



CHALLENGES IN ENSURING METROLOGICAL TRACEABILITY IN HERITAGE MATERIAL ANALYSIS

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Compositional Analysis of Heritage objects

Heritage Objects Provides information on:

- Raw material selection
- Manufacturing techniques
- Creative development
- Geographic and authorship origin.



Challenges [1-3]:

- Nondestructive techniques
- Sample heterogeneity
- Matrix effects
- Concentration ranges
- Comparability in long-time
- Metrological traceability

The **aim** of this poster is to present some examples in analytical calibration using multivariate techniques for element quantification in ancient glasses, highlighting limitations related to the availability of reference materials, as well as addressing challenges and opportunities in the field of heritage science.

1. INTRODUCTION

Krateriskos (Mid 14th century B.C.)
Glass
Landesmuseum Württemberg, Stuttgart

Portland Vase (1st century A.D.)
Glass
The British Museum, London

2. METHODOLOGY

- **RM Candidate Selection and Preparation** were selected based on their relevance to ancient glass, ensuring a wide concentration range and well-distributed values.
- **Glass RM candidates** were characterized to determine their elemental composition using acid/alkaline digestion and ICP-MS and ICP-OES.
- **Portable- X-Ray Fluorescence** measurements were performed using an Elio XGLAB (25 mm² active area, 135 eV resolution at Mn K α) under reproducibility conditions.
- **XRF Spectra** were processed to remove noise, baseline variations and obtain the deconvoluted signals.
- **Chemometric models** were trained using Partial Least Squares (PLS) to predict elemental concentrations.
- **Uncertainty Estimation** via Bootstrapping was applied to estimate prediction uncertainty.
- **Bias** was evaluated using Corning Certified Reference Materials(CRM) [4].



XRF Spectra from glass RM candidates

39 Calibrators set

4 CRM

Multivariate Calibration: PLS

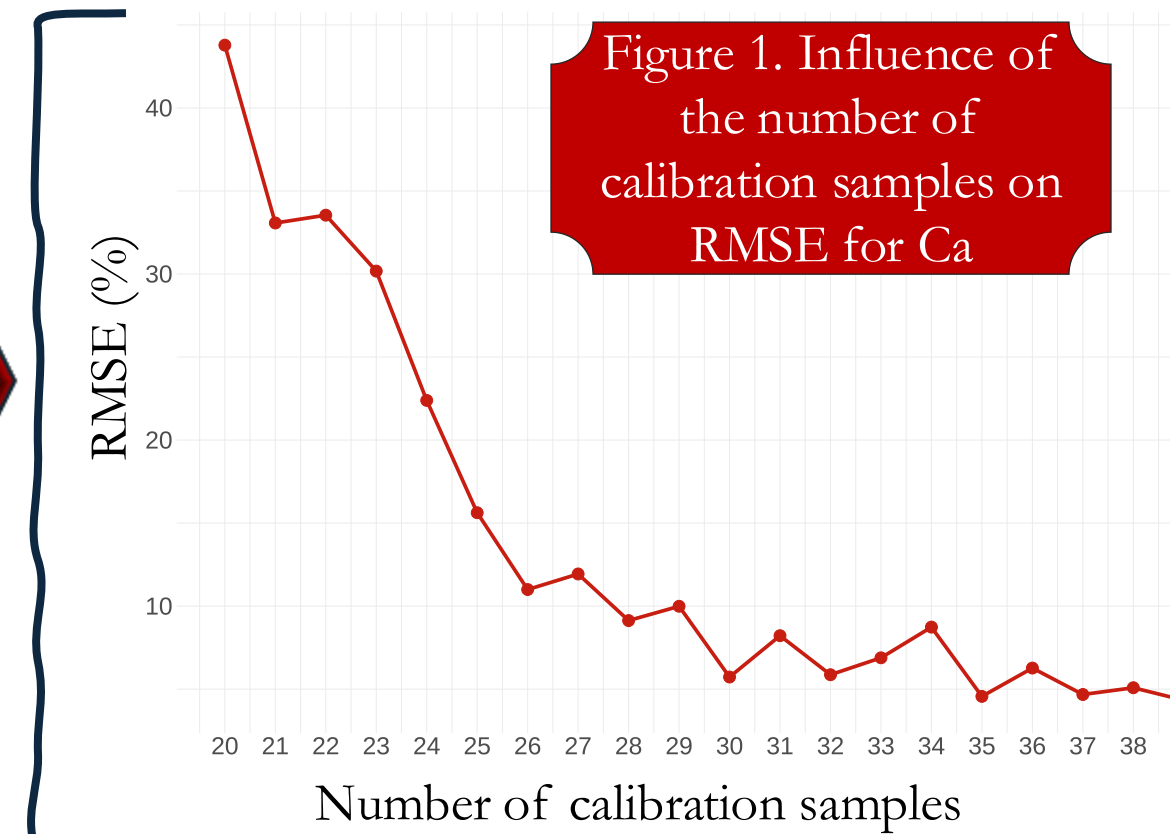


Figure 1. Influence of the number of calibration samples on RMSE for Ca

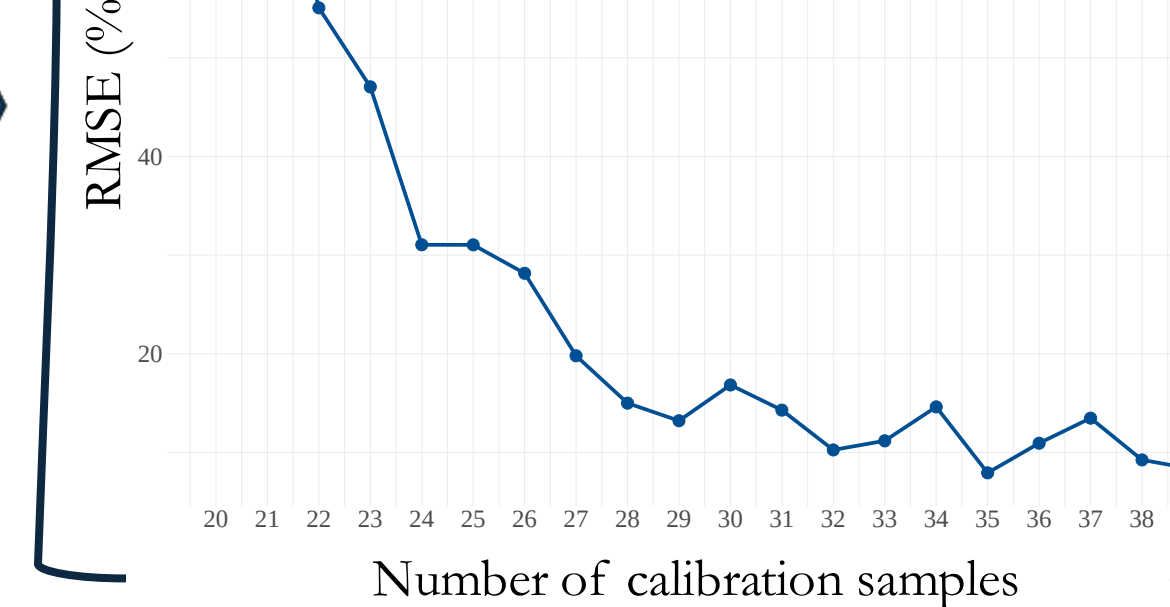


Figure 2. Influence of the number of calibration samples on RMSE for Pb

Bootstrapping

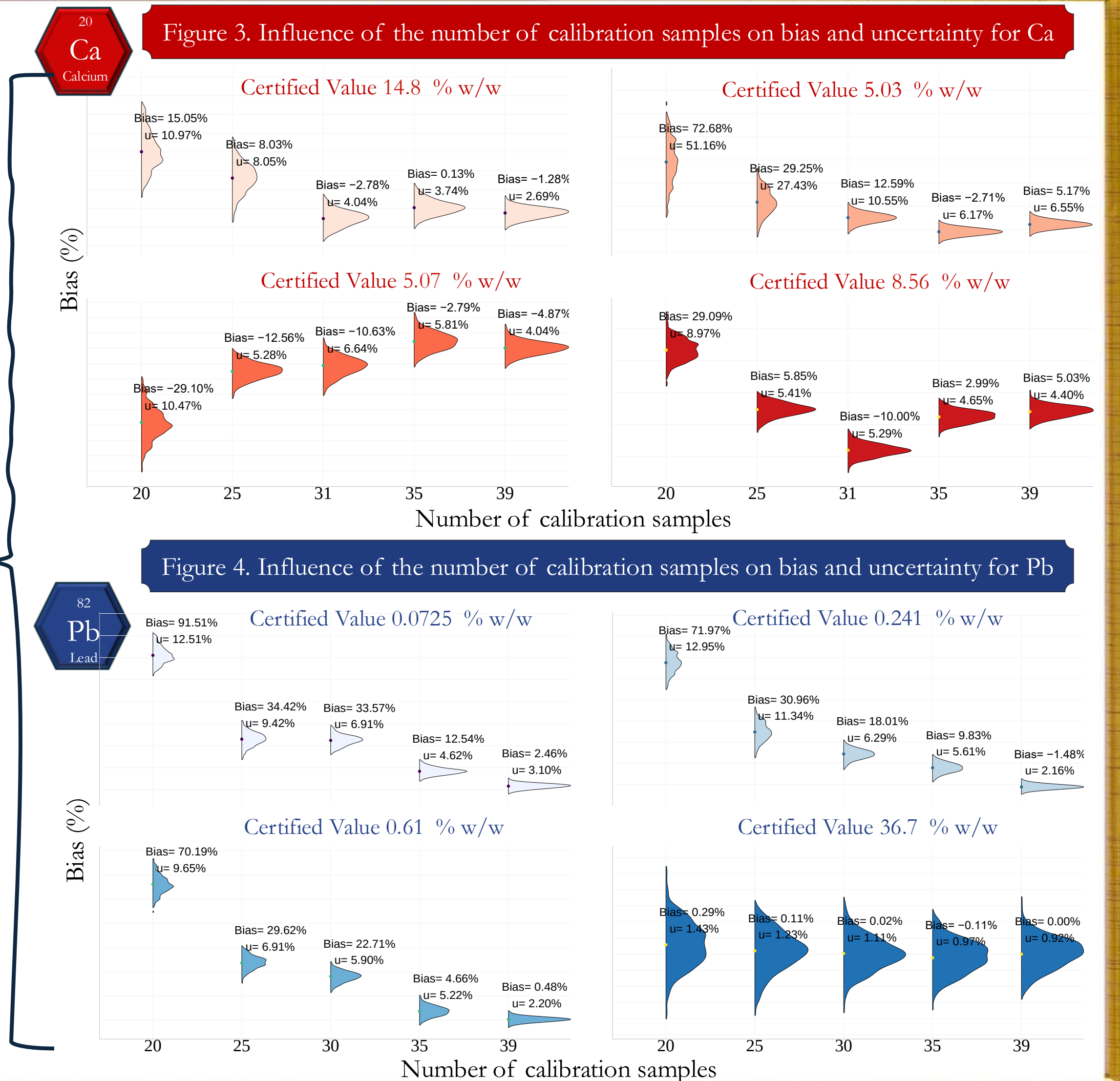


Figure 3. Influence of the number of calibration samples on bias and uncertainty for Ca

Figure 4. Influence of the number of calibration samples on bias and uncertainty for Pb

3. RESULTS

Completed glass vessels (1st century A.D.)
The Archaeological Museum , Beirut

- The **RMSE curves** show a significant decrease as the number of samples increases.
- For the glass with **Pb at 37.7%**, the number of samples has little influence, likely due to **low matrix effects** for this element and its **high concentration**.
- **Increasing the number of calibrators** reduces systematic error relative to the reference value and decreases uncertainty, highlighting the **importance of having a larger number of RMs** with diverse characteristics.
- Unfortunately, **only four CRMs** characterized by consensus are available for ancient glasses, lacking a metrological traceability chain, emphasizing the need of CRMs.

4. FINDINGS

Mysterius Asuka (1998)
Stanislava Grevenickova
Contemporary Glass Art Museum, Madrid

Perspectives (2025-2030)

Multiple contributors: NMIs, Universities & Industry
Blank canvas
Collection of possibilities

5. NEW OPPORTUNITIES

- **Historical Glass RMs:** Develop RMs for ancient glass to improve analysis accuracy.
- **CRM Traceability:** Improve CRM traceability to ensure consistency in heritage science studies.
- **Advanced Data Analysis:** Integrate digital metrology and machine learning for real-time data analysis.
- **Collaboration:** Promote cross-disciplinary efforts to enhance calibration and preservation.
- **Sustainability:** Adopt sustainable practices in RM development and updates.
- **Knowledge Transfer:** Make created materials available to heritage stakeholders for broader impact and application.

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