronology, accurately estimating natural radiation exposure is crucial for dating materials using Electron Spin Resonance (ESR). Traditional techniques like gamma and alpha spectrometry, despite their utility, are limited by sample size requirements and time inefficiency, especially in low-radiation contexts. This study explores the potential of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Plasma Mass Spectrometry (ICP-MS), using both Quadrupole (ICP-QMS) and High-Resolution (HR-ICP-MS) instruments, for analyzing uranium, thorium, and potassium concentrations in sediments.

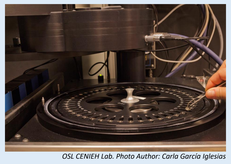
We compared various acid digestion methods using standard hot-blocks, microwave digestion, and single cell microwave technology on a selection of Sediment Reference Materials (NIST BRS 8704, OREAS 24d). Potassium detection was more accurate with ICP-OES (96% precision) than ICP-QMS (80%). In contrast, HR-ICP-MS significantly outperformed ICP-QMS in measuring uranium and thorium (U and Th recoveries of 99% and 94% vs. 83% and 81%, respectively). Moreover, microwave-assisted digestion methods showed slight advantages in uranium and thorium recovery.

Our findings suggest that a four-acid microwave-assisted digestion, combined with potassium measurement via ICP-OES in radial mode and uranium and thorium quantification using HR-ICP-MS, offers the most accurate and time-efficient approach measuring radioelement concentrations in Quaternary sediment for trapped-charge dating purpose. This methodology is particularly relevant for cave, river, and stream sediments even with expected low uranium levels.

Trapped Charge Dating Techniques In Quaternary Geochronology

ESR Quartz in rocks or sediments and biogenic materials (e.g. teeth)
OSL Quartz/Feldspar in rocks or sediments

ESR CENIEH Lab. Photo Author: Carla Garcia Iglesias



OSL CENIEH Lab. Photo Author: Carla Garcia Iglesias

The accumulated Dose D_A of a material exposed to radioactivity after its burial is time dependent.
The number of charges trapped in the sample material is directly correlated with its time of exposition and the radioactive profile of the media in which the material has been buried.

Independently to analytical technique used, the AVERAGE DOSE RATE must be estimated in order to establish the model Time = f(D_A)

Trapped Charge dating techniques measure only the dose rate at T = 0 (present day). Consequently current dose rate should be determined and different assumptions about in which extend the dose rate has been constant along time should be taken.

Thus, a precise knowledge about the sources of radioactive dose turns crucial to determine the dose rate in addition to the bulk gamma dose determined in situ, specially in highly variable scenarios.

The main radioactivity elemental contributors are Uranium, Thorium and Potassium:

Isotope	Relative Abundance [%]	Half Life [yr]	Specific Activity [Bq mg^{-1}]
^{235}U	0,72	7,10·10^{8}	79,960
^{238}U	99,28	4,51·10^{9}	12,437
Natural U	-	-	12,2
^{232}Th	100	1,41·10^{10}	4,057
^{40}K	0,0117	1,428·10^{9}	262
Natural K	-	-	0,0313

Typical factors used to convert from activity concentration to absorbed dose rate:

Isotope	Conversion Factor nGy.h^{-1} / Bq.kg^{-1}
^{238}U	0.38
^{232}Th	0.52
Natural K	0.04

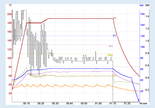
Analytical Techniques and Procedures

SAMPLE PREPARATION

Blocks / Racks of Heated Closed Vessels Acid Digestion
- 60 mL PTFA reactors
- 100 – 200 mg sample amount
- 140 ºC 12 h

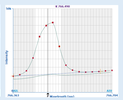
Microwave Assisted Acid Digestion
- 15 mL PTFA reactors
- 100 – 200 mg sample amount
- Programmed temperature ramp
- Single Reactor Cell UltraWAVE 2 Milestone

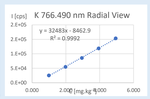
Single Step multi reagent digestion: HNO_3 – HCl – HF – H_2O_2
Final dilution in 50 g deionized water



QUANTITATIVE ANALYSIS

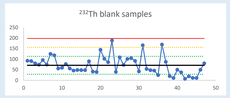
ICP – OES radial view

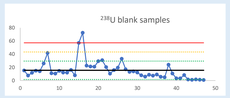


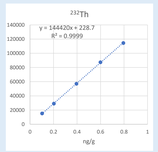


HR – ICP – MS

PARAMETERS	HR-ICP-MS operating conditions
RF power	1250 W
Nebulizer	Micro Mist concentric PFA, 0.1 mL min^{-1}
Spray chamber	Quartz cyclonic, 20 mL, Peltier cooled PC3 (ESI)
Acquisition mode	E-scan - LR



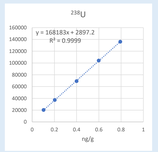




In solution:

^{232}Th
LOD = 0.13 pg.g^{-1}
LOQ = 0.44 pg.g^{-1}

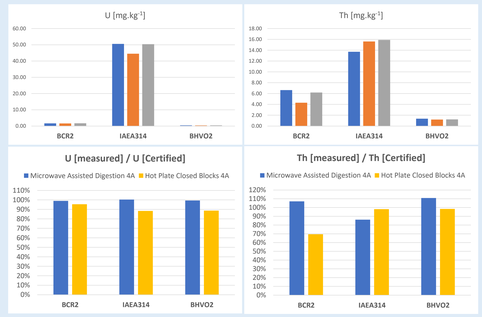
^{238}U
LOD = 0.04 pg.g^{-1}
LOQ = 0.12 pg.g^{-1}



Results

ACID DIGESTION

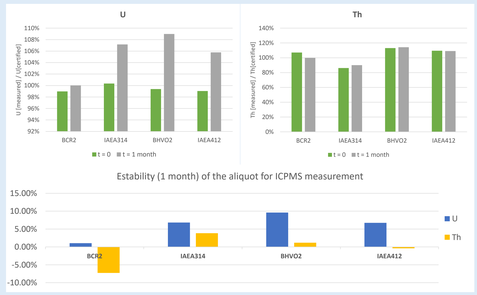
Microwave Assisted vs. Classic Heated Block Vessels
Same 4 A treatment



MW assisted digestion leads to results closer to certified values

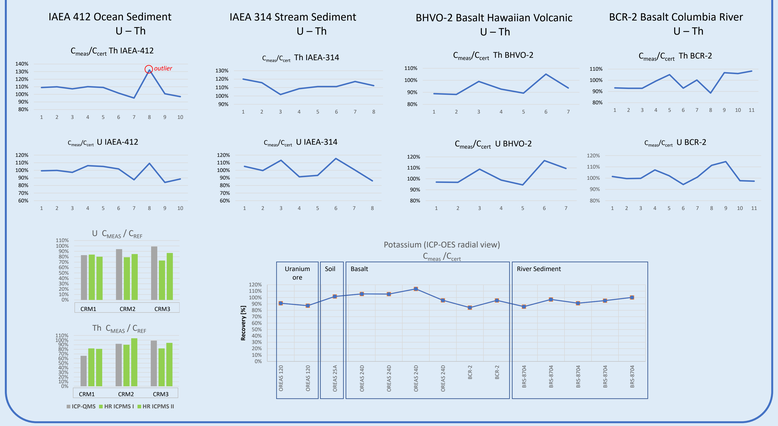
ESTABILITY OF THE SOLUTIONS

Aliquots were measured, stored at 4 ºC and measured again after 30 days.



Results are affected by large storage time, when up to 10% increment has been shown.

RECOVERY STUDIES



VARIABILITY OF THE DOSE RATE AS A RESULT OF THE ELEMENT CONCENTRATION REPORTED

CRM	IAEA 412	IAEA 314	BHVO2	BCR2	BRS8704	OREAS 120	OREAS 25A	OREAS 24D
D_A [Gy·ka^{-1}]	2.088	3.589	31.318	3.980	7.353	9.933	28.223	11.236
				Simulated Δ D_A				
Δ [U,Th,K] = 10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %
Δ [U,Th] = 10 %	6.29 %	8.51 %	0.89 %	2.19 %	2.65 %	6.43 %	3.07 %	1.05 %
Δ [U] = 10 %	3.18 %	7.85 %	0.48 %	1.06 %	1.44 %	6.19 %	1.21 %	0.59 %
Δ [Th] = 10 %	1.68 %	0.39 %	0.21 %	0.58 %	0.63 %	0.14 %	0.96 %	0.23 %
Δ [K] = 10 %	0.01 %	-	1.10 %	2.03 %	2.02 %	0.93 %	0.44 %	1.54 %
Mixed variability								
Δ [U] = 8 %								
Δ [Th] = 10 %	5.71 %	7.06 %	1.45 %	3.17 %	3.54 %	5.76 %	3.09 %	1.85 %
Δ [K] = 6 %								

Lessons Learned

- ✓ Microwave Digestion leads to improved recoveries than Block Digestion.
- ✓ Microwave Digestion advantages the Block Digestion in terms of Productivity, Safety and Cleanliness.
- ✓ Sample amount used can be reduced to mg level without loss of precision.
- ✓ Combination of ICP-OES and ICP-MS help to cross check both techniques.
- ✓ Radial view ICP-OES should be selected for potassium analysis.
- ✓ Statistical Control Charts as an unvaluable tool to control the process.
- ✓ Stability of the U, Th solutions is limited to a couple of weeks even cooled storage.
- ✓ The showcased method shows robustness and can be applied to different matrices of interest in geoarchaeological environments (cave, stream sediments).
- ✓ The dose rate is less sensitive to small variations of potassium, on the other hand uranium plays a crucial role for the dose rate interpretation.

Next Steps

- ❑ Reduce the sample amount to mg or submg level.
- ❑ Study the effect of sample grain size.
- ❑ Study the effect of the occurrence of refractory oxides in the samples.
- ❑ Expand the Reference Materials to be studied.
- ❑ Apply evaluation methods to reveal the effect of every single element on the paleodose.

Some Literature

G. Adamiec, M. Aitken. Dose-Rate conversión factors: update. Ancient TL, 1998

O.V. Kuznetsova and Y.V. Bychkova. M. Jonas. Development and Validation of a SF-ICP-MS Method for Analyzing the Diagenesis-Designating Metals in Marine Sediments. Analytical Letters, 2019

M. Jonas.Concepts and methods of ESR dating. Radiation Measurements, 1997

A. Pearce. Recommended Nuclear Decay Data. NPL Report IR 6, 2008

K.E.H. Penkman et al. Dating the Paleolithic: Trapped charge methods and amino acid geochronology PNAS, 2022