Methodological innovations in pXRF studies

edited by
Michaela Schauer, Nadia Cantin
and Thomas Faucher



Centre d'Études Alexandrines

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Introduction

Although pXRF has become a widely used tool across archaeology and heritage science through archaeometry, conservation science and geology, there has been a long-standing gap: the lack of a dedicated international forum focused specifically on methodological standards, challenges, and innovations in the use of portable X-ray fluorescence.

The conference Methodological Innovations in pXRF Studies held on 24 September 2024 at the Vienna Institute for Archaeological Science (VIAS), University of Vienna, was a significant step forward in addressing this issue.

The conference aimed to establish a platform where specialists, researchers, and practitioners could come together to address technical hurdles, share solutions, and foster community around best practices. Particular attention was given to improving and providing guidelines for data acquisition, processing, and interpretation across diverse research materials and contexts. The event also sought to create bridges between disciplines and between experienced users and early-career researchers.

To support broad outreach and engagement, the conference was organised through an international network of partners. In addition to the VIAS (through the FWF ESPRIT research project 476, *Standardising Portable X-ray Fluorescence Analysis for Archaeometry* (SPXRFA), led by Dr. Michaela Schauer), the Mediterranean Portable X-ray Fluorescence Ceramic Users Network (pXRF-CUN), led by the CEAlex and represented by Mai Abdelgawad, Nadia Cantin and Thomas Faucher, contributed expertise and visibility through the CNRS International Research Network (IRN). The Research Network Human Evolution and Archaeological Sciences (HEAS) helped bring together key institutions, including the Natural History Museum Vienna (NHMW) – with

* Michaela Schauer, Irmgard Hein: Vienna Institute for Archaeological Science (VIAS), University of Vienna, Austria; Michaela Schauer, Karina Grömer, Daniel Oberndorfer: Natural History Museum Vienna (NHMW), Austria; Michaela Schauer, Irmgard Hein, Karina Grömer, Doris Jetzinger, Katharina Rebay-Salisbury: Research Network Human Evolution and Archaeological Sciences (HEAS), University of Vienna, Austria; Nadia Cantin, Thomas Faucher, Mai Abdelgawad: Centre d'Études Alexandrines (CEAlex), CNRS/Ifao-UAR 3134, Alexandria, Egypt; Doris Jetzinger, Katharina Rebay-Salisbury: Department of Prehistoric and Historical Archaeology, University of Vienna, Austria.

Dr. Karina Grömer and Daniel Oberndorfer – as well as Dr. Irmgard Hein (VIAS), who promoted engagement in Egyptology and ceramic analysis. From the Department of Prehistoric Archaeology (IUHA), Dr. Katharina Rebay-Salisbury and PhD candidate Doris Jetzinger supported student and early-career researcher involvement.

While initial projections estimated 40–50 attendees, the event drew far greater interest: over 70 researchers from five continents participated, underscoring the global relevance of the conference theme. This overwhelming response affirmed the need for a dedicated platform focused on pXRF methods. A major outcome of the event was the founding of the Global pXRF Network, which has since grown into a worldwide community of over 170 members – establishing a collaborative forum for standard-setting, data sharing, and methodological training.

The conference programme was designed to balance focused presentations with open discussion. A total of 12 oral presentations were selected, each followed by a dedicated discussion period, along with seven poster contributions. All presenters were invited to contribute to this volume, and 12 full papers were accepted by the editors for publication and submitted to an external peer-review process.

Thematic focus

The conference placed the spotlight firmly on the methodological side of pXRF studies – a much-needed focus given the technique's widespread but uneven use across archaeological sciences. Instead of treating pXRF as a quick or auxiliary tool, the event centred on refining how the instrument is applied, from fieldwork to lab analysis.

The rationale behind this focus was clear: while pXRF has become routine in many disciplines, the underlying workflows, calibration strategies, and data treatment approaches often remain inconsistent, underdeveloped, or are never shared. To move beyond surface-level use, the conference addressed core challenges such as ensuring data quality, understanding device limitations, and developing shared benchmarks.

Crucially, the event aligned with broader shifts in the field towards transparency, reproducibility, and collaborative infrastructure. Emphasis was placed on:

- Developing best practices for data quality assurance, precision and reporting;
- evaluating calibration strategies across different devices and materials;
- exploring statistical and computational tools, including machine learning;
- supporting open science principles, such as FAIR and CARE.

The conference brought together both established experts and early-career researchers to foster a more standardised, methodologically rigorous, and innovative application of pXRF in heritage and archaeological sciences.

Scope and content of the volume

The 12 papers in this volume reflect the wide methodological and contextual range of pXRF research presented at the conference.

The volume is structured in two main parts. "Part 1: Exploring methodologies" focuses on workflows, calibration strategies, and data processing techniques, aiming to improve the precision, accuracy, and overall quality of pXRF research. "Part 2: Applying pXRF in practice: case studies in challenging conditions" presents real-world applications of pXRF in diverse research environments, highlighting challenges, adaptations, and methodological reflections.

Section 1 – Advances in practical workflows and field strategies begins with a contribution by Michaela Schauer, who defines a practical workflow for daily data quality assessment. She introduces benchmarks for daily device performance monitoring and explores strategies for assessing data precision for elements and unknown samples. Her approach is supplemented by an R script as a contribution to best practice and transparent reporting of pXRF data quality. In the following paper, Luisa Dallai, Roger Doonan, and Vanessa Volpi focus on *in situ* geochemical fieldwork using pXRF. They present a framework for best practice, including sampling strategies, survey resolution, the use of certified reference materials, and the integration of site-specific laboratory analyses for quality control.

Section 2 – Improving data accuracy: some solutions addresses calibration and accuracy challenges. Rebecca Scott and Laura Kay investigate the performance of a pXRF device using preset analytical modes based on the fundamental parameters (FP) method. Focusing on titanium white acrylic paint, they show that once a sample reaches infinite thickness, reliable data can be achieved. Below this threshold, however, results are imprecise and inaccurate. Their findings raise critical questions about interpreting pXRF data from multilayered surfaces and emphasise the need for pre-analysis pilot studies using mock samples. Detlef Wilke advocates for the use of spiked fired clay samples for calibration in ceramic analysis. His paper discusses the benefits of such samples for modifying single chemical variables in ways that natural reference materials do not allow, and argues for the necessity of working with spectral data to improve accuracy. He also outlines various correction and normalisation options used in this context.

Section 3 – Collaborative research: inter-device comparisons and networks highlights community-based standardisation efforts. Mai Abdelgawad and colleagues present the results of an interlaboratory study based on 18 fired brick samples developed by the pXRF-CUN. These were measured by 11 different devices from four manufacturers. The study demonstrates both the variability of device performance and the potential for cross-device calibration. It underscores how accuracy is influenced by instrument settings, protocols, and device-specific sensitivity. Michelle Richards and Andrew McAlister present a pilot study from the Australasian Archaeological Research pXRF Collective which tested six devices from three manufacturers using 19 silicate rock reference standards, showing that compatible results can be achieved through correction factors or raw spectrum calibration. The authors conclude with a short guidance list on how to achieve FAIR and CARE-compliant pXRF datasets. The section closes with a note on the founding of the Global pXRF Network, initiated during the conference. In their contribution, Michaela Schauer and colleagues introduce the volunteer-based initiative as a collaborative platform for knowledge exchange, training, and best practice development in archaeometry and heritage sciences. The network's

aims – to connect specialists and novices, host teaching events, support standardisation efforts, and centralise reference resources – are described alongside the structure of its core team.

Section 4 – Integrating machine learning in pXRF studies focuses on the integration of AI into pXRF workflows. Katharina Streit and Brandon Lee Drake apply neural networks to a small assemblage of Dark Faced Burnished and Wadi Rabah Ware from the sixth millennium BC in the southern Levant, demonstrating that even limited datasets can benefit from machine learning approaches. Anno Hein explores artificial neural networks, support vector machines, and random forests for grouping and classification of Roman transport amphorae from the Eastern Aegean, showing the potential of automated group definition in archaeometric research.

Part 2: Applying pXRF in pratice: case studies in challenging conditions opens with Holger Becker and Federica Pendolino, who present the day-to-day reality of working with pXRF in museum and research project settings. Drawing on experience from the LVR Landesmuseum Bonn, they emphasise the need for standardised procedures when dealing with highly varied materials and research questions. In the next contribution, Thomas Faucher and Alexandre Bodet examine the use of pXRF in numismatics. They discuss two case studies involving ancient coins, showing the limitations of non-destructive surface analysis in the presence of corrosion. Despite surface alterations, they argue that precise measurements can still enable semi-quantitative grouping. Ilian Finkeldey investigates chemical changes induced by conservation treatments on Nordic Bronze Age objects from Schleswig-Holstein. Although the bronzes showed little visible corrosion, pXRF analysis revealed alterations in light elements attributable to restoration processes. His work demonstrates the importance of distinguishing between corrosion- and conservation-related chemical changes and highlights the need for interdisciplinary collaboration in interpreting pXRF data from heritage objects.

Reflections and perspectives

Several overarching themes emerged from the Methodological Innovations in pXRF studies conference, spanning methodological contributions, case studies, and informal discussions. Foremost among them was a strong emphasis on data quality and standardisation. Across contexts – from fieldwork to museum labs – participants consistently highlighted the need for well-defined workflows, appropriate calibration strategies, and transparent reporting of instrument settings and uncertainty metrics. Ensuring the reliability and reproducibility of pXRF data remains a central concern for the community.

Equally prominent was the growing role of collaborative, cross-institutional research. Initiatives such as the pXRF-CUN interlaboratory study, the Australasian Archaeological Research pXRF Collective, and the newly launched Global pXRF Network illustrate a clear shift toward shared protocols, open data infrastructures, and mutual support. These efforts signal the formation of a more connected and methodologically rigorous international pXRF community.

Another notable development was the integration of machine learning and AI tools into analytical workflows. Although still emerging, several papers showed their value for classification and pattern recognition, particularly in ceramic analysis. As these computational methods become more accessible, they are likely to play an increasingly important role in pXRF data interpretation.

Perhaps the most important outcome of the conference, however, was the strength of interdisciplinary dialogue. The exchange among archaeologists, conservators, chemists, geologists, and data scientists proved essential to confronting shared challenges and rethinking assumptions about the method's scope and limitations. Combined with the active involvement of early-career researchers and students, this created not only a snapshot of where the field stands today, but a foundation for where it is headed.

It is our hope that this volume – and the work and conversations it reflects – will continue to support the development of a well-connected, critically engaged, and methodologically ambitious pXRF research community.

Acknowledgements

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Part 1

Exploring methodologies

1

Advances in practical workflows and field strategies

Michaela Schauer

Workflow and benchmarks for daily device monitoring and data precision assessment in hand-held pXRF studies

Abstract

Ensuring high data quality is essential in hand-held portable X-ray fluorescence (pXRF) analysis, particularly in archaeology and heritage science, where geochemical data directly influence the understanding of our own past. This paper introduces a transparent workflow for evaluating element and sample precision as well as device performance, designed for users working primarily with analytical data. The proposed approach focuses on internal quality control, offering step-by-step routines using standardised benchmarks. The methodology supports both qualitative and quantitative applications and is delivered via a flexible R script to promote usability, comparability, and routine adoption. This contribution is intended not as a final framework but as a foundation for better practice and transparent reporting in pXRF studies.

Keywords

Data quality assessment, standardisation, workflow, device performance, sample precision, element precision

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Introduction

Hand-held, portable X-ray fluorescence (pXRF)[1] is widely used in archaeology and heritage science as it enables quick, cost-effective, minimal to non-destructive *in situ* chemical analysis of artefacts but also in the field, for example, to identify site activity zones. Quality and reliability of pXRF data of those studies are contingent on two fundamental aspects: accuracy, defined as the closeness of a measurement to a known or accepted value, and precision, which refers to the consistency of repeated measurements on the same sample. In recent years, there has been significant focus on ensuring accuracy in pXRF data with these efforts being crucial for producing quantitative data comparable across studies and instruments[2]. In contrast, precision, especially at the level of repeated measurements on the same object, but also on the definition of reliable elements for interpretation of datasets has received less attention[3], despite being equally important for both qualitative classification and quantitative interpretation[4].

This gap is particularly problematic in studies working with inhomogeneous materials such as, for example, archaeological pottery. Pottery is structurally and compositionally complex: inclusions, voids, surface treatments, and zoned compositions etc., all can influence the response of pXRF measurements. Therefore, coarse, handmade cooking vessels with large mineral or organic temper often show significant internal variability as, depending on the location of the pXRF measurement spot, the excitation volume may intersect different phases (e.g. clay matrix, inclusions), resulting in substantial variation between repeated measurements on the same object. In contrast, fine tableware with dense, homogeneous fabrics tends to yield much more consistent data[5]. A common strategy to mitigate this is to perform multiple measurements per sample and use their mean as the representative value[6]. Yet, in such cases as mentioned above, mean values alone are often not sufficient to characterise the composition of a sample. It might appear accurate, i.e. close to a laboratory standard or a reference group, but fail to be precise due to high measurement value scatter. This can lead to misinterpretation, especially in provenance studies or chemical grouping as pottery samples with undetected high internal variability cannot be reliably assigned to specific compositional groups: if individual measurements cross the boundaries of multiple geochemical groups, a mean-based group attribution may falsely suggest secure classification. Therefore, without evaluating intra-sample precision, such interpretations remain questionable, yet little work has been done so far to define benchmarks for this factor[7]. Besides sample heterogeneity, element precision also has to be addressed in regard to geochemical pottery studies, as elements detected with poor precision will lead to burring of compositional groups[8]. In addition to these material-related factors, pXRF instruments themselves can exhibit daily variation, for example, due to detector drift, or instability

1. In this article, the phrase pXRF refers specifically to hand-held devices.
2. Speakman, Shackley 2013; Hunt, Speakman 2015; Drake, MacDonald (eds.) 2023; Schauer *et al.* 2024; Frahm 2024; Wilke in this volume.
3. For examples see Stapfer *et al.* 2019; Daszkiewicz, Schneider 2020; Quinn 2022.
4. See e.g. Johnson *et al.* 2024; Frahm 2024.
5. Stapfer *et al.* 2019; Daszkiewicz, Schneider 2020.
6. Speakman, Shackley 2013; Stapfer *et al.* 2019; Daszkiewicz, Schneider 2020; Quinn 2022; Frahm 2024.
7. Wilke, Rauch, Rauch 2016.
8. Quinn 2022.

in excitation conditions. These effects further complicate data interpretation, especially when internal consistency is assumed without verification[9].

The precision monitoring (device/element) and benchmarking (element/sample) procedures proposed in this paper directly address these issues. By setting a threshold for acceptable precision, researchers can systematically identify samples and elements whose internal scatter is too high to support confident interpretation[10]. They enable transparent and reproducible decisions about data inclusion, and ensure that group structures are not distorted by imprecise input. The workflow is designed for researchers working with pre-processed pXRF output (analytical data), i.e. elemental concentration data provided by a specific device and measurement mode. It therefore does not replace calibrations/correction procedures which are essential for producing accurate analytical data suitable for quantitative analysis[11], but complements it by offering a toolset to assess data consistency and detect instrument drift. A custom R script demonstrates by example and supports implementation and documentation of internal quality control procedures[12].

Methods

Well documented Data Quality Assessment (DQA) procedures for device monitoring and element precision, but especially defining intra-sample variation for pXRF applications are still rare. However, internal quality control routines can significantly improve transparency, reproducibility, and confidence in pXRF results[13]. This paper proposes a streamlined DQA workflow tailored to typical pXRF usage in archaeology, grounded in the first two phases of Total Data Quality Management (TDQM): data quality definition and measurement[14]. It does not attempt to replicate full laboratory uncertainty budgets but instead offers a practical toolset; the following sections describe the components of this workflow in detail. The paper outlines first the conceptual framework of uncertainty used to define which error sources can realistically be addressed by the workflow. It then introduces a protocol for monitoring short- and long-term device performance, before explaining how precision can be assessed at both element and sample level. The paper also distinguishes between calibrations/coefficient corrections used to define data accuracy and discusses day-to-day device monitoring based on control limits. Finally, the full implementation of the workflow is presented, including data processing steps and empirical thresholds, supported and demonstrated by the accompanying R-script[15].

9. Helfert 2013; Daszkiewicz, Schneider 2020; Quinn 2022.
10. Wilke, Rauch, Rauch 2016; Stapfer *et al.* 2019; Daszkiewicz, Schneider 2020; Quinn 2022.
11. Speakman, Shackley 2013; Wilke in this volume.
12. Schauer 2026.
13. Vlachos, Michail, Sotiropoulou 2002; Halevy 2003; Hemraj, Dhondee 2006; Abdel-Fatah 2010; Balaram, Satyanarayanan 2022.
14. Nikiforova 2020; Bronselaer 2021; Wang, Strong 1996; Drake, MacDonald (eds.) 2023.
15. For workflow and example, see Schauer 2026.

Components of uncertainty addressed in this paper

In pXRF analysis, especially within archaeology and heritage science, the full quantification of measurement uncertainty through formal uncertainty budgets is often impractical. This is due to a variety of constraints, including unpredictable field conditions, the lack of standardised sample preparation for minimal to non-destructive applications, and the fact that many researchers work with analytical data produced by proprietary (e.g. producer specific) software. Therefore, this paper proposes a realistic, structured approach to internal quality control[16]. To ground this approach conceptually, the model proposed by Drake, Mayer and Shugar is introduced, in which the estimated value, including all relevant sources of uncertainty, is expressed as:

$$\hat{c}_i = c_i + e_h + e_c + e_q + e_i$$

This model identifies four main contributors to deviation from the true value (C_i):

- e_h: heterogeneity-related uncertainty (e.g. matrix variability);
- e_c: spectral acquisition uncertainty (e.g. counting statistics);
- e_q: quantification model uncertainty (e.g. calibration error);
- e_i: unmodeled influences (e.g. instrumental drift or environment)[17].

In accordance with GUM[18], the combined standard uncertainty is theoretically estimated by summing the squared contributions of these independent components:

$$u_c = \sqrt{u^2(e_h) + u^2(e_c) + u^2(e_q) + u^2(e_i)}$$

While this framework is appropriate in laboratory settings, its full implementation is often unfeasible in field-based or minimally controlled environments. Therefore, quality control strategies for pXRF based on monitoring rather than full modelling are often advertised. Consequently, this paper focuses on two accessible components: sample heterogeneity e_h and instrumental influences as part of e_i[19].

Sample heterogeneity (e_h) is the dominant source of uncertainty, especially in non-destructive or minimally invasive pXRF applications. Variability in surface texture, such as evenness, particle size, mineral inclusions, or surface coatings affect the excitation volume and contribute to this error. To address this, replicate measurements are taken at different positions on the same object, providing an empirical estimate of intra-sample precision. Therefore, e_h cannot be assessed when only a single measurement per sample is taken (e.g. geochemical *in situ* analysis)[20].

Instrumental or environmental influences (e_i) encompass those factors not captured by e_c or e_q including detector drift, temperature fluctuations, power instability and environmental effects[21].

16. For a general introduction to measurement uncertainty see GUM 2008; Markovicz 2008; Drake, Mayer, Shugar 2023.
17. Drake, Mayer, Shugar 2023.
18. GUM 2008.
19. Álvarez *et al.* 2007; Markovicz 2008.
20. GUM 2008; Markovicz 2008; Drake, Mayer, Shugar 2023.
21. Drake, Mayer, Shugar 2023.

Routine monitoring through repeated measurements of matrix-matched reference materials (see below) allow users to detect shifts or malfunctions in device performance over time[22].

Finally, this paper also considers Limit of Detection (LOD) and Limit of Quantification (LOQ). LOD refers to the lowest concentration at which an element can be reliably detected, while LOQ refers to the lowest concentration at which it can be reliably quantified. Manufacturer-provided LODs are based on ideal conditions and specific to the mode, setting, and material used[23]. In particular, measurement time strongly influences LOD, as detection limits decrease with the square root of increased acquisition time – longer measurements result in lower LOD and, consequently, LOQ[24]. Additionally, LOD in pXRF varies between samples due to differences in composition and geometry, which affect the intensity of X-rays received by the detector[25]. Manufacturer-provided LODs are therefore rarely directly applicable to archaeological matrices but may serve as rough references even if these values are lower than the actual LOD[26]. Following established practices in pXRF literature[27], LOD and LOQ can be calculated empirically from the standard deviation (i.e. measurement uncertainty or error values provided by the device) based on repeated measurements at the same spot on matrix-specific standards in order to capture random statistical variation. The standards used differ depending on material type and should contain no to very low concentrations of the elements in question[28]. More advanced LOQ estimation methods require raw spectral access or data derived from calibration/correction procedures and are therefore beyond the scope of this paper[29].

Device monitoring through precision

Precision is defined as the agreement of test results obtained under stipulated conditions and therefore refers to the variability between replicate measurements. Repeatability describes the condition where all variables of a measurement remain constant[30]. In pXRF analysis, this is addressed by repeated measurements of the same sample under identical conditions[31] and is used to evaluate pXRF devices in regard to short-term or within-run precision, also known as s-drift. This drift monitoring captures temporary fluctuations in instrument sensitivity during a single session, typically over several hours[32]. Reproducibility, by contrast, refers to the consistency of results when measurement conditions vary, such as time, operator, or location[33]. In pXRF applications, reproducibility is monitored as long-term precision, or l-drift, which captures gradual changes in device performance

22. Markovicz 2008; Drake, Mayer, Shugar 2023.
23. For the settings used in this study, no manufacturer-provided LODs were available. However, the supplier provided a guide for manually calculating LODs from the calibration spectra specific to the device and mode used. The author followed this guide, applying the ASTM E2926 standard to generate the values (ASTM International – E30.01 Committee 2017), and is grateful to Josef Schuller and Dr. Kathrin Schneider for their support and guidance.
24. Stapfer *et al.* 2019.
25. Bevins *et al.* 2022.
26. Da Silva, Triantafyllou, Delmelle 2023.
27. Seyfarth 2023.
28. Stapfer *et al.* 2019.
29. Goren, Mommsen, Klinger 2011; Da Silva, Triantafyllou, Delmelle 2023.
30. EPA 2007; Pollard, Heron, Armitage 2017; ISO 5725-1:2023.
31. Frahm 2014; Pollard, Heron, Armitage 2017; ISO 5725-1:2023.
32. Johnson 2014.
33. Frahm 2014; Pollard, Heron, Armitage 2017; ISO 5725-1:2023.

over time. In practice, both s-drift and l-drift are assessed by repeatedly measuring the same standard sample[34].

pXRF application guidelines recommend the use of Standard Reference Materials (SRMs) or Site-Specific Calibration Standards (SSCSs) to monitor instrument stability[35]. These standards (or monitors) should be matrix-matched, meaning if different materials or measurement modes are used, standards must be selected accordingly. Routine monitoring typically includes measuring at least one standard per day[36]. Recommendations vary, suggesting three[37] to seven[38], or at least one measurement of the selected standard at the beginning and end of each session[39], and after interruptions (battery changes, device restarts etc.)[40]. Some protocols further recommend analysis of SSCSs in seven replicates every three to five days[41].

The results of these replicate measurements should be compared to previously acquired data from the same standard, using the same instrument and settings[42]. Precision is then expressed statistically using the Relative Standard Deviation (RSD) or its equivalent, the Coefficient of Variation (CV)[43]. This metric reflects the spread of measurements around the mean and captures random error specific to the instrument, configuration, and measurement conditions[44].

Sample and element precision in this paper

The non-destructive analysis of archaeological artefacts, particularly on freshly exposed surfaces such as pottery breaks, is highly susceptible to sample heterogeneity. Variations in particle size, mineral composition, density, and chemical makeup can cause matrix effects, including elemental enhancement, absorption, and spectral interferences[45]. These effects introduce significant measurement variability. Therefore, repeated measurements at different, non-overlapping positions on the same sample are recommended to create an empirical estimate of intra-sample variability[46]. While the number of required replicates can be determined statistically[47], three repeated measurements are commonly considered sufficient in pXRF studies of archaeological materials. Sample-level precision,

34. Johnson 2014.
35. In regard to archaeological artefacts, the author is not aware of specific, official pXRF related DQA standards. Yet, for the pXRF analysis of contaminated soils a variety of standards do exist (Ge *et al.* 2005; EPA 2007; ISO 13196:2013; MENZ 2024).
36. Ge *et al.* 2005; EPA 2007; MENZ 2024.
37. Ge *et al.* 2005.
38. EPA 2007.
39. Ge *et al.* 2005; EPA 2007; MENZ 2024.
40. MENZ 2024.
41. Ge *et al.* 2005.
42. Markovicz 2008; Ramsey 2008; Frahm 2014; Johnson 2014; Frahm 2024; MENZ 2024. To support CV interpretation, instrument blanks, ideally containing only non-detectable elements, should be measured to check for contamination of the measurement window (Markovicz 2008; MENZ 2024) or lab-induced interferences as well as to define LOD/LOQ. Commonly pure silicon dioxide or quartz (Markovicz 2008; EPA 2007) as well as plastic blocks are used. Protocols recommend measuring the blank multiple times but at least at the start and end of each session (Ge *et al.* 2005; EPA 2007; MENZ 2024). However, this can pose practical issues, as devices interrupt the measurement if the response is insufficient.
43. Pollard, Heron, Armitage 2017; ISO 5725-1:2023; Jenner 1996.
44. Pollard, Heron, Armitage 2017; Frahm 2024.
45. Markovicz 2008.
46. EPA 2007; Drake, Mayer, Shugar 2023.
47. Markovicz 2008.

defined as the degree of agreement between these replicate measurements, is quantified using the CV with lower CVs indicating more consistent results[48].

In addition element-level precision must be considered. This is influenced primarily by the matrix, i.e. the elemental composition of the sample, but also by elemental concentration. Precision tends to decrease as concentrations approach the LOD with the LOQ being the relevant criterion to define precisely measured elements. For this reason, CV, LOD and LOQ are used in this paper to evaluate the reliability of elements in a specific dataset[49].

Accuracy in this paper

Accuracy is defined as trueness, meaning the closeness of agreement between the mean of repeated measurements and known or accepted Reference Values (aRVs)[50]. While norms and guidelines acknowledge that laboratory-based analyses also face limits regarding precision and accuracy, these methods are typically used to establish aRVs for calibration and coefficient correction procedures[51]. SRMs or SSCSs (see above) are commonly used for this purpose: they must represent the chemical range of the material or site in question[52], and a reference set typically includes 10 to 30 well-characterised samples. In some cases, spiked materials or pure element standards are employed[53].

Accuracy is generally assessed using linear regression analysis, where Pearson correlation coefficient (r^2), slope, and intercept quantify the agreement between measured values and aRVs[54]. Once established, calibration or correction coefficients can be applied across studies and datasets that meet the same criteria, such as same matrix, sample preparation, measurement protocol, and elemental concentrations falling within the concentration range. It cannot be overstated that creating high quality calibrations/corrections is essential when working with analytical data, particularly to ensure that values used for archaeological interpretation are reliable. Moreover, measuring shared calibration/correction standards is key to enabling comparability across devices and studies, avoiding isolated, siloed analyses. Yet, at the same time, qualitative approaches also exist, where internal data consistency (e.g. precision) is prioritised, and accuracy is of secondary importance[55].

Developing a calibration/coefficient correction takes time and cannot be part of an every-day routine. Established methods for their development are already widely published and are therefore not addressed here[56]. Instead, this paper focuses on routine device monitoring to ensure consistent performance within a given project. For this purpose, accuracy is benchmarked through Control Limits (CL), which are calculated from repeated measurements of SRMs or SSCSs used throughout

48. EPA 2007.
49. Daszkiewicz, Schneider 2020; Quinn 2022.
50. Markovicz 2008; Frahm 2014; ISO 5725-1:2023. It has to be stressed that no method can provide an absolute true value of an analyte. Therefore the term accepted Reference Value (aRV) is used for this paper.
51. Markovicz 2008; MENZ 2024.
52. Ge *et al.* 2005; EPA 2007; Abdel-Fatah 2010; MENZ 2024.
53. EPA 2007; Abdelgawad *et al.*; Wilke in this volume.
54. EPA 2007; Markovicz 2008; MENZ 2024.
55. Frahm 2013; Speakman, Shackley 2013; Drake, MacDonald (eds.) 2023; Frahm 2024; Abdelgawad *et al.*; Richards, McAlister in this volume.
56. See e.g. Markovicz 2008; Ramsey 2008; Speakman, Shackley 2013; Frahm 2014; Pollard, Heron, Armitage 2017; Eslami, Wicke, Rajabi 2020; Bliujiene *et al.* 2023; Drake, MacDonald (eds.) 2023; Frahm 2024; Schauer *et al.* 2024; Hnila *et al.* 2025; Abdelgawad *et al.*; Richards, McAlister; Wilke in this volume.

a study[57]. Following existing guidelines, additionally the Percent Relative Difference (%RD) is monitored[58].

Practical application

The following outlines a DQA strategy to evaluate element and sample precision as well as daily device performance based on analytical data focusing on Steps 1 and 2 of the TDQM cycle (see above). Following a fit-for-purpose philosophy, it is designed to be time efficient. The workflow including all relevant calculations and examples are provided as accompanying R-Script[59]. The example data was collected using the Bruker Tracer 5g (serial no. 900G6390) of the Vienna Institute for Archaeological Science, operating in MudrockDual mode (Major (15kV/27.9µA, no filter): 60s; Trace (40kV/38.85µA, Ti 25µm/Al 300µm): 60s) with an 8 mm collimator[60]. The device is equipped with a 20 mm² silicon drift detector (SDD) and a graphene window, providing an energy resolution of <140eV at 250.000 cps (measured at MnKα). Measurements were conducted between 26 February and 14 May 2025 (30–45% rel.hum.; 20–27 °C), as part of the FWF ESPRIT Project 476[61]. The dataset includes pottery samples from the collection of the project and reference standards supplied by the manufacturer. Where the device output reported "< LOD", "0.0000001" was used to enable downstream analysis.

LOD and LOQ for element precision

To assess element precision, the workflow presented here follows established procedures for empirical LOD and LOQ estimation: the former is calculated as 3*SD[62], the latter as 3.3*LOD. For this purpose, SRMs or SCCSs should be selected to include no to low concentrations of relevant elements using blanks or spiked samples (see above) as well as matrix-matched standards[63]. Elements for which most values fall below LOD or respectively LOQ are flagged as unsuitable for quantitative

57. Ge *et al.* 2005; EPA 2007.
58. EPA 2007.
59. Schauer 2026.
60. It should be noted that the author is aware of the limitations of this measurement mode (Hunt, Speakman 2015). However, the procedure proposed here focuses on precision, and in this regard as demonstrated in this paper, device and mode perform reliably.
61. For workflow and example see Schauer 2026.
62. The SD referenced here is the 1δSD (MeanSD), calculated as the mean of the individual standard deviations (e.g., in the example below the three SDmeans) from each standard used in the LOD calculation. To ensure the empirical LOD is not underestimated, the 3δSD reported by the device is used as the basis, providing a conservative and statistically robust threshold (see Schauer 2026).
63. EPA 2007; Georgakopoulou *et al.* 2017; Stapfer *et al.* 2019; Quinn 2022; Seyfarth 2023. The choice of standards is critical for reliable LOD determination. In the example below, the LOD for Si is unexpectedly high (see Schauer 2026) due to the use of a pure SiO_2 standard, which contributes not only the characteristic peak but also substantial background noise. A different result would emerge using, for example, a pure aluminum standard. Also, more generally, LODs should follow a predictable trend relative to atomic number (Z), with lower LODs for higher-Z elements and higher LODs for lighter elements. This relationship should form a smooth curve without abrupt deviations. When irregularities occur, such as the unusual LODs in the example below for Fe and Ni with the later being lower than the former (see Schauer 2026), they must be investigated. In this case, these abnormalities are likely caused by the use of compositionally complex reference material with high values of specific elements far from the actual LOD. This underscores the importance of using spiked or single-element standards for LOD benchmarking.

interpretation of the given dataset and measurement setting[64]. This is particularly important for trace elements, which occur naturally in minimal concentrations[65]. That said, elements frequently falling below detection or quantification thresholds can still yield valuable insights: while most samples may show concentrations below LOD, a few may present detectable or even elevated concentrations, which can be archaeologically significant. However, before using such elements for interpretation, potential calibration errors or device malfunctions must be ruled out as well. Even if only usable qualitatively, all elements should be reviewed as part of the interpretive process.

For the example for empirical LOD/LOQ estimation three reference standards for silicon-rich matrices, commonly used in pXRF soil-mode calibrations for ceramic materials are employed: two matrix-matched standards (Bruker MudrockStandard/SRM SdAR-M2[66]) and one blank (SRM pure SiO_2)[67]. Step-by-step guidance for these calculations is available[68]. In the example pottery dataset, LOD and LOQ thresholds were applied to assess element suitability for interpretation. Elements with more than 20% of individual values falling below the LOD (as presented by the device)[69] are excluded, as insufficiently detectable data undermines data reliability: Co and Ba exceed this threshold by far and were therefore flagged as unsuitable for further statistical analysis (**fig. 1a**). Elements close to the threshold, such as P, require additional scrutiny. Using LOQ with the same threshold definition (≤20%), further refined element selection for this specific example: Ba, Co, Mo, Nb, U, Cr, V, As, P, Pb, Mg, Cu and S are excluded from quantitative interpretation due to benchmark violation (**fig. 1b**)[70]. Eliminating such elements reduces the risk of misclassification and strengthens the robustness of archaeological interpretations. In the case of Y, being close to the benchmark, more analysis is sensible (see above).

CV for element and sample precision

The CV is used in this approach to assess both intra-sample and element-level precision. It quantifies the relative spread of replicate measurements and is calculated as:

$$CV = \frac{SD}{Mean} * 100$$ [71]

- for each element across repeated measurements at different positions on the same sample and;
- as a mean CV across all samples in the dataset for each element individually.

64. Bevins *et al.* 2022.
65. EPA 2007.
66. International Association of Geoanalysts 2017.
67. Three standards were used to define LOD/LOQ in previous studies, in some pottery case studies, they were calculated using selected, representative sherds from the specific site (Stapfer *et al.* 2019).
68 Schauer 2026.
69. The measurement uncertainty is specific to an individual measurement, depends on the SD derived from counting statistics and is used to define its precision in regard to unsystematic or statistical error. In pXRF studies, this value is typically reported as a confidence interval of 2δ, corresponding to a certainty interval of 95.4% (Frahm 2024).
70. It is important to note that not all elements reported by the algorithm are truly present at meaningful levels. In many cases, as evident in the example presented here, elements such as Mg appear only as minimal peaks when the spectrum is reviewed (see Schauer 2026). In the author's view, such elements should be treated with caution when interpreting analytical data.
71. EPA 2007; Markovicz 2008; Rouillon, Taylor 2016; Frahm 2024.

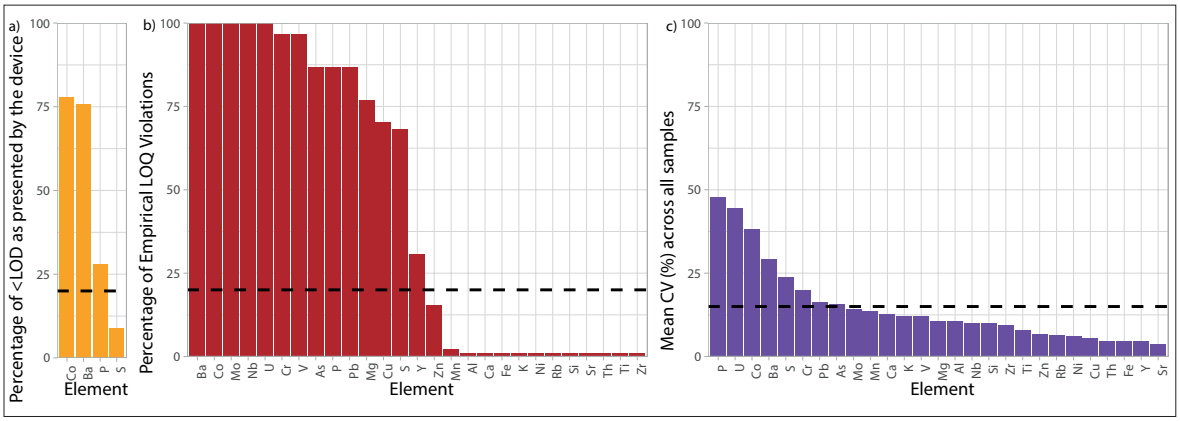


Figure 1: Example of LOD (**a**), LOQ (**b**) and CV (**c**) monitoring charts for element precision

In regard to element precision, pXRF benchmarks are generally set at CV≤20% for highly heterogeneous materials (pottery, stone, etc.) or *in situ* soil measurements[72] with a CV≤15–20% being acceptable by most studies[73], even if for some pottery studies a CV≤5% is recommended when internal patterning is the focus[74]. CV≤10% is proposed for more homogenous matrixes (obsidian, homogenised powders, etc.)[75].

In this workflow the element precision benchmark is defined at CV≤15%[76]. This threshold applies across the entire dataset, e.g. it represents the mean of all sample-specific CVs. At the sample level, no more than 20% of the reliably detected elements in a single sample may exceed the predefined, material-dependent CV threshold[77]. If this condition is violated, additional measurements must be taken and/or the individual measurement contributing most to the variation be excluded[78]. During data interpretation, it must be verified whether the elements relevant for group discrimination in each sample are measured with sufficient precision.

Revisiting the example, following the mean CV per element, P, U, Co, Ba, S and Cr violate the benchmark (**fig. 1c**). For Pb, As and Mo, the closeness to the benchmark needs revisiting the monitoring results of LOD/LOQ which, all together, make very clear that those elements also cannot be reliably used for interpretation of this dataset. Yet, in the case of Y, this element shows low CV and comparably few LOD violations and is therefore included. So, for this dataset, this leaves Si, Ti, Al, Fe, Mn, Ca, K, Ni, Zn, Rb, Sr, Y, Zr and Th as reliable, precisely defined elements for data analysis.

In the example dataset, most samples meet the 15% CV benchmark for most elements, with fewer than 20% of element values per sample exceeding the threshold. However, six samples violate

72. EPA 2007; Helfert 2013; Bevins *et al.* 2022.
73. EPA 2007; Helfert 2013; Wilke, Rauch, Rauch 2016; Daszkiewicz, Schneider 2020; Bevins *et al.* 2022; Quinn 2022.
74. Bishop *et al.* 1990; Georgakopoulou *et al.* 2017.
75. EPA 2007. The CV can also be used to characterise chemical groups (Biagetti *et al.* 2021; Wilke, Rauch, Rauch 2016).
76. It hast to be noted that, more nuanced CV thresholds should be developed that account for concentration levels, where higher concentrations warrant stricter criteria. However, to the author's knowledge, empirically defined, matrix-specific concentration-dependent CV benchmarks rarely exist for archaeological materials (Stapfer *et al.* 2019; Daszkiewicz, Schneider 2020). This highlights the need for further research, ideally drawing on established practices in analytical chemistry to develop suitable thresholds for pXRF in cultural heritage contexts.
77. For workflow and example see Schauer 2026.
78. Stapfer *et al.* 2019; Daszkiewicz, Schneider 2020; Quinn 2022.

this criterion and require re-measuring. For TP_67a, one measurement (File 3583) clearly differs from the other two[79]. In this case, one additional measurement should confirm the deviation, and if consistent, the outlier can be excluded. For TP_59a, where all three measurements are relatively close but still altogether exceed the CV threshold, a fourth replicate will likely stabilise the result. More complex cases occur when all three measurements diverge significantly. Here, at least two new measurements are necessary to identify and exclude the outlier(s) with confidence.

Monitoring pXRF device performance

Shewhart Control Charts (SCCs) are recommended in the literature to monitor device performance in terms of value consistency[80]. They allow visualising short-term (s-drift) and long-term variation (l-drift; see above) by plotting repeated measurements of the same standard in chronological order. Horizontal lines mark the mean (M, Control Limit (CL)[81] or nominal value[82]) with ±2δSD-lines defining Upper (2UCL) and Lower Control Limits (2LCL). If the reported values are within ±2δSD, the instrument is performing well; if they are consistently higher or lower, this may indicate a problem with the instrument, mode or reference material. Device, standard(s), and procedure should be reviewed if:

– Four consecutive values exceed ±1δSD;
– two exceed ±2δSD;
– one exceeds ±3δSD.

Mean and SD can be represented by matrix-matched aRVs or be obtained from repeated pXRF measurements of a standard[83]. Some protocols mention 30 measurements of a matrix-matched SSCS or SRM to create the SCCs[84], pXRF manufacturers require only 10 arrays[85].

This paper proposes to establish SCCs from at least 10 measurements on matrix-matched SRMs/SCCs using the same settings as employed in the respective study without moving the standard to catch the statistical random error. To establish UCL and LCL, only M and SD are required. For transparency, reporting median (MD), CV, Standard Error of the Mean (SEM), and measurement uncertainty (error) statistics (M, MD, SD) are recommended (**Table 1**)[86]. Literature[87] and empirical data support establishing 2UCL/2LCL at ±2δSD, with devices often performing consistently enough to even meet UCL/LCL at ±1δSD (**fig. 2**). Though rarely published, sharing SCCs data would enhance the understanding of device performance[88].

79. Schauer 2026.
80. Barreiros *et al.* 2001; Piercey 2014; Guthrie 2020; ISO 7870-2:2023.
81. Piercey 2014; Guthrie 2020; ISO 7870-2:2023.
82. Analyticon 2015.
83. Piercey 2014; Guthrie 2020; ISO 7870-2:2023.
84. Ge *et al.* 2005.
85. Analyticon 2015.
86. For workflow and example, see Schauer 2026.
87. Piercey 2014. Others also accept ±3δSD as quality benchmark (Guthrie 2020; ISO 7870-2:2023).
88. Eslami, Wicke, Rajabi 2020. Experience shows that CLs often need to be defined locally, as environmental conditions can influence device sensitivity. This is especially important in field projects with tight time constraints, where this procedure must be factored into planning.

Element	M	SD	SEM	CV	LCL	UCL	CV2	LCL2	UCL2	CV3	LCL3	UCL3	MD
Ti	1377	59	19	4.3	1318	1436	8.6	1259	1495	12.9	1200	1554	1363
Mn	917	25	8	2.7	892	942	5.5	867	967	8.2	842	992	912
Ca	6787	197	62	2.9	6590	6984	5.8	6393	7181	8.7	6196	7378	6832
Zn	902	20	6	2.2	882	922	4.4	863	942	6.6	843	961	900
Rb	154	4	1	2.4	150	158	4.9	147	162	7.3	143	165	156
Zr	221	8	3	3.6	213	229	7.2	205	237	10.9	197	245	219

Element	MU_M	MU_SD	MU_MD	Empirical_LOD	Manufacturer_LOD	Empirical_LOQ
Ti	22	0	22	93	8	307
Mn	12	0	12	42	8	139
Ca	47	1	47	138	13	455
Zn	8	0	8	18	2	59
Rb	2	0	2	9	1	30
Zr	3	0	3	9	2	30

Values in ppm/CV in %	CV/LCL/UCL=1δSD	CV2/LCL2/UCL2=2δSD	CV3/LCL3/UCL3=3δSD
CV= Coefficient of Variation	LCL=Lower Control Limit	UCL=Upper Control Limit	LOD=Limit of Detection
M=Mean (CL)	SD=Standard Deviation	SEM=Standard Error of the Mean	
MD=Median	MU=Measurement Uncertainty (2δSD)		LOQ=Limit of Quantification

Table 1: Example documentation of Control Limits

Following the procedure to monitor CLs, manufacturers recommend measuring the respective standard three times at the start of each session to verify that the mean falls within the designated test range[89]. To streamline routine checks, a set of elements should be selected based on the measurement mode, the matrix analysed and/or the specific elements targeted in the session[90], and the standard used. The selected elements should also adhere to these additional criteria: broad coverage of excitation energies, minimal peak overlaps and interferences, reliable detection (CV ≤ 10% (1δSD)[91]), and concentrations in the standard that meet or exceed the manufacturer LOQ, if possible the empirical LOQ (see above). They should also be practical to monitor as very different concentrations may be difficult to interpret due to device screen limitations or rounding. For example, using a geochemical setup such as Bruker's MudrockDual with the soil standard SdAR-M2, for efficient data checking and when working with pottery, suitable elements include the light elements Mn, Ti, and Ca (Major), and the trace elements Rb, Zn, and Zr (Trace; Table 1).

The evaluation procedure itself is brief: pXRF instruments can automatically report the mean, allowing a swift comparison of the values of the selected elements on the device screen with (2)LCL/(2)UCL-boundaries. In cases where values for more than 1/3 of the elements monitored fail the

89. Ge *et al.* 2005. Some pXRF studies mention comparable, yet slightly different approaches: see e.g. Eslami, Wicke, Rajabi 2020; Bliujiene *et al.* 2023; Hnila *et al.* 2025.
90. Analyticon 2015.
91. Mommsen, Maran 2000–2001.

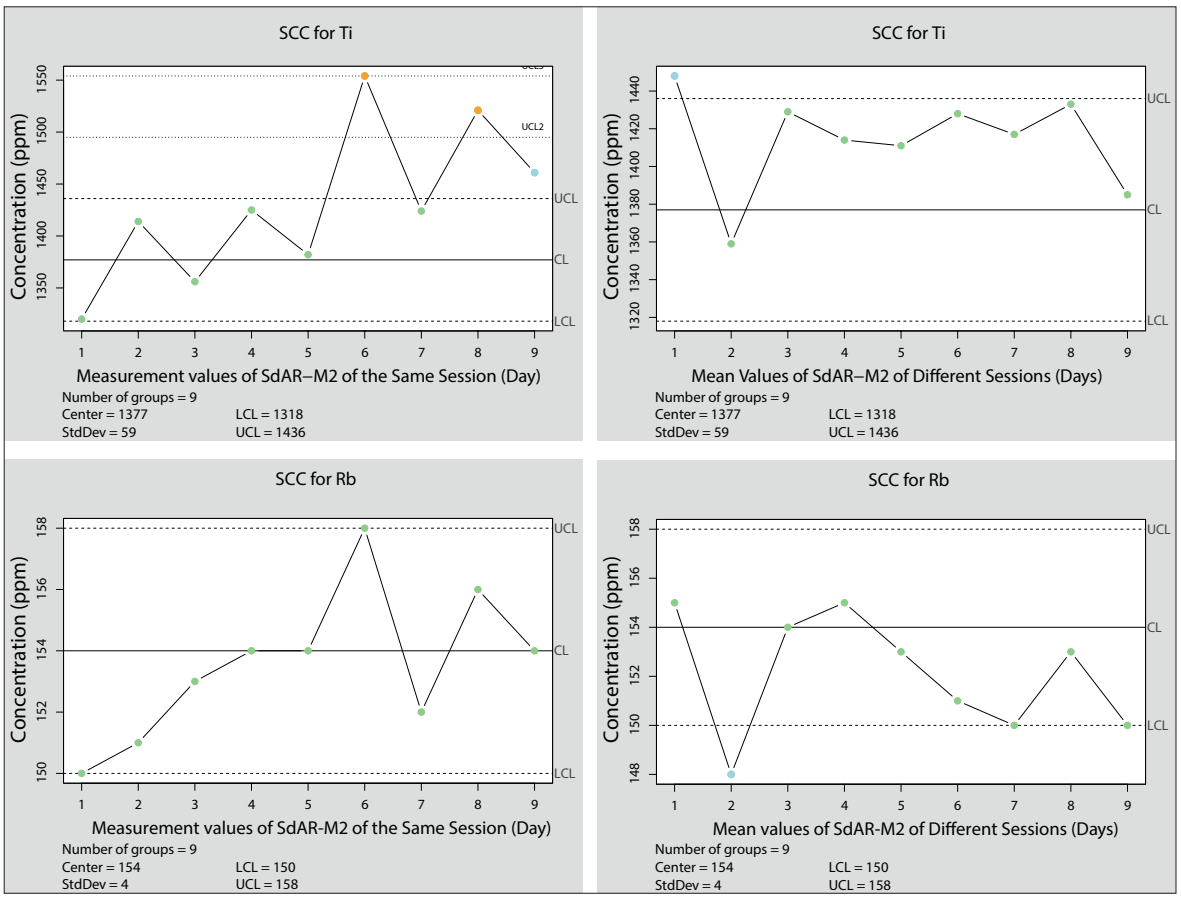


Figure 2: Examples of SCCs to monitor s-(left) and l-drift (right) showing drift-effects are minor for the example data[92]

criterion, additional measurement should be taken. While the procedure outlined can be repeated during the session, it must strictly be conducted before unknown samples are analysed and the SCCs must be updated and checked daily (fig. 2).

Additionally, pXRF literature recommends using the Percent Relative Difference (%RD) to assess systematic error by comparing the mean CL (CL_{mean}) to the mean of repeated pXRF measurements ($V_{observed}$) from the same standard using the formula:

$$\%RD = \frac{(V_{observed} - CL_{mean})}{CL_{mean}} * 100$$ [93]

While pXRF guidelines require %RD to be below 20%[94] the author recommends using higher standards with %RD<3% being defined as excellent, 3–7% very good, 7–10% good, and >10% as

92. For workflow and example see SCHAUER 2026.
93. EPA 2007; PIERCEY 2014; FRAHM 2024.
94. EPA 2007.

%RD	Si	Ti	Al	Fe	Mn	Mg	Ca	K	P	S	V	Cr	Ni
Mean (ppm)	245940	1377	48028	19130	917	2628	6787	35575	247	2098	68	44	50
Empirical LOD (ppm)	3657	93	2403	195	42	4293	138	435	231	195	48	30	12
03/20/2025	4	5	2	0	1	19	1	2	-9	0	5	-4	1
04/02/2025	-4	-1	-6	-2	-4	20	-4	-5	-13	-6	4	5	-1
04/03/2025	2	4	1	-1	0	22	0	1	-18	-1	7	-2	1
04/04/2025	2	3	0	0	0	-4	0	1	-14	-2	1	-18	-1
04/11/2025	3	2	2	-1	0	-6	0	1	-12	-3	-5	-9	3
05/05/2025	4	4	4	-2	-1	12	0	1	-1	0	1	-11	-3
05/06/2025	-1	3	-3	-2	-3	16	-3	-2	-23	-5	1	-18	3
05/08/2025	0	4	-1	-1	-1	22	-2	-1	-5	-3	2	-11	1
05/14/2025	-4	1	-5	0	-2	21	-4	-4	-29	-3	7	-13	-1

%RD	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Mo	Ba	Pb	Th	U
Mean (ppm)	287	902	412	154	152	54	221	21	24	1526	460	18	5
Empirical LOD (ppm)	15	18	12	9	9	9	9	9	9	657	15	3	24
03/20/2025	-2	-1	-1	1	0	-1	1	-1	3	-5	1	-4	-57
04/02/2025	2	3	0	-4	0	-3	-11	3	-5	-5	-5	-4	-13
04/03/2025	0	0	0	0	0	1	-1	3	-1	-2	0	2	-13
04/04/2025	0	1	0	1	0	1	-6	3	-5	-10	1	2	9
04/11/2025	1	0	0	-1	0	1	-2	3	-1	-5	0	2	-13
05/05/2025	-1	0	-1	-2	0	-1	-4	-1	-5	-3	-2	-4	-13
05/06/2025	0	0	0	-3	0	1	-4	3	-1	-5	-2	2	-57
05/08/2025	0	1	-1	-1	0	1	-4	3	-1	-3	-1	2	-78
05/14/2025	0	1	-1	-3	0	-1	-5	-1	-5	-3	-3	-4	-100

-3% ≤ %RD ≤ 3%	3% < %RD ≤ 7% -7% ≤ %RD < -3%	7% < %RD ≤ 10% -10% ≤ %RD < -7%	10% < %RD %RD < -10%

Empirical LOD= Empirical Limit of Detection defined for a specific device, measurement mode and matrix
Mean= Mean of Control Limits calculated for SdAR-M2

Table 2: Example documentation of %RD supporting I-drift monitoring

insufficiently accurate (**Table 2**[95]). Yet, %RD should be interpreted with caution. As shown in the example dataset, elements such as P or U, whose concentrations lie close to or below the empirical LOD, as well as elements like Cr or Mg, which are present in low concentrations or are affected by methodological limitations, naturally yield higher %RD. If these elements are essential for a study,

95. JENNER 1996; PIERCEY 2014.

a different matrix-matched standard with higher concentrations of these elements or spiked samples should be used[96].

Conclusion

The proposed DQA procedure supports internal quality control in everyday pXRF use by:

1. Identifying elements with high measurement uncertainty though LOD, LOQ and CV monitoring);
2. detecting non-representatively measured samples with too high internal variability through CV
3. enabling routine device monitoring of short- and long-term drift effects through SCCs and %RD.

Once control limits are defined, daily device monitoring becomes straightforward and should be conducted before analysing unknowns. Sample and measurement precision should be reviewed during or after each session to allow for re-measurement where necessary. While Excel is sufficient, the provided R script offers a faster and more efficient solution: with consistently formatted data, results can be processed within minutes.

Applying transparent procedures not only improves data quality but also strengthens our understanding of pXRF performance. The procedures outlined here are not new in principle, but they provide a structured foundation. Future research should focus on refining precision benchmarks, adapting methods to a wider range of materials, and encouraging routine implementation across the discipline.

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96. For workflow and example, see SCHAUER 2026. It is worth mentioning that for some elements, such as P and Zr, consistently negative values were observed, indicating reduced sensitivity during the monitored period without evidence of a systematic drift.

Data availability statement

The supplementary material for this chapter is available in Schauer (2026): "Device monitoring, sample and element precision for analytical data in hand-held pXRF studies: evaluation in R. Supplementary material to Schauer 2026", V1.0 at https://doi.org/10.5281/zenodo.18442146.

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Luisa Dallai, Roger Doonan, Vanessa Volpi

Innovation strategies and the use of hand-held portable X-ray fluorescence (HH-pXRF) in archaeological fieldwork

Abstract

Hand-held portable X-ray fluorescence (HH-pXRF) offers unprecedented access to chemical analysis and the potential to transform the way archaeological investigations are conducted. Its use in the field demands a thoughtful innovation strategy that addresses new questions or questions formerly unapproachable by conventional laboratory analysis. Rather than being a direct alternative to laboratory-based analyses, HH-pXRF promotes innovation in archaeological project design; previous studies demonstrate its diagnostic value in identifying archaeological features, as soil geochemistry reflects both anthropogenic activity and natural influences.

Using case studies, this paper highlights the importance of site-landscape specific methodologies that are sensitive to geological conditions, archaeological questions, and project-specific constraints. We suggest that strategies should be flexible, to accomplish a considerable range of possible archaeological applications, especially those that are field-based.

Selected examples will focus on a vast territory in southern Tuscany (Italy) that, since 2009, hosted a number of multidisciplinary research activities, aiming to develop a flexible toolkit design to aid archaeological research. Between 2017 and 2018, as part of the ERC project nEU-Med, a substantial set of more than 12000 HH-pXRF analyses was carried out in the Cornia and Pecora coastal plains, covering an area of approximately 350 hectares, as well as on inland hills with long-term mining activities. HH-pXRF results were analysed in combination with geomorphological data and the archaeological record, to support a diachronic reconstruction of the historical landscape.

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Keywords

HH-pXRF, soil chemistry, landscape archaeology, multidisciplinarity

Introduction

The mapping of chemical element variability of soils across whole landscapes to prospect for archaeological sites is a long-established method in archaeology. Early analyses were performed almost 100 years ago, when phosphorus, mapped for agricultural purposes, was noted to correlate well with buried archaeological sites of all ages, and the variability of phosphate was used to reveal the presence of settlements[1]. After little uptake in wider archaeology, the 1970s saw a science-based approach to cultural systems in archaeological research that fostered a renewed interest in the geochemical analysis of soils[2]. While some studies looked again at using patterns of variability to prospect for sites[3], most interest was directed towards using geochemical analysis as a method to identify specific cultural activities by attributing the absolute concentration and combination of elements, including heavy metals such as Cu, Zn, Pb and other lighter elements such as P, Ca, and K[4]. Despite encouraging results, the approach was complicated by the challenge of equifinality, as Bintliff and Degryse highlight: "for every element potentially indicative of a particular form of human behaviour, multiple alternative causes have been claimed, some of which are not necessarily anthropogenic"[5].

Starting from the 1980s, the use of XRF within archaeology had a dramatic impact and an extensive use in soil analyses[6]. Today, thanks to technical improvements, a new generation of instrumentation is capable of producing an enormous number of analyses in a relatively short time. As a consequence, archaeologists have greater access to chemical data, once the domain of well-funded and furnished laboratories, and while analysis can be undertaken by a variety of practitioners with different degrees of competence, this growing availability increases the opportunity for inappropriate use.

Being aware of the scientific debate on reliability and internal consistency of HH-pXRF data that has accompanied its growing popularity[7], our paper will focus on the informative potential of the technique as part of a multidisciplinary toolkit for archaeological fieldwork. As other contributions in this volume will focus on precision, accuracy and reproducibility[8], we will comment in particular on the use of HH-pXRF on site, as an added value to archaeological project design and implementation. Field procedures, sampling strategies and survey resolution will be discussed and some space will be dedicated to data visualisation, the use of certified reference materials (CRMs) and external confirmatory testing. While discussing these different points, examples will be provided, intended as practical on-field deployments of each specific issue, suggesting guidelines for best practices in HH-pXRF analysis.

1. Arrhenius 1929.
2. Clarke 1973.
3. Craddock *et al.* 1985; Bartlett 1988.
4. Cook, Heizer 1965.
5. Bintliff, Degryse 2022, p. 6.
6. Frahm, Doonan 2013.
7. Speakman, Shackley 2013; Williams, Taylor, Orr 2020; Frahm 2024.
8. Richards, McAlister; Schauer in this volume.

Case studies

Case studies will drive us to the territorial context of southern Tuscany (central Italy), and particularly in the wide district of the so-called "Colline Metallifere" (i.e. the metal bearing hills) and to the coastal valleys of the Pecora and Cornia rivers (**fig. 1**). In this area since the mid-1980s, the University of Siena has developed several research projects, aimed at the diachronic study of the relationship between settlement patterns and the exploitation of environmental resources, in particular mining and metallurgical ones[9]. Between 2015 and 2020, the territory became the privileged research context of the ERC project nEU-Med (https://neu-med.unisi.it), which fostered a multidisciplinary investigation approach, and an extensive use of HH-pXRF geochemical analyses. On-site and laboratory-based geochemistry was coupled with traditional archaeological survey, geophysics, geoarchaeology and stratigraphic excavation, and results interpreted in the light of historical sources[10]. More than 12000 HH-pXRF soil analyses were performed with an Olympus INNOV-X Delta Premium DP-6000-C HH-XRF equipped with a 40kV 4W X-ray tube (200mA, Rh anode) and a large-area SSD detector. The instrument was used in the field set in "soil mode" (3-beam), which utilises Compton Normalisation for low concentrations (ppm to 3%) of elements in light matrices, detecting elements ranging from phosphorus (P) to uranium (U). Given the purposes of the research and the expected territorial coverage, the time for each measure was set at 30 seconds; this was considered a good compromise between accuracy and project objectives[11] (**fig. 2**). Results obtained were georeferenced on-site, with metric or centimetric GPS and managed through a designed data base. Geochemical maps generated in GIS environment (QGIS) proved to be extremely useful for identifying the anthropised context and describing geomorphological features.

Investigation included a multi-scale strategy from site-scale to territory. Samples were designed to answer a variety of historical questions, including functional characterisation of spaces within individual sites, identification of specific operational chains (i.e. analysis on mining/metallurgical contexts) and the reconstruction of geomorphological features of the historical landscape[12]. Relying on this consistent and multidisciplinary dataset, the Colline Metallifere territory can provide different practical examples of the implementation of HH-pXRF analysis in archaeological research.

Project design and implementation

The use of HH-pXRF for soil analysis in archaeological projects necessitates a shift in thinking. Taking the instruments into the field produces large-scale data acquisition and fosters a more nuanced understanding of the spatial distribution of elements across archaeological landscapes, something that was simply not possible at this scale with laboratory-based chemistry. It is then a fundamental principle in project design that there should be efforts made to maximise the number of samples taken, as HH-pXRF allows for the analysis of thousands, significantly increasing the

9. Dallai, Donati, Volpi 2018.
10. Bianchi, Hodges 2020.
11. Frahm 2024.
12. Dallai, Donati, Volpi 2018; Dallai, Volpi 2019; Dallai, Volpi 2022; Poggi, Volpi, Dallai 2025.

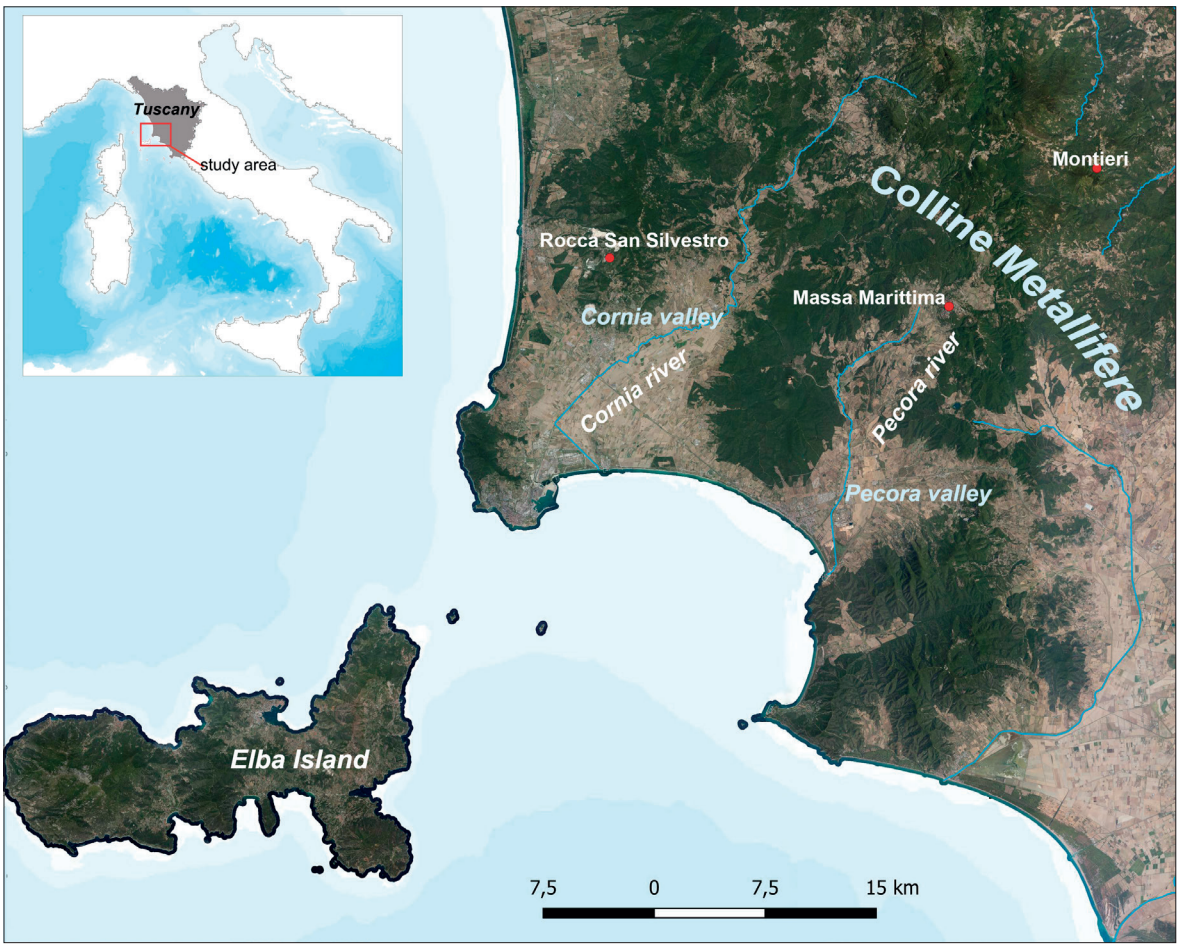


Figure 1: The Colline Metallifere study area in southern Tuscany (Italy), with toponyms cited in the text

resolution and/or coverage of geochemical surveys, and to allow flexibility so that strategy can be informed on the fly responding, to geochemical results and modifying its programme of enquiry[13].

However, prior to deployment in the field, any well-designed project has to undertake a comprehensive desk-based assessment of the study area that includes soil type and variability, both bedrock and superficial geology, recent land-use and the kind of archaeology anticipated from all periods. The analysis of published sources (i.e. in the UK the BGS publishes detailed maps of soil type variability – https://www.bgs.ac.uk/datasets/bgs-civils-strength; in Italy, the ISPRA provides geothematic maps that can be downloaded and managed in any GIS platform – http://portalesgi.isprambiente.it) can greatly contribute to assessing the baseline of soil variability. If a study area extends over different soil units, then the ability of geochemistry to distinguish anthropogenic deposits will be more challenging; likewise, the presence of mineralisation or modern contamination, as experienced in the

13. Boyd *et al*. 2021.

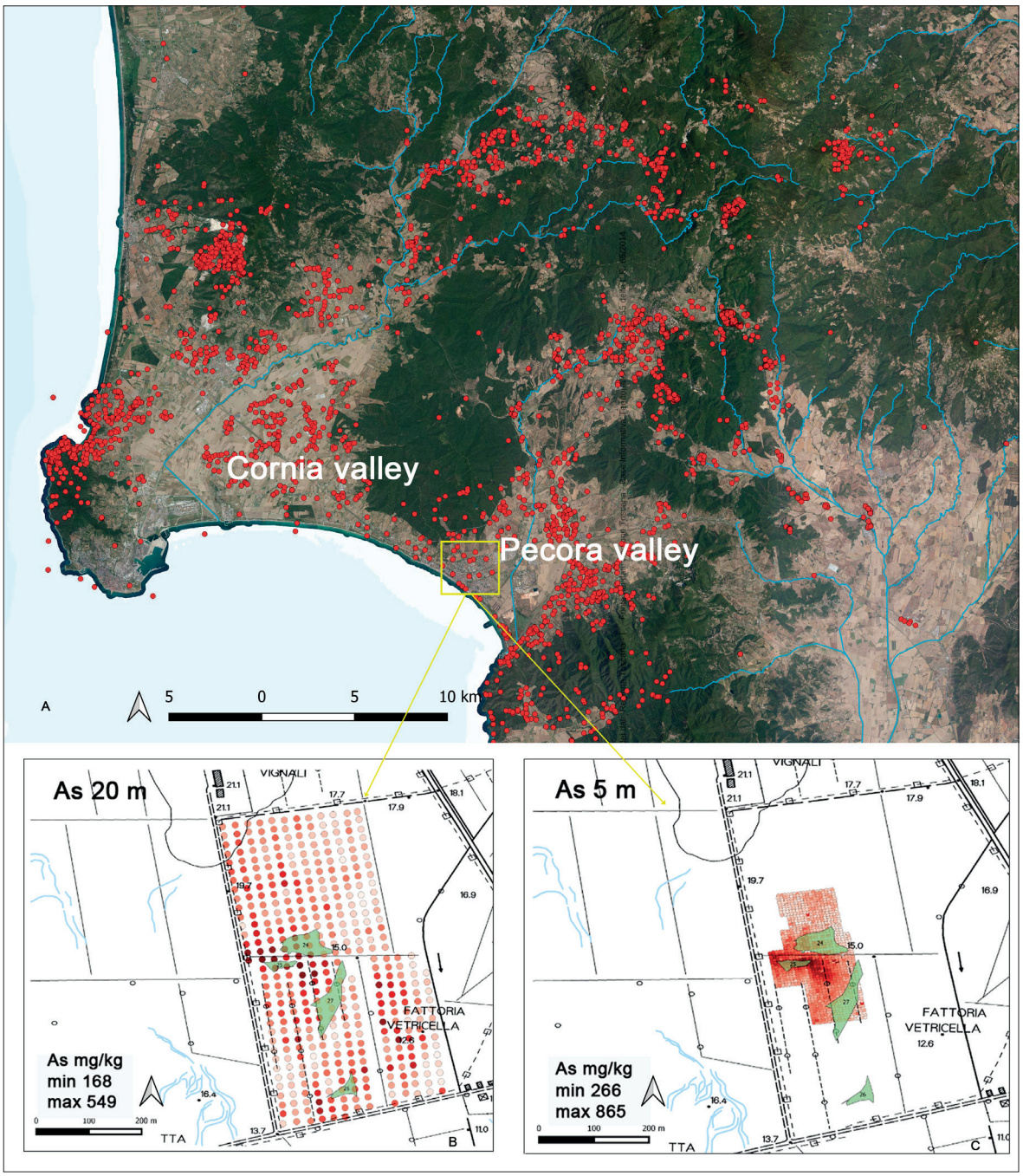


Figure 2: Territorial samples under investigation in Cornia and Pecora valleys in southern Tuscany (Italy): **A**. overview of the territorial context and archaeological database (red dots); **B**. Pecora valley: HH-pXRF results for As displayed on a 20 m sampling grid; **C**. HH-pXRF results on a 5 m sampling grid

Colline Metallifere district and in other ancient mining areas, are likely to complicate the analysis and interpretation of geochemical data sets[14].

In the lower Pecora valley, on-site HH-pXRF analysis was aimed at better characterising the environment in which settlement patterns developed over the centuries. Although a soil map was available from the National Geological service, the needs of the project required a more accurate reassessment to allow the identification of geochemical variations possibly related to geo-pedological features and/or human presence. The design of on-site research included a multidisciplinary survey that combined geochemical and archaeological fieldwork, covering an area of approximately 140 hectares; over 2800 HH-pXRF measurements were performed and georeferenced with a metric GPS. Survey was undertaken in the months of September and October, on dry tilled soil, in order to minimise the effect of moisture on chemical values[15]. Moreover, at this time of the year soils are not yet fertilised, and this reduces the interference when taking the readings of P, Ca, K and Mg[16]. The soil was particularly dry and hard, and measurements were taken directly on the surface, after removing a few centimetres with a trowel, as manual core drilling was not possible.

Chemical data were imported into QGIS to produce maps of the spatial distribution of the different elements and results were evaluated in combination with geomorphological analysis[17].

Measurements allowed us to obtain a detailed description of geochemical soil variability, fostering a comprehensive evaluation of environmental dynamics. In particular, the average reading for Ca, As, K, Mn and Fe, provided a "background" value, enabling a preliminary territorial classification; in addition, analysis was performed on a set of diagnostic elements potentially correlated to anthropic activities (Ca, As, K, Mn, Fe, Cu, Pb and Zn)[18]. Geochemical values allowed a very clear distinction between dry-sandy soils (Ca 4000 mg/kg; As 87 mg/kg; K 1.4%; Mn 977 mg/kg; Fe 3.2%) and clay soils (Fe 3.3%, Mn 1.600 mg/kg and K 1.5%), helping to define environments potentially suitable for settlements, such as alluvial fans and river terraces[19] (**fig. 3**).

A further screening of Ca distribution highlighted a promising area of investigation, where consistent Ca, Fe, Mn, As and K patterns partly overlapped the traces of an ancient river identified through aerial photos and geophysics; Ca in particular showed concentrations not referable to environmental dynamics. Trial excavations informed by geochemical data identified remains of limestone walls related to a Roman rural dwelling and a vast cemetery, partly damaged by plough soil activities, dating to early medieval period[20] (**fig. 4**). In sum: mapping the variability of specific geochemical proxies can be extremely useful in obtaining information about soil characteristics and geomorphological features in the area under investigation (e.g. Zr and Rb reflect grain-size changes; Ca is useful for identifying sedimentary inputs influenced by fluvial dynamics)[21]. Being aware of which are the key proxies that can be related to soil background, their variability becomes a powerful tool to unveil the environmental or anthropogenic origin of geochemical variations.

14. Minvielle Larousse *et al*. 2024.
15. Bastos, Melquiades, Biasi 2012.
16 Schneider *et al*. 2016.
17. Pieruccini *et al*. 2018.
18. Misarti, Finney, Maschner 2011; Oonk, Slomp, Huisman 2009; Cannell 2017; Cuenca García 2018; Carvalho *et al*. 2004.
19. Pieruccini, Susini 2020.
20. Dallai, Carli, Volpi 2020.
21. Poggi, Volpi, Dallai 2025; Dallai, Volpi 2022; Volpi *et al*. 2024.

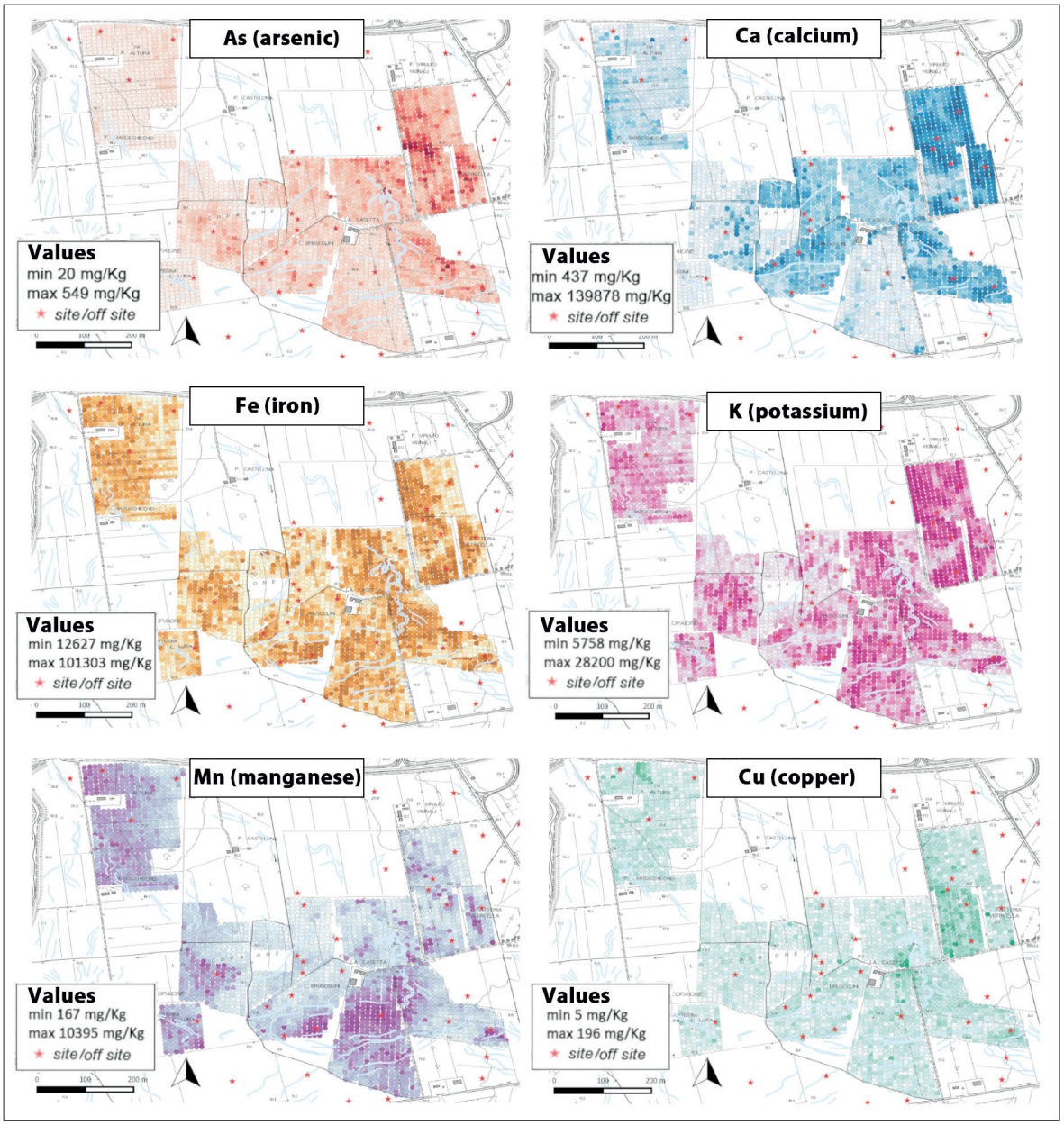


Figure 3: Pecora valley. HH-pXRF values for As, Ca, Fe, K, Mn and Cu design structured anomalies on the territorial samples selected by the ERC nEU-Med project

Field methods: samples, strategies and survey resolution

A critical aspect of sampling strategy that should be addressed when prospecting with HH-pXRF is whether to work on core samples or simply to analyse a prepared surface of topsoil. Early studies tended to use cored samples in the belief that these would provide better data, as the analysed sample was "nearer" to the archaeological horizon. However, subsequent studies have shown this assumption to be complex, as soil processes allow elements, such as phosphorus and heavy metals,

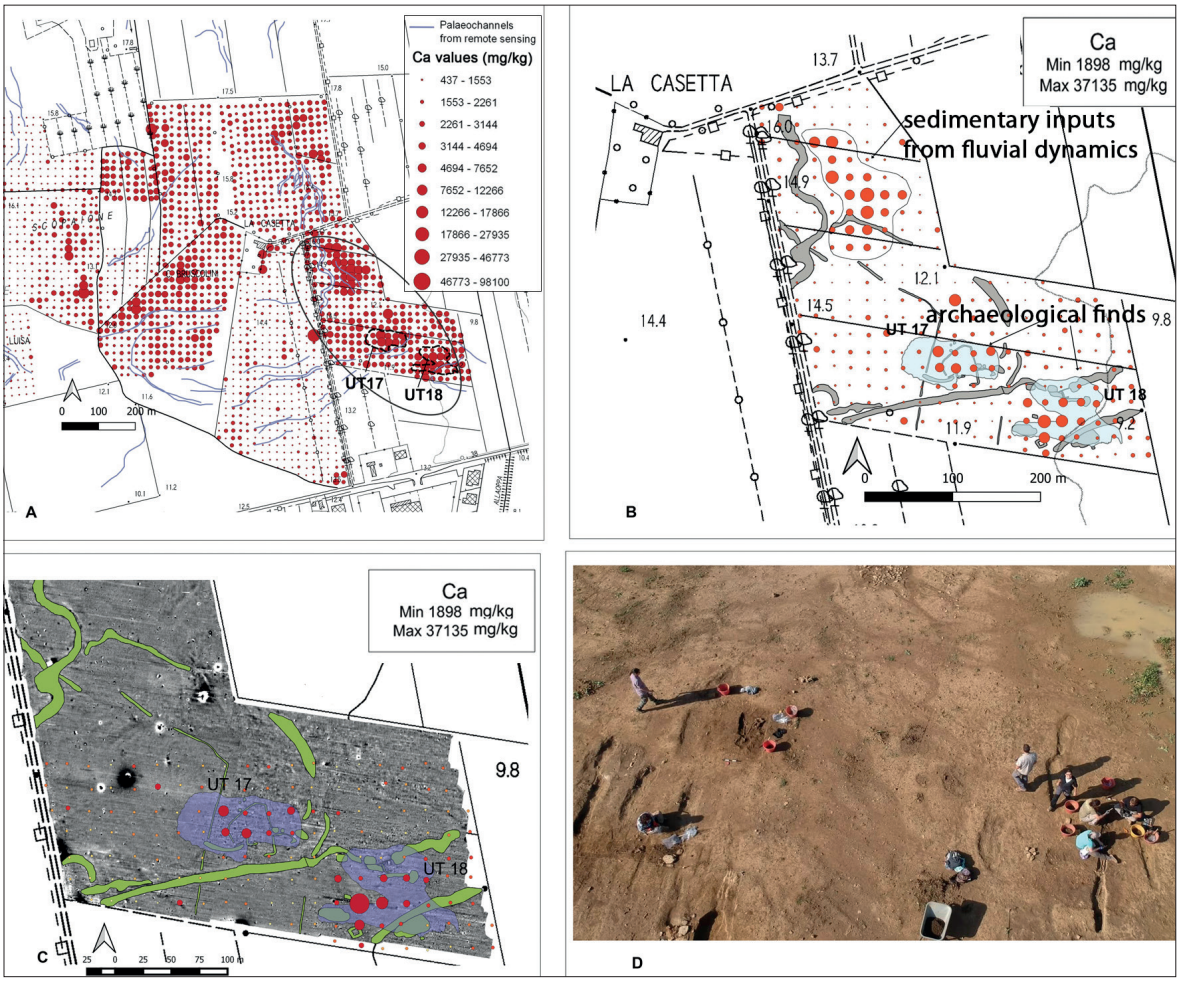


Figure 4: Pecora valley. **A**. Ca variability in the study area. **B**, **C**. Geochemistry (Ca patterns) and geophysics highlight elemental patterns related to environmental (palaeochannels) and anthropic features. **D**. Archaeological excavation identifing remains of a medieval cemetery (photo credits: University of Siena, DSSBC)

to be transported from buried horizons to the topsoil[22]. We can therefore assume that, while coring might in some instances provide results that show a better signal to noise ratio[23], HH-pXRF analyses still demonstrate the ability to provide archaeologically meaningful results based on the mapping of chemical variability derived from topsoil, as in the example of the Pecora valley. The key advantage is that topsoil analyses are minimally invasive and rapid, meaning that within any set budget, the number of analyses deployed on topsoil is likely to be three-fold greater than a technique that relies on cored samples, and resolutions can be either correspondingly higher or the extent of the survey to be greater[24].

22. Bintliff, Degryse 2022.
23. Cannell *et al*. 2020, Volpi *et al*. 2024.
24. Bourke, Ross 2016.

When dealing with an archaeological project that involves geochemical soil analysis, the sampling interval is a critical consideration and will directly impact the utility of the results[25].

Most project designs will rely on a systematic grid for sampling, be it for landscape survey or to interpret the use of space on exposed archaeological surfaces[26]. Moreover, field strategy must take into consideration the management of a substantial daily geochemical analysis data set, designed to be statistically reliable and useful at both descriptive and predictive levels. Choosing an appropriate sampling interval is paramount and should be informed by a number of considerations, namely:

– The specific research question;
– the types and extent of activities expected;
– the anticipated spatial scale of the chemical signatures related to those activities.

Coarse sampling grids offer the ability to cover large areas rapidly, but if the chosen sampling interval is too large, the mapped changes in soil variability may be of insufficient resolution to offer interpretive value[27]. Equally, if sampling resolution is too high, then it may be that the extent of survey coverage is limited by time and costs, resulting in an insufficient area covered to be able to address archaeological questions.

For the investigation of wider landscapes, as in the Pecora valley survey, the sampling interval was set at 20 m, but the grid was then narrowed down to 5 m, as research was focusing on specific research contexts and geochemistry was meant to address trial excavations.

When trying to identify different functional areas within a settlement, such as domestic spaces, workshops, or waste disposal areas, a finer suitable sampling interval is necessary to effectively capture the spatial variations in elemental concentrations that define these areas. For the analysis of exposed archaeological contexts, where the investigator aims to understand how space was used within a structure, resolution can narrow down to the point of analysing chemical variability within the limits of a single stratigraphic unit.

For stationary activities, either sitting or standing, it is considered that processing of materials takes place within arm's length, and the most appropriate sampling interval may be 0.5–1m, while for more contained mobile activities, it is considered that actions take place within a few steps, so a resolution of ~1m might be fitting[28]. Indeed, one of the most interesting aspects in designing the strategy for using HH-pXRF in the field is precisely the option of adapting the sampling space to the needs of the research and its questions.

A combination of different sampling scales has been accomplished within the project centred on the renowned medieval fortified site of Rocca San Silvestro (fig. 1), where from 2023 a comprehensive geochemical survey has been included in the research project Miners[29].

The site is well-known to archaeological literature, thanks to the investigations carried out in the 1980s on the site and in the surrounding territory, where a systematic survey identified over 200 mine

25. Doonan, Waddington, Craver, 2026.
26. Boyd *et al.* 2021.
27. Haslam, Tibbett 2004.
28. Save *et al*. 2020.
29. Miners is a project developed by the Siena Research Unit co-ordinated by Prof. Giovanna Bianchi within the ARC project: *Pursing Public Health in the Preindustrial World, 1100–1800* (Monash University, Melbourne, Australia-P.I. Prof. Guy Geltner).

entrances[30]. Extensive archaeological investigation led to the functional interpretation of most of the spaces within the castle, whose economy was tightly linked to mining exploitation; some of these were interpreted as productive ones and related to the roasting and smelting of lead and copper ores.

At Rocca San Silvestro, over 1300 HH-pXRF analyses have been performed within the site, following virtual grids of analysis of 1x1 m that covered ore-processing contexts, residential areas and spaces of uncertain function; 10x10 m grids were designed to analyse territorial samples heavily impacted by pre-industrial mining activities, for a total of 250 measurements. For each square, one measurement of 30 seconds was taken with a HH-pXRF Olympus Vanta M fitted with a wide-area SDD, anode in Rhodium (Rh) and 50 kV power, set in soil mode[31] (**fig. 5, A–D**).

Based on the evaluation of structured patterns of elements directly correlated with the processing of local mineral deposits (i.e. Pb, Cu and Zn) and on archaeological data, an initial statistical processing allowed the classification of three different groups. Considering Pb in particular, spaces where archaeological research identified traces of metallurgical activities were characterised by an average value of 537 mg/kg, while an average value of 126 mg/kg was recorded in residential ones. Despite a lower grade of contamination, this latter clearly highlights the significant lead pollution correlated to the economic activities performed within the site. Some other areas showed an average value of 334 mg/kg. According to the archaeological investigation, their function was uncertain, while the new data clearly highlight a possible productive role, thus promoting an overall reassessment of the distribution of different functions (i.e. residential or productive) within the site[32] (fig. 5, D).

Data visualisation and interpretation

HH-pXRF data obtained from the field research in the Colline Metallifere was crucial to support both historical-archaeological and environmental interpretations; thanks to the georeferencing of each measurement and the use of GIS, on-site research could rely on constantly updated maps of geochemical values. In order to produce such thematic maps, which were essential for our research, we thought about what the most useful output could be, as data visualisation of soil chemical variation is a critical aspect to consider. Given the relative infancy of the use of HH-pXRF geochemical data to map and interpret variability, it is important to be transparent in the presentation of results and to resist any temptation to overly process results.

Although specific research questions and dissemination purposes can in some contexts request the use of interpolated maps, in most cases, and in our experience in particular, the use of minimally processed results plotted in a clear manner, where each measurement is displayed as a discrete value, seems the most sensible choice for visualisation. Interpolation techniques, like kriging, can smooth out individual high data points as well as fill in blank areas, or areas that have returned values below detection limits, creating a misleading impression of a continuous anomaly extending across the space.

30. Francovich 1991.
31. Bianchi *et al*. 2024.
32. *Ibid*., p. 62–68.

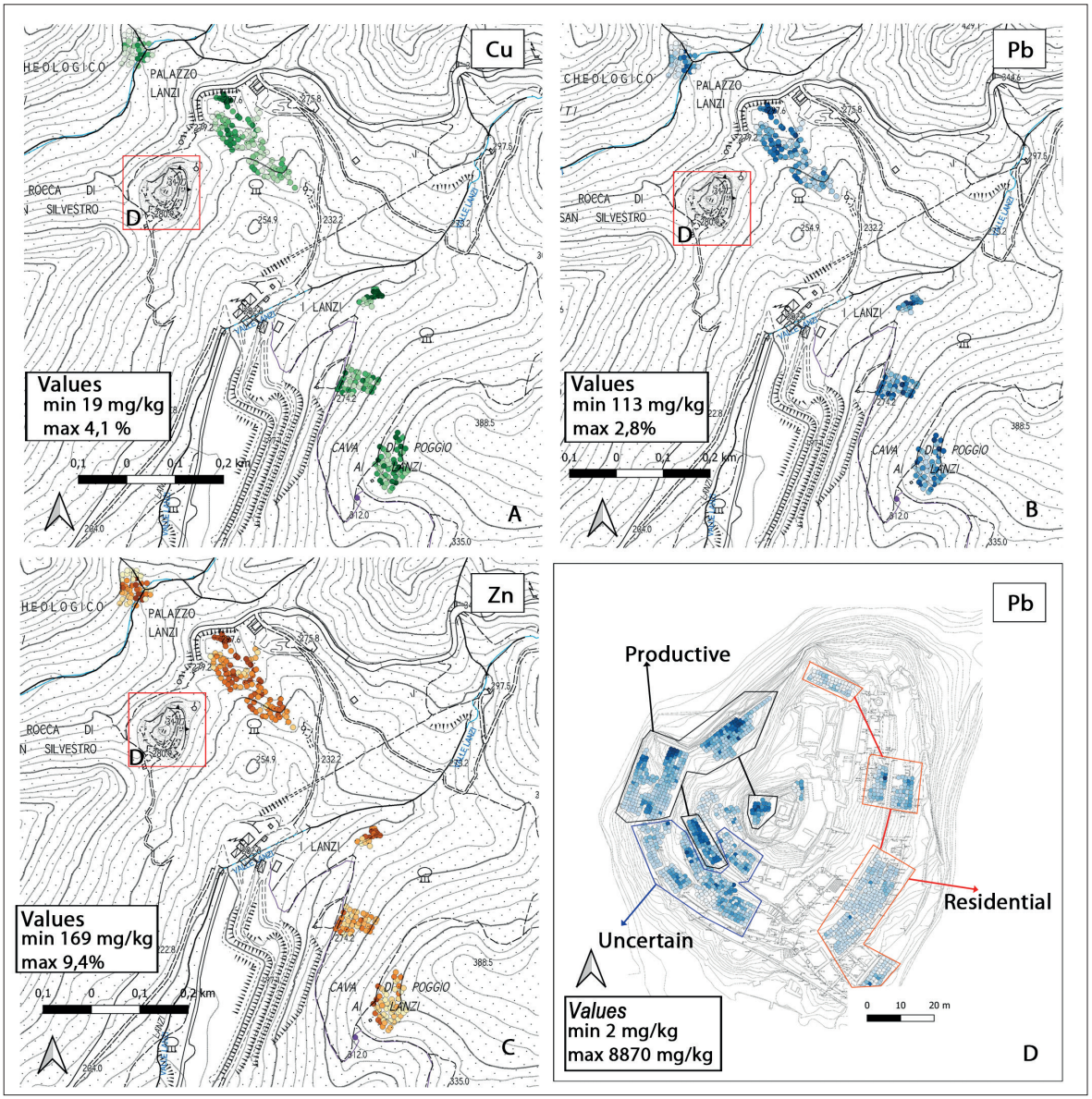


Figure 5: Rocca San Silvestro. **A–C**. HH-pXRF values recorded on ancient and modern mining areas; **D**. Pb patterns and functional interpretation of spaces within the site

By contrast, presenting raw data allows for a more nuanced understanding of spatial patterns and the identification of "structured anomalies", rather than smoothed and interpolated "hot spots"[33]. This is especially important because HH-pXRF data is often collected at points on a discontinuous survey grid, unlike the near-continuous data stream of a gradiometer survey. Moreover, discriminating soil chemical variability rather than accurately determining absolute values across an area is precisely the aim of a survey using on-site HH-pXRF analysis; soil dynamics constantly modify

33. Carver, Doonan, Waddington 2021.

chemical values, and this can give rise to changes in absolute values, while preserving the structure of chemical variation.

Relying on minimally processed results ensures transparency and allows the data to be assessed fairly. In the Tuscan example, and particularly in the Cornia valley survey, structured patterns of elements like Ti, Fe, Ca, K have been plotted and analysed at territorial scale to emphasise boundaries between different soils, helping to define the original limits of historic lagoons now completely reclaimed; subsequent statistical treatment of element ratio (e.g. Rb /Sr, Mn/Fe, Ca/Ti, Sr/Ti, Zr/Rb, Zr/Ti and K/Rb) has proved this first interpretation to be reliable and solid[34].

Analytical controls and the use of Certified Reference Materials (CRMs)

HH-pXRF measurements are generally trustworthy, despite small variations between different type and brands of instruments[35], but it is important to recognise that the analytical routine may be subject to errors of various natures, including user variation. Poise, balance and stability are key skills that any operator needs to master; these can be assessed or monitored by both determining instrumental precision (with the instrument in a bench-top adaptor) and with the instrument being used in hand-held mode. It is usual to expect poorer precision and accuracy in hand-held mode due to user instability, but with practice and care this can be minimised (**fig. 6, A**).

In addition to a careful use of the instrumentation, the analysis of CRMs allows researchers to assess instrument, and user, performance by comparing HH-pXRF readings of CRMs to their certified values. Through this process, researchers can identify any biases or inconsistencies in instrument performance or use routine. This is particularly important when using instruments with empirical calibrations, as deviations from certified values can indicate the need for adjustments; maintaining data consistency and ensuring that measurements taken at different times are comparable is essential for an appropriate use of the technique. CRMs should be relevant to the soil types being analysed, to cover the expected range of elemental concentrations found in the study area and enhance the accuracy of data interpretation. In the Tuscan field experience, we have performed regular instrument calibration using NIST standards (https://www.nist.gov/standards). CRMs are usually analysed at the start and end of on-site surveys, and day to day to monitor, and correct, if necessary, accuracy, precision and systematic errors such as drift. Moreover, while commercially available CRMs are valuable, the creation of in-house standards, tailored to specific project needs, can further improve data accuracy and relevance. As for instrumental method and settings, explicit reference to CRMs analyses strengthens the transparency and reproducibility of research, allowing other researchers to evaluate data quality and assess comparability with other studies[36].

34. Volpi *et al*. 2024.
35. Richards, McAlister in this volume.
36. Save *et al*. 2020.

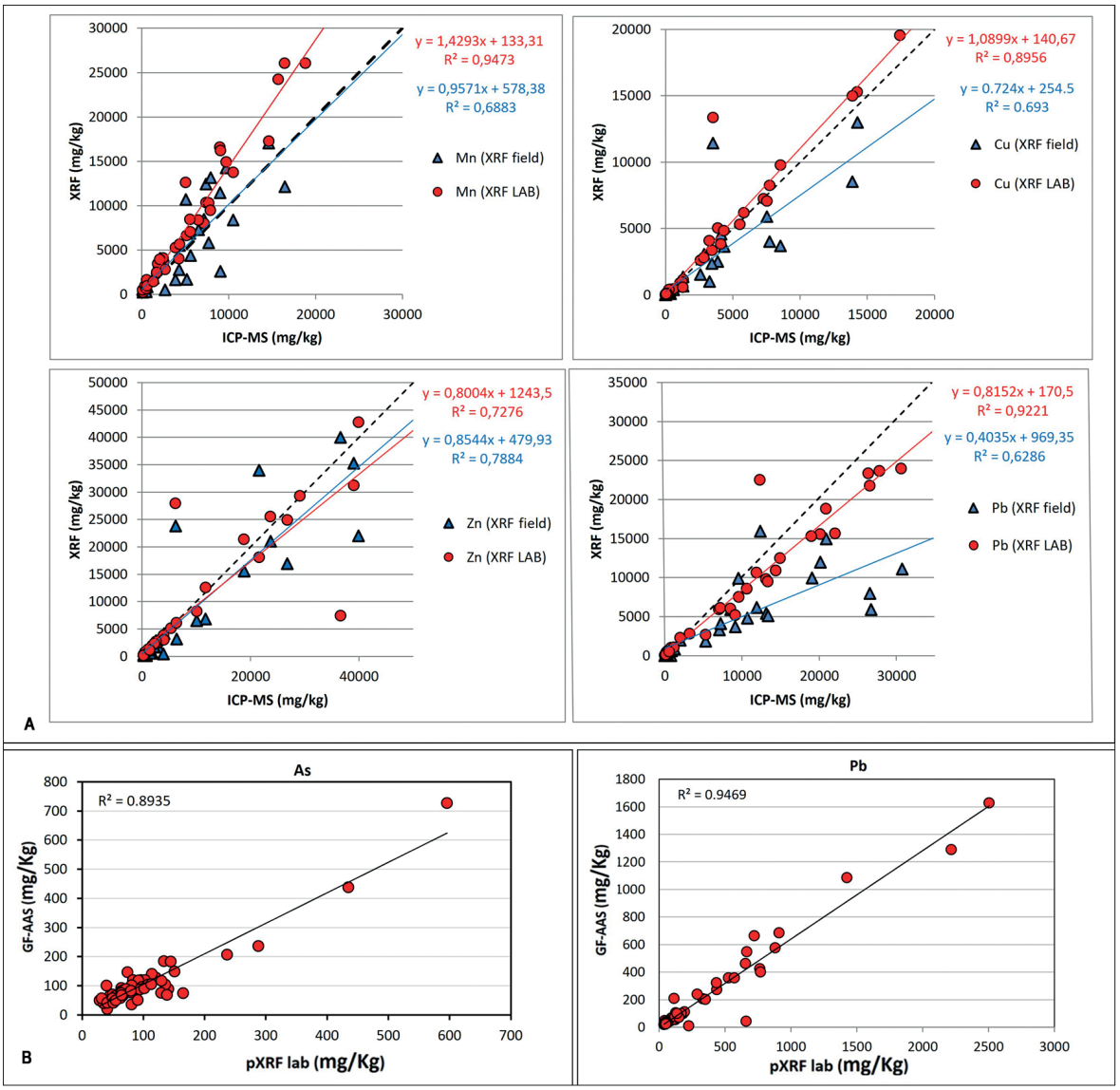


Figure 6: Montieri. **A**. Comparison of Mn, Zn, Cu and Pb concentration values in fluvial sediments obtained from on-site HH-pXRF, lab HH-pXRF and ICP-MS measures. **B**. Comparison of As and Pb concentration values in fluvial sediments obtained from GF-AAS and lab HH-pXRF

External confirmatory testing

While cross-calibration among instrumentation is challenging, there are benefits for the occasional use of external confirmatory tests to validate analyses done for wide-area landscape survey, following international standards of competence such as ISO/IEC 17025 or MCERTS for UK (https://www.gov.uk/government/publications/mcerts-performance-standard-for-laboratories-undertaking-chemical-testing-of-soil).

External confirmatory testing may add to costs of any survey, and they should not be seen as always being essential, as there will be occasions when the use of certified reference materials and/or

in-house standards might be thought to be sufficient. In the Colline Metallifere research, the need for an accurate evaluation of soil contamination in an ancient mining context close to the present-day settlement of Montieri (fig. 1), offered the opportunity to compare HH-pXRF results with ICP-MS and GF-AAS.

The project design integrated archaeological prospecting for the identification of ancient mines, HH-pXRF analysis and sampling of river sediments. Sediments were collected at a depth of approximately 1 m, along four watercourses downstream from the village (ditch A, B, C, D, **fig. 7, A**)[37]. A total of 56 soil samples were taken at regular distances of 10–15 m with a hand-held core drill and analysed on-site, with an Olympus INNOV-X Delta Premium DP-6000-C HH-pXRF equipped with a 40kV 4W X-ray tube (200mA, Rh anode) and a large-area SSD detector set in benchtop soil mode (3 beams, 30 seconds). Samples were then cross-analysed in the laboratory with HH-pXRF, ICP-MS and Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS)[38]. In order to ensure the quality of data obtained, operating protocols EPA 6200 were used. In the laboratory, HH-pXRF values were obtained from samples dried at room temperature, sieved at 125µm and placed in appropriate holders; for each sample three measures were taken. Samples for GF-AAS were prepared following a careful procedure: 100 mg of sieved soil was added with 1.5 mL of HNO_3 65% and 0.5 mL of H_2O_2 33% in a Teflon vessel, and attached in a Milestone Ethos microwave digestion system for 20 minutes. Samples were cooled and stored in a 50 ml test tubes with distilled water; the residual insoluble precipitate was separated by centrifugation at 3500 rpm for about 3 minutes. The GF-AAS analysis was performed by Perkin Elmer AAnalyst 100 instrument, equipped with a graphite furnace and auto-sampler Perkin Elmer A72. Results proved that on-site HH-pXRF measurements are reliable, overall, despite some variations deriving from operating conditions. Laboratory HH-pXR Fand ICP-MS values show a good correlation, particularly for Cu, As, Zn and Pb, among the main indicator elements of metallurgical pollution; HH-pXRF and GF-AAS results for Pb and As show excellent correlation (**fig. 6, A–B**). While proving HH-pXRF reliability, external confirmatory tests produced absolute values that were crucial for environmental monitoring purposes; for its part, archaeological interpretation was primarily based on elemental pattern analysis, as "structured anomalies" of Pb, Zn and Cu were clearly visible on two of the four streams analysed (B and C), with values degrading from the source downstream (**fig. 7, B–D**).

Some final remarks and the need for guidelines

In the study of archaeological soils, HH-pXRF has enabled a shift in the way the chemical variability is understood. The time and expense associated with laboratory-based analyses have meant that archaeologists have often taken low numbers of soil samples to characterise archaeological contexts and rarely used geochemistry to undertake landscape-wide high-resolution surveys. By contrast, the new generation of HH-pXRF permits the rapid analysis and reporting of thousands of samples directly on-site, to quickly inform survey or excavation strategy. As a consequence, the kinds of questions

37. Benvenuti *et al*. 2014.
38. Analysis was performed at the Department of Biotechnology, Chemistry and Pharmacy at Siena University under the supervision of Prof. A. Donati, who was in charge for the evaluation of former mining impact on the environment in the Colline Metallifere district. http://www.archimin.unisi.it/.

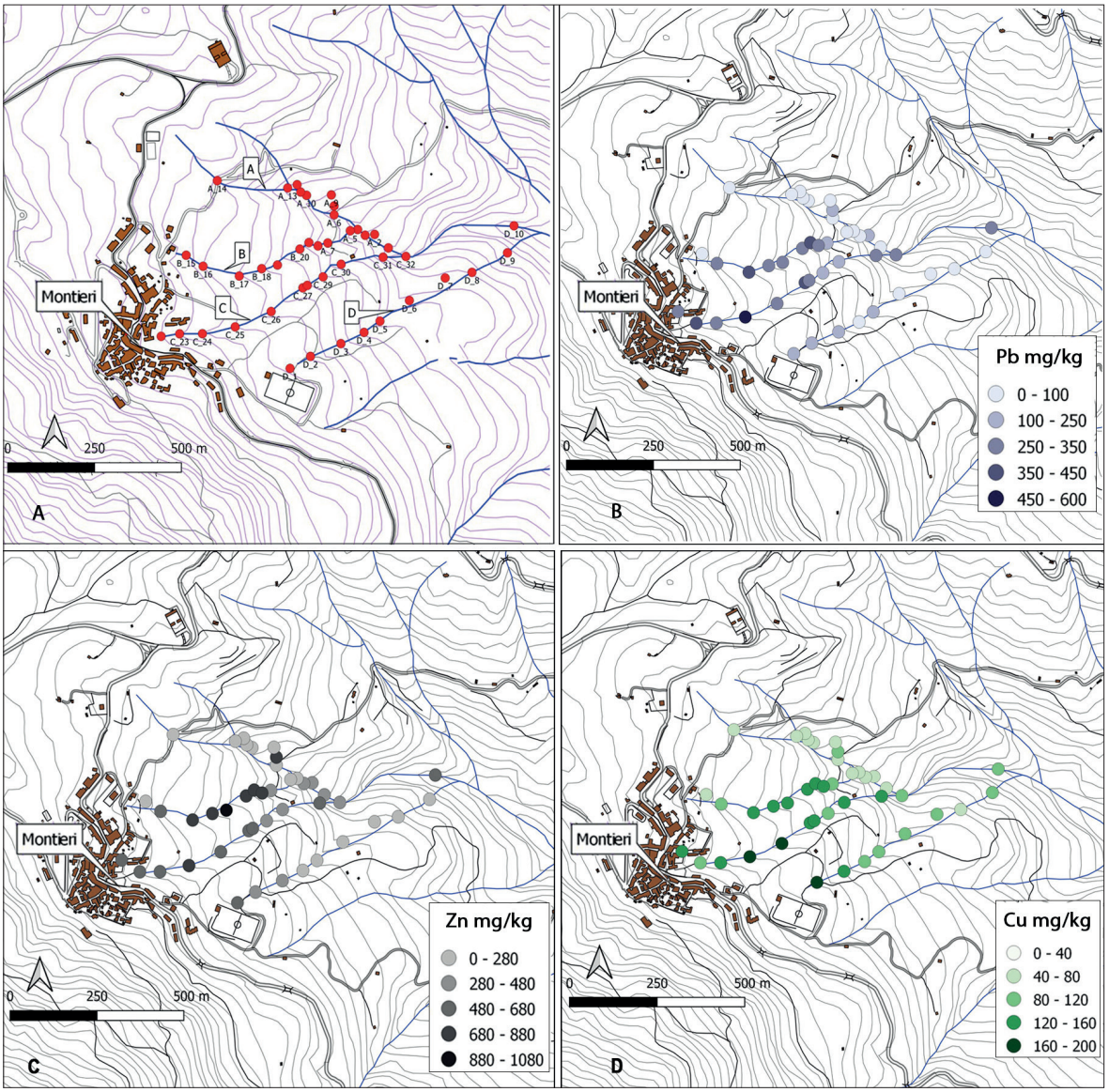


Figure 7: Montieri. A-Sample locations; B-D, Pb, Zn and Cu concentration values along the streams

asked, and the type of datasets generated, are significantly different to those from traditional studies. This is an important point and highlights how HH-pXRF is best used, i.e. as an instrument that offers new ways of working, rather than a budget alternative to laboratory analyses[39], and we believe that its inclusion in any respectable project design should be recognised as an opportunity.

In our examples we have illustrated how the technique was used as a flexible and powerful tool of an overall archaeological survey strategy, providing useful data to support a comprehensive interpretation and reconstruction of the historical landscape. In doing this, we have always referred to chemical variability of a context/landscape, beyond absolute values, highlighting the value of the

39. Frahm, Doonan 2013.

"structured anomaly" as a cornerstone of interpretation, and emphasising the attention given to the "structure" of neighbouring data points rather than any single "hot spot".

The increasing number of archaeological projects including HH-pXRF analysis needs an effort to define good practices and to discuss limits, concerns and opportunities offered by the technique, particularly in its deployment in the field. We strongly believe that a set of shared guidelines, based on practical experiences, could offer insight into the best use of the instrumentation in archaeological fieldwork and instil greater confidence in HH-pXRF data, promoting its wider acceptance as a valuable tool for archaeological soil analysis.

It is precisely in this spirit that we intended our paper as a contribution to the ongoing academic and professional debate.

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Author contribution

Luisa Dallai: conceptualisation, investigation, writing – original draft preparation, reviewing and editing, visualisation, supervision;
Roger Doonan: conceptualisation, reviewing and editing;
Vanessa Volpi: investigation, formal analysis, reviewing and editing.

Data availability statement

Data supporting the findings of this study are available from the corresponding author (L.D.) upon reasonable request, but are not publicly accessible due to their partial association with sensitive sites.

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2

Improving data accuracy: some solutions

Rebecca Scott, Laura Kay

Painting by numbers: investigating the reliability of fundamental parameters in paint analyses

Abstract

The fundamental parameters (FP) method is often used with portable XRF instrumentation. In some cases, it can be extremely difficult for the operator to access and process the spectral data independently. Since FP is cited as a "standardless" method, there becomes a temptation to rely on the "numbers" generated. This issue is further compounded with instruments where operators must utilise an inbuilt "mode" for analysis. Portable XRF has been used in several studies to determine the composition of paint: both in gallery paintings and as decoration on objects and artefacts. Most studies use the technique to determine the presence/absence of elements within a given painted region, to ascertain the type of paint and whether further analysis is required. It is generally accepted that even if the accuracy of the pXRF data is questionable, the precision is not. Patterns in the data are felt to be reliable. This research explored the extent to which FP combined with a pre-set mode provided an accurate quantitative representation of the composition of varying volumes of Titanium White acrylic paint. Results indicated that once the infinite thickness of the sample was reached the data was precise. Below this threshold the data was neither accurate nor precise. Consideration is given to reliability of data from multilayered painted pieces, and the implications of using FP-generated data to investigate paint. Recommendations for good practice include running pilot tests on mock and/or trial samples to ascertain the strengths and limitations of the available spectrometer prior to *in situ* work.

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Keywords

Fundamental parameters, critical depth, paint, ceramics, pXRF

Introduction

Portable XRF (pXRF) technology is nothing new, one of the earliest applications can be seen in the archaeometallurgical fieldwork of Helmig, Jackwerth and Hauptmann[1]. However, the technology has improved and miniaturised over the years[2]. These instruments are now affordable to a wide variety of archaeological, museum, and heritage workers[3]. A quick internet search will reveal a range of pXRF manufacturers, with many of these having several different models of instrument available. Despite being marketed to the general heritage community; these spectrometers are rarely designed with this domain in mind[4]. Many pXRF spectrometers are still being marketed as "point and shoot" devices, suggesting the user can analyse and quantify the chemical composition of samples with an "off-the-shelf" device "straight from the box"[5].

The authors noted that whilst some users of pXRF instruments appeared very conscious of the strengths and limitations of the factory settings, others do not seem to consider them at all when reporting their results. The primary author's own experiences with pXRF were mainly utilising a Bruker Tracer III SD. In other words, full control over the operating parameters, no access to fundamental parameters (FP) calibrations, and a reliance on peak area counts and ratios. However, a change of circumstance brought a change of available instrumentation. Now the authors use a Niton XL3t GOLDD; an instrument which requires pre-set operating modes and only provides FP data. The authors experienced a general frustration when trying to access raw data and spectra. Is this perhaps a reason why the limitations, particularly of pre-set mode and FP based spectrometers, are rarely discussed?

Conventional FP based methods of analysis require homogeneous samples, and flat (preferably polished) surfaces[6]. Archaeological materials rarely meet these requirements. Where sub-samples can be taken and subjected to destructive sample preparation methods, pXRF will rarely be the analytical method of choice. According to Balasubramanian and Muthukumaraswamy (2016)[7] FP analyses are very powerful if the correct conditions are met, they specify:

1. The sample must be a single layer – not containing, for example, any contamination, paint, or rust;
2. the sample must not contain any abnormalities in terms of shape – ideal samples are flat and smooth;
3. the sample must not allow any incident X-ray beams to pass through it – i.e. it must be of infinite thickness for the X-ray beam;

1. Helmig, Jackwerth, Hauptmann 1989.
2. Scott *et al.* 2016.
3. Forster *et al.* 2011; Nicholas, Manti 2014; Shugar, Mass 2012.
4. Scott *et al.* 2016.
5. Hunt, Speakman 2015; Shackley 2012.
6. Szalóki, Radócz, Gerényi 2019.
7. Balasubramanian, Muthukumaraswamy 2016.

4. pure samples of the elements that require quantification need to be available[8]. If using multi-element standards, these need to be matrix-matched to the samples and the preparation method must be reproducible[9].

Unfortunately, there is still a perception that users can collect accurate quantitative data without any development of customised calibrations[10]. This perception amongst novice and/or inexperienced users is often reinforced when FP is mentioned, due to the impression that FP implements quantitative analyses without the use of standards[11].

Artists' materials start out as highly complex, composite materials[12]. After hundreds or even thousands of years, alterations occur, often resulting in high levels of surface porosity and/or layered microstructures, making them particularly unsuitable for non-destructive, surface techniques, such as XRF[13]. Despite this, XRF is one of the most used techniques for the elemental analysis of paintings, ceramics, manuscripts, statues, and metal artefacts[14]. Yet, the very nature of many works of art makes them too thin to meet the infinite thickness requirements, therefore quantified analyses of these materials is only possible with thin film standards[15]. Quantified analyses of heritage materials in general require the best reference standards along with a very accurate knowledge of their composition[16]. This suggests that paint and paintings are probably not suitable for analysis either with a pre-set mode (unless it is a custom creation), or FP-based analyses (due to the sample thickness). This research uses a Niton XL3t GOLDD with pre-set analytical mode to explore the extent to which FP would provide an accurate quantification of the composition of different volumes of Titanium White paint.

Methods

A Thermo Scientific Niton XL3t GOLDD + (pXRF with Ag anode; 6–50kV, 0–200μA max X-ray tube) was used, and four of the pre-set modes were tested (Mining Cu/Zn; Mining Ta/Hf; Soils; TestAll Geo). These modes, whilst not ideal for paint, were the only modes available on the instrument. This reflects the reality of many users, especially if they or their research were not considered at the time of purchasing the instrument. Each "new" mode must be purchased from and installed by the manufacturer, resulting in people using the instrument as is.

The two "Mining" modes are designed for samples where the concentrations of elements are >5000 ppm. The "Soils" mode is more suited for samples with low concentrations of elements

8. Balasubramanian, Muthukumaraswamy 2016.
9. Rousseau 2013.
10. Shugar, Mass 2012.
11. Takahara 2017.
12. Shugar, Mass 2012.
13. *Ibid*.
14. Molari, Appoloni 2019.
15. Shugar, Mass 2012.
16. Galli, Bonizzoni 2013.

(<5000ppm)[17]. "TestAll Geo" is recommended by the manufacturer as the general testing mode. Each mode is pre-set to determine a specific list of elements. Preliminary tests of the four modes using six colours of Derwent acrylic paint indicated that the TestAll Geo mode reported the widest range of elements, and Titanium White paint had a small number of measurable elements (i.e. was the least complex paint composition).

XRF sample cups with polypropylene film were filled with Titanium White paint from 3mm to 18mm in depth in 3mm increments. Each depth was measured in TestAll Geo mode for 150 seconds per scan, with a minimum of three scans taken across the sample cup surface. The TestAll Geo mode will cycle through four filter ranges "High Range" (50kV, 40μA) which optimises measurements of elements from barium (Ba) to silver (Ag); "Main Range" (50kV, 40μA) which optimises elements from manganese (Mn) to bismuth (Bi); "Low Range" (20kV, 100μA) from titanium (Ti) to chromium (Cr); and "Light Range" (8kV, 200μA) for light element analyses[18]. The amount of time which the spectrometer spends within each range can be determined by the user, however, for this research the factory settings were used (30 seconds each for Low, Main, High Ranges, 60 seconds for Light Range).

In order to measure thinner layers of paint, a series of brush strokes were built up on polypropylene film from one brush stroke up to approx. 2mm thick. The paint was brushed directly onto polypropylene film and again three scans were taken across the surface. The instrument was used with the manufacturer supplied test stand with built-in shielding (**fig. 1**).

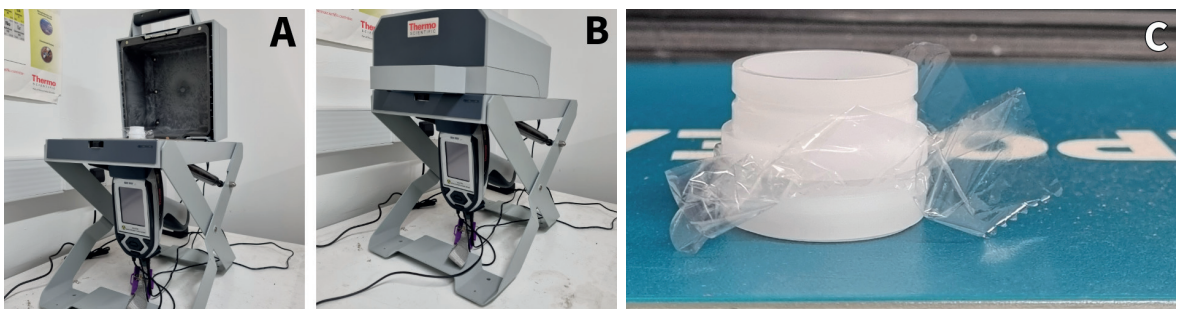


Figure 1: **A**. The Niton XL3t GOLDD+ attached to the manufacturer issued test stand with a sample cup on top of the nose cone of the instrument. **B**. The instrument with the protective shielding closed. **C**. A close-up of a double open-end sample cup. In this instance polypropylene film covers one end of the cup, allowing sample material to be added at the other

The critical depth of penetration (i.e. the depth at which 99% or more of the initial X-ray signal is absorbed) can be derived from the Beer-Lambert formula. Since at least 99% of the initial signal is attenuated, the equation can be simplified. The critical depth of penetration was therefore calculated for the elements of interest in the sample using the formula:

$$4.61/((\mu/\rho)\rho)$$

17. Thermo Scientific 2010.
18. *Ibid*.

Where μ/ρ is the mass attenuation coefficient of the matrix, and ρ is the density of the sample material. The mass attenuation coefficient was determined from the NIST Standard Reference Database 126[19]. The mass attenuation values were taken from the data for photographic emulsion (a light sensitive substance combined with an organic binder, applied as a coating to a substrate). This was chosen as being the most similar material to paint but acknowledging that the values would introduce a degree of error into the calculations.

Results

According to the Derwent acrylic paint data safety sheet, barium (Ba), sulphur (S), and titanium (Ti) are the elements measurable with pXRF which may be present in their Titanium White acrylic paint. A sample of the paint sent off for SEM-EDX analysis confirmed the presence of Ba (26.52%), Ti (16.06%), S (7.63%), Si (5.14%), Al (0.66%), Cu (0.42%) and K (0.33%). The TestAll Geo reported values for the elements specified within the mode, which included Ba, S, and Ti amongst others, whether these elements were present or not. **Figure 2** indicates the elements reported by the TestAll Geo mode.

The critical depth of penetration was determined for a number of the elements using NIST data for a photographic emulsion matrix (**Table 1**). Since only Ti, Ba, S and Si had been expected within the paint in higher concentrations, it was decided to focus the investigation on those elements which were found in quantities of >0.5%.

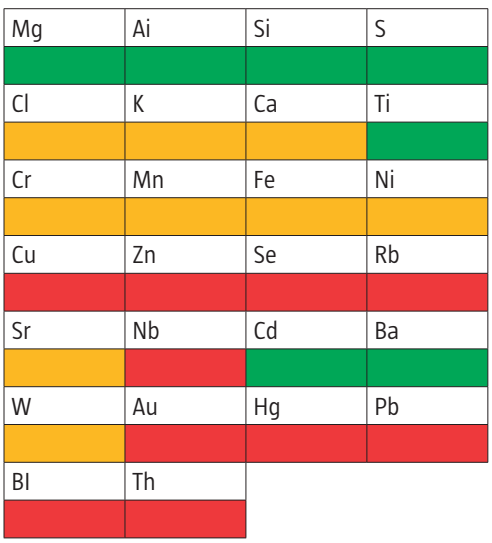


Figure 2: The elements reported in Titanium White paint using the TestAll Geo mode. The colours indicate the concentration of the element present in the paint as determined by the pXRF. Red – the element was below the limit of detection. Orange – the element was reported as being <0.5%. Green – the element was reported as >0.5%

Element	% in paint via pXRF	Critical Depth (mm)
Magnesium (Mg)	>0.5	3.9
Aluminium (Al)	>0.5	3.9
Silicon (Si)	>0.5	3.9
Sulphur (S)	>0.5	3.9
Titanium (Ti)	>0.5	5.9
Barium (Ba)	>0.5	11.8
Manganese (Mn)	<0.5	5.9
Iron (Fe)	<0.5	11.8
Nickel (Ni)	<0.5	11.8
Lead (Pb)	Below detection	11.8

Table 1: A selection of the elements reported via the TestAll Geo mode, the percentage present in Titanium White paint as determined by the pXRF, and the theoretical critical depth of penetration in mm for a photographic emulsion matrix

19. Hubbell, Seltzer 1996.

The average of three scans from each thickness of paint were plotted. **Figure 3** shows the results for 1 – 10 brush strokes of paint (the brush strokes have been nominally converted to mm for the sake of plotting the data), and the measured depths of paint up to 18mm. The results presented are elements reported by the pXRF as being present in the paint in concentrations of consistently more than 0.5%.

The results indicate a wide variation in the reported concentrations over thinner layers of paint, stabilising to consistent concentrations at approx. 6mm of paint. Titanium White paint is known to contain Ti, S, Si and Ba, it should not contain Mg. The results indicate that the FP calibration is overestimating the concentration of all the elements (except Ba) in the thinner layers. When compared to the SEM-EDX data, the stabilised pXRF data is underestimating the concentration of all the elements. A full set of results can be found in Appendix 1.

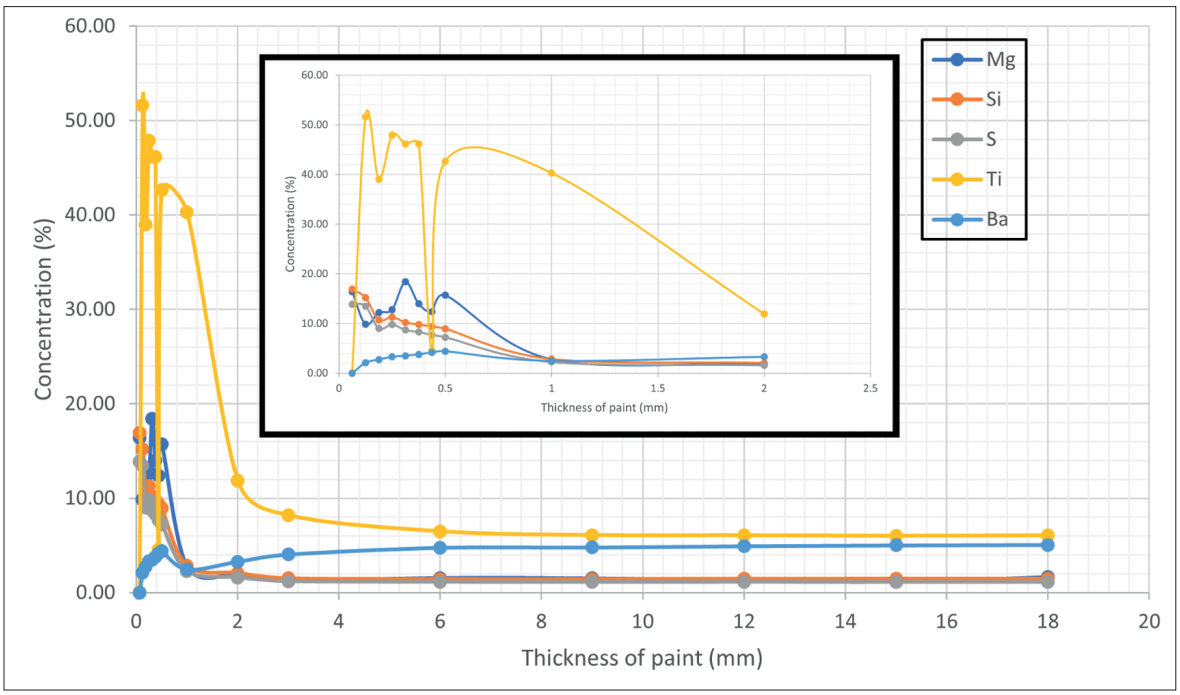


Figure 3: The concentration of Mg, Si, S, Ti, Ba as reported by the pXRF in TestAll Geo mode for depths of paint ranging from 1 brush stroke to 18mm. These are for the mean measurements of each thickness. The inset image shows greater detail on the 1 – 10 brush strokes, after this point the paint was measured in sample cups

Discussion

The results have highlighted two challenges in pXRF usage which are sometimes overlooked by analysts. Firstly, the use of pre-set modes is potentially hindering the generation and subsequent interpretation of data. Titanium White paint was deliberately chosen as the sample material, because it contained only a few elements detectable with pXRF. The use of the pre-set mode means the instrument is "looking" for the elements listed in the mode. Many of these modes have been created for a specific type of application – in terms of the Teesside University instrument geological work.

Whilst TestAll Geo may be a good option for a general testing mode[20], it is not necessarily suitable for a paint where determination of the pigment is dependent on the presence/absence of certain elements[21]. Whilst the instrument determines the concentration of Mg, Si, and S, to be approx. 1 – 1.5% after the critical depth of penetration is reached; over the range of a few brush strokes, the instrument reports approx.10–20% of these elements. The SEM-EDX reported Si (5.14%) and S (7.63%). Even if the analyst is only using the data in a qualitative way, such as detecting presence/absence of elements, this over- and under-estimation, combined with a potential lack of access to the spectra, can result in misidentification of the pigments. In addition, certain light elements will only be quantifiable if the pXRF instrument is combined with a He flux. McGlinchey notes that instruments which "auto-identify" peaks make certain assumptions about the background scatter and can result in false positives[22]. Even users who routinely use XRF to determine the thickness of thin films have noted that the instruments can over- and/or under-estimate the thickness by 6–10%[23].

It should be remembered that the presence of 'other' elements in a spectrum may also be the result of contamination from sample preparation, from the equipment itself, and/or any air gaps[24]. For example, mylar films can be contaminated with P, S, Ca and Ti[25]; and whilst polypropylene film is less prone to contamination, suppliers have mentioned the presence of Ca, Zr, P, Fe, Zn, Cu, Ti, and Al[26]. In this research polypropylene film was used with the sample cups to hold the Titanium White paint. Testing of both the film and no sample at all indicated that As and Cu were potentially present in the polypropylene, whilst Sr, W, Ba were present in the X-ray shielding of the instrument. The pXRF in TestAll Geo mode indicated that Ti and Al were present above 0.5% (but in the case of Al these measurements were not consistent). Ca (not expected in the sample) and Fe (not expected in the sample) were reported as present below 0.5%, these could potentially be from the polypropylene film, however the critical depth needed to measure these elements accurately has not been reached. This problem also arises when measuring the blank samples. The TestAll Geo mode reported values for Cu and Zn (the latter not expected in the sample) as both being below the detection limit. Yet the SEM-EDX results indicated 0.42% Cu present in the paint. Note, that Zr and P were not reported. This could be because they are not present in the sample, nor are they present as contaminants in the polypropylene, or it could be they were present, but they are not defined in the pre-set mode and therefore not reported. This is where the analyst would need to look at the spectra, to make an informed decision about the elements being reported.

The second challenge is the reliance on the fundamental parameters generated data. For bulk samples, where the analyte intensity will not change with sample thickness[27], FP techniques can give accurate data assuming the critical depth of penetration is met[28]. However, SEM-EDX analysis of the paint suggests the pXRF was under-reporting the concentrations of the elements in the samples.

20. Thermo Scientific 2010.
21. Molari, Appoloni, Rodriguez 2020.
22. Mcglinchey 2012.
23. Vrielink *et al.* 2012.
24. Lopes *et al.* 2016.
25. De Almeida *et al.* 2020.
26. *Ibid.*
27. Takahara 2017.
28. Balasubramanian, Muthukumaraswamy 2016.

Even though the theoretical determination of the critical depth of penetration has a degree of error (due to using photographic emulsion as a proxy matrix), the pXRF results clearly stabilised over the reported depth range. If analysing thin film samples, where X-ray intensity is linear and the film is thin enough for matrix effects to be ignored, FP analysis can be used on proviso the composition of the film is known in advance[29]. The problem with heritage materials such as paint is that they are often too thick to be classed as thin films and too thin to be analysed as bulk material. If the complexity of multi-layered samples is introduced, the absorption, enhancement, and scattering effects within and between each layer also need to be considered[30]. If researchers only have access to an instrument which produces FP output and difficulty accessing the spectra, there is little option but to rely on the FP generated numbers. Ideally, users would interrogate the spectra to note potential variations caused by changes in sample thickness and/or check peak assignments and spectral interferences. As the results in Figure 3 indicated, once the critical depth of penetration for each element had been met, the numbers generated stabilised and could be reported with more certainty. Below this threshold the data was not reliable. Ti was present in the sample as expected, but not at concentrations of 40–50% as reported.

The underestimation of Ba is interesting, particularly as it is present in the paint and in the safety housing surrounding the sample stand. The most likely explanation is due to the close proximity of the Ba L lines to the Ti K lines. Although the software should compensate for matrix effects to a certain extent, it is probable in this instance that the FP algorithm is struggling to resolve the overlapping peaks. This is where the ability to access and review the spectra properly becomes essential.

In the analysis of painted surfaces, the identification of the pigments used is important for a variety of reasons, including determining the artist's working methods (how paint was mixed) and pigment availability, as well as providing information for conservation purposes[31]. The current method of determining pigment using pXRF is via the presence/absence of elements in the spectra[32]. This method often relies on studying the ratios of the X-ray line intensities[33]. However, with an instrument, such as the Niton XL3t, where it is difficult to access the raw data and spectra, these sorts of qualitative interpretations become increasingly challenging. If the samples contained enough material measurable by pXRF and the data could be collected to ensure the trace element peaks were developed, then FP calibrations would provide reasonably accurate data[34]. However, the often thin nature of the paint samples, combined with the various organic materials in the binding medium, would result in inaccurate data. This is because FP calibrations will normalise the quantities to 100%, thereby altering the true compositional quantities[35]. Even if, as in the case of the Niton XL3t, the reported values give a 'balance' in the normalisation process, i.e. all the elements that are not measurable with the pXRF, this is still an estimation on the part of the algorithm. The potential impact of this on qualitative studies should always be considered. For example, the results (fig. 3) indicate that Titanium White paint contains approx. 6% Ti, approx. 5% Ba, and approx. 1%

29. Takahara 2017.
30. Vrielink *et al.* 2012.
31. Molari, Appoloni, Rodriguez 2020.
32. Galli, Bonizzoni 2013; Mcglinchey 2012; Molari, Appoloni 2019, 2021; Molari, Appoloni, Rodriguez 2020; Stulik, Kaplan 2012; Trentelman, Schmidt Patterson, Turner 2012.
33. De Almeida *et al.* 2020; Mcglinchey 2012; Molari, Appoloni 2019; Molari, Appoloni, Rodriguez 2020.
34. Shugar, Mass 2012.
35. *Ibid.*

S, if infinite thickness of the sample is achieved. Over the range of a few brush strokes, the results suggest approx. 46% Ti, approx. 3% Ba, and approx. 10% S. Even if the data were used in a qualitative way, the ratios between the elements would not be consistent, and ultimately could lead to misattribution of the pigments. McGlinchey notes that a tell-tale sign of poorly understood pXRF data is when the concentration of elements present in paint is reported as adding up to 100%[36]. It should also be remembered that pre-set modes determine concentrations for the elements listed in the mode. This combined with the FP normalising to 100% means that seemingly good results can still be inaccurate, as indicated by the SEM-EDX analysis of the paint.

As with any analytical study, the experimental set-up should be tailored to each individual project. Images created using multiple pigments and colourants applied as mixtures or overlapping strokes in layered structures, as is typical with paintings, are more complex than other applications where it can be assumed that the elements are uniformly distributed[37]. The penetrating nature of X-rays means elements in the top-most layer will fluoresce, however the signal detected by the instrument will also include elements from pigments in underlying layers and substrates[38]. The depth of measurement is deeper in light element matrices compared to heavier element matrices[39]. This means that if the layers in the painting are of mixed matrices, i.e. some layers contain Pb-based paint whilst others do not, it will be extremely difficult to attribute the data to the correct layer. Matrix effects, such as absorption and secondary fluorescence, are accounted for in FP algorithms[40]. However, FP assumes a homogeneous sample. This is a problem that all analysts who utilise pXRF for paint studies encounter (even if they are relying on interpretation of the spectra). Even if the pXRF cannot identify the organic media used in the paint binders, these elements can still cause matrix attenuations[41]. This is because fluorescence count rates are influenced by all the elements present in the sample[42], directly measured or otherwise. Likewise, even if the pXRF correctly detects the presence of an element, it cannot discriminate between compounds, for example, red lead (Pb_3O_4) and litharge (PbO)[43]. Ultimately, pXRF users analysing multilayer complex materials, such as paint, must make a choice: report qualitative data, report quantitative data with a high degree of error, or attempt to create reference materials that match the unknown's heterogeneity and composition[44].

Whilst this research has focused on the analysis of paint, the potential pitfalls of using pXRF in a poorly planned experiment can be applied to other heritage materials. Instruments which only utilise pre-set modes are designed with specific purposes in mind. This is not to say they cannot be utilised by the heritage community, but caution must be applied. In many instances it would be useful to work with mock-up samples to determine the limitations of the instrumentation being used[45]. This stage is particularly important if the pXRF is to be used *in situ*[46]. If analysts have an idea of the

36. Mcglinchey 2012.
37. Mcglinchey 2012; Trentelman *et al.* 2012.
38. Trentelman, Schmidt Patterson, Turner 2012.
39. Takahara 2017.
40. Rousseau 2001, 2009, 2013.
41. Mcglinchey 2012.
42. Vrielink *et al.* 2012.
43. Shugar, Mass 2012.
44. *Ibid*.
45. Mcglinchey 2012.
46. Scott *et al.* 2016, 2018; Scott, Eekelers, Degryse 2016.

expected composition of the samples, then attempts should be made to determine the critical depth of penetration for the elements in the sample. Whilst this step is less relevant where samples are of infinite thickness, it should be essential for samples that are less likely to meet the bulk sample criterion. An anecdotal example of the importance of this step is when the primary author was asked by a student to analyse some zeolites (aluminosilicates) spiked with varying concentrations of Cu. The result was that the Cu could clearly be seen in the sample, but the pXRF reported no difference in the concentrations of Cu. When the author calculated the critical depth of penetration for the student, it became apparent that the volume of material was too small. In fact, the amount of material the student needed to produce to get accurate concentrations of Cu measured on the pXRF was so great, it was cheaper and easier for the student to use an alternative analytical technique. In the current study, the theoretical critical depths were calculated as 3.9mm (S), 5.9mm (Ti) and 11.8mm (Ba). This was based on the NIST data for photographic emulsion. However, the experimental data indicated that for all the elements under consideration in paint, the critical depth was achieved around the 6mm mark. At least, this is where the pXRF signal stabilised, suggesting critical depth had been met. However, Figure 3 shows the mean concentration of Ba (as determined by the pXRF) to be around 5%, whilst the SEM-EDX data reported the Ba in the sample to be 26.52%. As with the zeolite example, the pXRF is seeing the Ba in the paint sample, but unable to accurately measure the concentration even once the theoretically calculated critical depth has been reached. This highlights that caution should be taken when calculating the critical depth of penetration from a proxy material (photographic emulsion). In reality, the critical depth of penetration for Ba in the paint sample had not been reached. So, whilst the theoretical calculation of the critical depth of penetration of the elements in the sample is highly recommended, the values should only be taken as a guideline.

Whilst pXRF can be an excellent screening tool, caution should be exercised over quantified data, particularly FP generated data. If the conditions necessary for a robust FP-based analysis are not met, then the data will be error prone. When pXRF analyses were conducted on Zhu Zhu Pets in 2009, it was suggested the toys contained unsafe levels of antimony, this led to legal battles, as the report was based on inaccurate data[47]. The use of FP, which normalises data to 100%, can impart a false sense of completeness, demonstrating a misunderstanding of what the instrument is capable of doing[48]. If very thin layers are analysed, then the FP method needs to be adapted to suit the samples[49]. It should be remembered that FP works well on a pure metal sample but becomes increasingly more complex with multiple elements present[50]. As Ager *et al.* point out, pXRF can be an excellent tool in an interdisciplinary research project, but proper analysis can only be achieved if there is a close collaboration between all parties[51]. For example, not all pXRF analysts are heritage specialists and may lack the necessary understanding of the specific material. Likewise, not all heritage experts have the relevant understanding of the limitations of the instrument. The instrumentation is often calibrated for a specific application and the relevant expertise is needed to interpret the results[52].

47. Shugar, mass 2012.
48. Mcglinchey 2012.
49. Szalóki, Radócz, Gerényi 2019.
50. Balasubramanian, Muthukumaraswamy 2016.
51. Ager *et al.* 2020.
52. West 2019.

Conclusion

Portable XRF is not new, however, most pXRF spectrometers are not designed specifically for use in the heritage laboratories. As such, the instruments may be utilised inappropriately and/or not to their maximum potential. A lack of consideration of the limitations of the instrumentation for a specific application will lead to a misunderstanding between what is expected and what it is possible to achieve[53]. This is particularly the case with spectrometers which utilise pre-set modes. The reality of many heritage-based pXRF users is that the instrument they have access to was not acquired with their specific research needs in mind. The result is that any pre-set modes may not be ideally suited to the materials they are being used with, and the acquisition of new modes may not be cost effective. Pre-set modes will report data for the elements specified within the mode. Whilst it may be possible to moderate these modes, the user needs an awareness of what elements to expect in the sample. If the user does not have easy access to the spectral data, it is hard to check whether the presence/absence of elements if being correctly reported. Users also need a sound knowledge of potential sources of unexpected elements in the data, i.e. is the element in the sample, has it been introduced as contamination, is it part of the sample preparation, and/or additional materials such as polypropylene film, etc.?

Additionally, pXRF spectrometers which favour a reliance on fundamental parameters to report data can be problematic. There is often an assumption that FP data is infallible, however, if the sample preparation criteria for robust FP analyses are not met, then this will rarely be the case. FP, as with other XRF analyses, requires homogeneous, flat surfaces, and infinite thickness, criteria rarely met in samples of archaeological material. In particular, the critical depth of penetration should not be ignored. Whilst the theoretical calculation of this may not be without error, it will give an indication of the volume of material necessary for a robust analysis. This research showed that below the critical depth of penetration, the reported FP data was inaccurate and unreliable, meaning that not even the ratios between elements were consistent. Part of the problem lies in the fact that the FP algorithm normalises the measured data to 100%, thereby introducing some error. Add to this the fact that any organic materials present in the sample, whilst hypothetically calculated by the FP algorithm as being present, cannot have the relevant matrix effect corrections applied, due to their unknown nature. Even experienced users of FP-based XRF analyses have reported the over- and under-estimation of elements when the analytical criteria for a robust study are not met.

Portable XRF is an excellent screening tool, however, good practice would encourage the use of pilot studies and preliminary lab testing of mock or trial samples. This would enable the user to determine the strengths and limitations of their specific instrumentation. It would allow the determination of the most appropriate sample preparation methods, and above all it would encourage consideration to be given to tailoring the experimental set-up to the specific needs of the research project.

53. Shugar, Mass 2012.

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Author contribution

Aspects of this research formed part of an undergraduate research dissertation. As such the author contributions can be summarised as follows:
Rebecca Scott: conceptualisation of the work and project administration; development of the chosen methodology; provision of resources and curation of the final data; formal analysis of the data and visualisation of the conference presentation and proceedings article; supervision of the data collection, analysis, and write up of the undergraduate dissertation; writing of the original draft of this paper and responsibility for reviews and subsequent edits;
Laura Kay: provision of resources; initial investigations; validation of collected data; formal analysis of data in relation to dissertation project; curation of data relating to dissertation project; review and editing of written draft of this paper.

Statement on the use of AI

During the preparation of this work, the authors did not use AI tools.

Data availability statement

The supplementary material for this chapter is available in Teesside University's Research Portal – PURE at https://research.tees.ac.uk/en/persons/becki-scott/.

SAMPLE	Al	Al std dev	Si	Si std dev	S	S std dev	K	K std dev	Ti	Ti std dev	Cu	Cu std dev	Ba	Ba std dev
1 brush stroke a	5.87		17.24		14.42		0.09		46.24		<LOD		1.59	
1 brush stroke b	6.27		17.08		14.13		0.09		43.79		<LOD		1.46	
1 brush stroke c	7.02		16.57		13.27		0.08		40.42		<LOD		1.33	
mean	6.39	0.58	16.96	0.35	13.94	0.60	0.09	0.00	43.48	2.92			1.46	0.13
2 brush strokes a	5.60		15.37		12.73		0.09		45.30		<LOD		1.61	
2 brush strokes b	5.94		15.08		12.58		0.08		46.14		<LOD		1.79	
2 brush strokes c	<LOD		15.56		13.78		0.09		51.35		<LOD		2.04	
mean	5.77	0.24	15.34	0.24	13.03	0.65	0.09	0.00	47.60	3.28			1.81	0.22
3 brush strokes a	25.99		9.67		8.02		0.06		36.10		<LOD		2.61	
3 brush strokes b	20.92		11.86		9.86		0.08		39.82		<LOD		2.74	
3 brush strokes c	15.06		10.79		9.17		0.06		41.09		<LOD		2.90	
mean	20.65	5.47	10.77	1.10	9.02	0.93	0.07	0.01	39.01	2.59			2.75	0.15
4 brush strokes a	10.19		11.67		10.07		0.07		46.14		<LOD		2.64	
4 brush strokes b	<LOD		12.05		10.64		0.07		52.80		<LOD		3.20	
4 brush strokes c	13.00		10.34		8.68		0.07		44.88		<LOD		4.06	
mean	11.59	1.98	11.35	0.90	9.80	1.01	0.07	0.00	47.94	4.25			3.30	0.72
5 brush strokes a	10.67		9.57		8.07		0.07		42.78		<LOD		3.17	
5 brush strokes b	6.34		10.55		8.91		0.08		47.98		<LOD		3.35	
5 brush strokes c	<LOD		10.63		9.09		0.08		47.76		<LOD		4.01	
mean	8.51	3.06	10.25	0.59	8.69	0.54	0.07	0.01	46.17	2.94			3.51	0.44
6 brush strokes a	15.89		9.08		7.79		0.07		42.94		<LOD		3.42	
6 brush strokes b	4.66		10.12		8.47		0.07		47.67		<LOD		3.84	
6 brush strokes c	14.17		10.21		8.64		0.07		47.13		<LOD		4.07	
mean	11.57	6.05	9.80	0.63	8.30	0.45	0.07	0.01	45.91	2.59			3.78	0.33

SAMPLE	Al	Al std dev	Si	Si std dev	S	S std dev	K	K std dev	Ti	Ti std dev	Cu	Cu std dev	Ba	Ba std dev
7 brush strokes a	24.44		9.11		7.58		0.06		41.31		<LOD		3.91	
7 brush strokes b	12.03		9.78		7.93		0.08		44.49		<LOD		4.07	
7 brush strokes c	17.54		9.28		7.57		0.07		42.11		<LOD		4.57	
mean	18.01	6.22	9.39	0.35	7.69	0.21	0.07	0.01	42.64	1.65			4.19	0.34
8 brush strokes a	14.91		8.95		7.14		0.06		40.27		<LOD		4.12	
8 brush strokes b	19.79		8.92		7.34		0.07		40.54		<LOD		4.51	
8 brush strokes c	18.16		8.96		7.27		0.05		40.59		<LOD		4.56	
mean	17.62	2.48	8.94	0.02	7.25	0.10	0.06	0.01	40.47	0.17			4.40	0.24
9 brush strokes a	1.00		2.75		2.20		0.04		11.51		0.00		2.39	
9 brush strokes b	0.91		2.87		2.27		0.04		12.00		0.00		2.39	
9 brush strokes c	1.01		2.93		2.32		0.03		12.32		<LOD		2.66	
mean	0.97	0.05	2.85	0.09	2.26	0.06	0.04	0.00	11.94	0.41	0.00	0.00	2.48	0.16
10 brush strokes a	0.60		1.97		1.54		0.04		7.74		0.00		3.44	
10 brush strokes b	0.72		2.24		1.74		0.03		9.00		0.00		3.03	
10 brush strokes c	0.61		2.00		1.56		0.03		7.94		0.00		3.38	
mean	0.64	0.07	2.07	0.15	1.61	0.11	0.03	0.00	8.23	0.68	0.00	0.00	3.28	0.22
3mm a	1.01		3.04		2.46		0.04		12.96		<LOD		2.64	
3mm b	0.50		1.52		1.21		0.02		6.49		0.00		4.05	
3mm c	3.28		6.95		0.04		0.04		16.32		<LOD		0.02	
mean	1.60	1.48	3.84	2.80	1.24	1.21	0.03	0.01	11.92	5.00	0.00		2.23	2.05
6mm a	0.46		1.45		1.13		0.03		6.08		0.00		4.85	
6mm b	0.50		1.46		1.13		0.02		6.07		0.01		4.79	
6mm c	0.45		1.45		1.14		0.03		6.09		0.00		4.66	
mean	0.47	0.02	1.45	0.00	1.13	0.00	0.03	0.00	6.08	0.01	0.01	0.00	4.76	0.10
9mm a	0.44		1.46		1.12		0.02		6.05		0.01		4.80	
9mm b	0.43		1.41		1.09		<LOD		6.00		0.01		4.86	
9mm c	0.51		1.50		1.14		<LOD		6.16		0.00		4.73	
mean	0.46	0.04	1.46	0.05	1.12	0.02	0.02		6.07	0.08	0.01	0.00	4.79	0.06

SAMPLE	Al	Al std dev	Si	Si std dev	S	S std dev	K	K std dev	Ti	Ti std dev	Cu	Cu std dev	Ba	Ba std dev
12mm a	0.52		1.45		1.13		< LOD		6.10		0.01		4.96	
12mm b	0.49		1.49		1.12		< LOD		6.12		0.00		4.94	
12mm c	0.39		1.48		1.14		< LOD		6.07		0.01		4.90	
mean	0.47	0.07	1.47	0.02	1.13	0.01			6.09	0.02	0.01	0.00	4.93	0.03
15mm a	0.48		1.46		1.11		0.02		5.99		0.00		5.03	
15mm b	0.52		1.50		1.13		0.03		6.01		0.01		5.04	
15mm c	0.46		1.49		1.13		<LOD		6.05		0.01		4.96	
mean	0.48	0.03	1.48	0.02	1.13	0.01	0.02	0.01	6.02	0.03	0.01	0.00	5.01	0.04
18mm a	0.47		1.47		1.13		<LOD		6.11		0.00		5.08	
18mm b	0.50		1.49		1.13		<LOD		6.03		0.00		5.09	
18mm c	0.51		1.50		1.13		0.03		6.03		0.01		5.02	
mean	0.49	0.02	1.48	0.02	1.13	0.00	0.03		6.06	0.05	0.00	0.00	5.06	0.03

Supplementary Table 1: Results (in %) and standard deviations of the pXRF analyses of triplicate measurements for different volumes of Derwent "Titanium White" acrylic paint

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Detlef Wilke

Empirical calibration with spiked fired clay blocks for improved inter-instrument compatibility in ceramic provenancing

Abstract

Portable XRF analysis is actually the sole universal method for non-destructive geochemical provenancing of archaeological ceramics. Measurements without prior substance-consuming sample preparation are not only a prerequisite for studying cultural heritage material, but also for high throughput analysis of large assemblages of archaeological settlement finds. For most of the archaeological regions worldwide, a plenitude of production sites must be considered, which makes it impossible to cover all these sites by a single laboratory with a single instrument. Therefore, it is important for cross-time and inter-laboratory data use, to calibrate instruments for discriminative minor and trace elements, thereby reflecting the peculiarities of XRF analysis of micro-heterogenous sample materials with uneven surfaces. Empirical matrix specific element calibration is only possible with spiked fired clay samples, since there is no geochemical reference material differing in the concentration of just a single element. Examples are given for the necessity of absorption and interference correction at varying Ca, Fe or Pb concentrations. Distance and density correction needs normalisation with the tube photons, the Compton or the Rayleigh scatter. The respective arithmetic corrections are only possible if the instruments provide raw data access for subsequent peak deconvolution into net counts per energy line. Since many clay deposits are very similar in the composition of the few minor and trace elements accessible with XRF analysis, careful calibration is crucial for positive and negative sample attribution to archaeological reference groups established with waster materials and by cluster analysis, respectively.

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Keywords

Matrix, absorption, enhancement, spectral interference, validation

Introduction

Geochemical or compositional provenancing of archaeological ceramics depends on the proposition that locally produced pottery reflects the geochemical pattern (colloquially called the "signature") of the local raw materials, particularly of the near surface clay deposits exploited by the ancient potters[1]. Whereas many ceramics due to their characteristic minor and trace element patterns are well distinguishable even at a short distance from their production sites, pottery made from Quaternary clayey sediments is frequently rather similar and difficult to distinguish. This is a worldwide phenomenon observed with sherds produced from poorly decolourised sediments and with low contents of stable heavy mineral grains as an index of the limited weathering of the geological feedstocks during the Quaternary period. Compositional provenancing of ceramic fragments of unknown origin in archaeological settlement contexts therefore depends on a reliable and reproducible quantification of as many discriminative elements as possible in order to distinguish even very similar fabrics, but perhaps made at different production sites a considerable distance from each other. Data sets must reflect the true abundances of the discriminative elements with reasonable uncertainties, suitable for the purpose.

There is no single ideal method for geochemical analysis of archaeological ceramics, or for XRF and pXRF (portable[2] X-ray fluorescence) analysis. However, pXRF analysis is non-destructive. Even very small fragments can be analysed, the total assemblage is available for further studies with hopefully new, improved non-destructive analytical tools, and there is sufficient steric flexibility to analyse archaeologically intact vessels, figurines, roof, floor and oven tiles and the like[3]. With respect to archaeological finds, the term non-destructive is taken literally. Indeed, it can be recognised in many regions of the world, that the confirmation of non-destructive analysis is meanwhile a precondition for convincing museum and depository representatives to provide already archived study material. As long as finds are still in the hands of the excavators, sample preparation may be more generous, including "fresh breaks/cuts/sections", which are often claimed as non-destructive sampling.

Neutron activation analysis (NAA) has its focus on the rare earth elements, but has some weaknesses with other stable heavy mineral elements. Wavelength dispersive XRF (WDXRF) is perfect for low-Z elements, including Al and Si, energy dispersive XRF (ED-XRF) for mid-Z elements, and inductively coupled plasma mass spectrometry (ICP-MS) probably covers the broadest range of elements, but all of these methods are destructive[4]. Minimally invasive laser ablation sampling as well as

1. Bishop, Rands, Holley 1982.
2. For large scale sherd analysis portable or hand-held instruments are preferentially placed in a bench-top stand with the measurement window in the upside position and the sample placed on top. Countries have issued different regulations regarding X-ray radiation safety.
3. E.g. Quinn *et al.* 2021.
4. ED-XRF is potentially non-destructive, as long as small ceramic fragments fit into the sample chamber of a stationary instrument.

non-destructive micro-XRF and proton induced X-ray emission (PIXE) are inappropriate whenever the ceramic paste is inhomogeneous with respect to accessory mineral grains of whatever size[5].

Calibration and validation

In late 2010 Steven Shackley[6] published a warning letter, and the debate on the point-and-shoot approach by pXRF users became highly controversial. The concern about reference standards and the quality of factory calibrations continued, but meanwhile the discussion has died down. However, the questions remain, how reliable are geochemical factory calibrations, and how diligently they need to be validated.

XRF raw data calibration is complex, and non-destructive pottery analysis adds additional levels of complexity. The concentration figures need to be precise and accurate in order to reflect even minor differences between rather similar reference groups. Pottery sherds, particularly earthenware, typically have a micro-heterogenous composition with often uneven surface and exhibiting surface modifications or contaminations, which in non-destructive analysis may distort the compositional results of the paste. Compared to NAA, XRF is short in number of appropriate discriminative elements, since the detection limit of present day XRF systems is in the range of 10 ppm. Even putting the adherence to scientific principles aside, we still need accuracy for a continued use of established data with new instruments, if an older device breaks or if we want to switch to a different brand. Similarly, inter-laboratory use of data needs accuracy based on diligent instrument calibration.

When Speakman and Shackley[7] criticised the naïve use of portable instruments and the likewise naïve trusting of the figures on the display for quantifying obsidian and pottery compositions, it was unclear whether obvious discrepancies were due to uncorrected matrix effects, uncorrected spectral interferences, uncertainties in the accepted values of the reference materials, or were due to the general complexity of mathematical assumptions as in case of fundamental parameter calibrations. Using a larger sample of geochemical reference materials for calibration and validation, respectively, some elements are quite good with coefficients of determination of the regression/correlation lines above 0.97, others are really poor. Among these are Zr and the low abundance trace elements Ga, Y and Nb, which we all need for the provenancing of pottery with XRF.

Certified reference materials

One source of uncertainty is the recommended values of the certified reference materials themselves, as for example in case of Zr. If given mass fraction data are plotted against the net counts, which means prior to any instrument calibration, the figures scatter a lot, and the regression line may not hit the origin. For sure matrix effects play a major role, but even for a single standard like NIST 2710,

5. Cf. Speakman *et al.* 2011.
6. Shackley 2010.
7. Speakman, Shackley 2013.

Zr values scatter considerably with independent analyses. Hunt *et al.*[8] have compared NAA, wavelength dispersive and energy dispersive stationary XRF at MURR and at the Atlanta laboratory and confirmed the scatter observed by GeoReM in Mainz[9]. For whatever reason the NAA value for Zr was particularly high. A critical evaluation of recommended Zr values in silicate standards had already been performed before by Potts, Webb and Watson who also applied a Zr standard addition procedure[10].

Inter-instrument and inter-laboratory deviations

Inter-laboratory calibration differences are ubiquitous, and make the use of cross-laboratory data difficult or even impossible. In **Figure 1** an example of Roman sherds from Urmitz-Weißenthurm near Koblenz, Germany, is given. The attempt was to provenance outlier sherds found in a Roman waster complex in Worms without having respective reference material from the suspected production site downstream of the Rhine[11]. The Urmitz-Weißenthurm material exhibits an Nb anomaly, most probably due to volcanic weathering compounds in the nearby Mühlheim-Kärlich clay deposits. Indeed, the clay samples taken there, make it very likely that the Worms waster sherds are settlement debris derived from Urmitz-Weißenthurm. Fortunately data of authentic sherds found at Urmitz-Weißenthurm from Wengxing Xu at the former Römisch-Germanisches Zentralmuseum (RGZM) Mainz and from Susanne Biegert at Gerwulf Schneider's former laboratory at Freie Universität Berlin were available. Both data sets with local sherds were analysed with wavelength dispersive XRF. As can be seen, the three datasets shifted from lower to higher Zr or higher to lower Nb concentrations. This is most likely due to calibration differences, but we cannot allocate the discrepancy to either of the two elements. Since the sherd samples are different, conversion factors cannot be calculated. As meanwhile none of the three instruments is still in operation and in its original configuration, a cross validation with a set of identical reference materials is also no longer possible. In an eight-dimensional rotation, the three datasets are very similar and partially overlap, but without prior knowledge they could also be interpreted as resembling three different clay deposits or production sites. Thus datasets used as reference groups for archaeological provenancing need to fit. Datasets need to be accurate with respect to reliable mass fraction values of the geochemical reference materials used for calibration.

A recent comparison of the factory calibration of a NITON XL3T GOLDD+ portable XRF instrument with the NAA routine by Hein *et al.*[12] confirmed significant differences between the two methods for most of the element concentrations obtained with an assemblage of 97 amphora fragments, which had been preselected by non-destructive XRF[13]. For many elements the slope c of the linear regression/correlation line of the pXRF values plotted against the NAA values strongly deviated from the ideal figure of 1.0, indicating significant calibration differences. Furthermore, the correlation value R^2 for most elements was low, as shown by a wide scatter of the individual data

8. Hunt *et al.* 2014.
9. *Ibid*.
10. Potts, Webb, Watson 1990.
11. Wilke *et al.* 2019.
12. Hein *et al.* 2021.
13. *Ibid.*, fig. 7a–c.

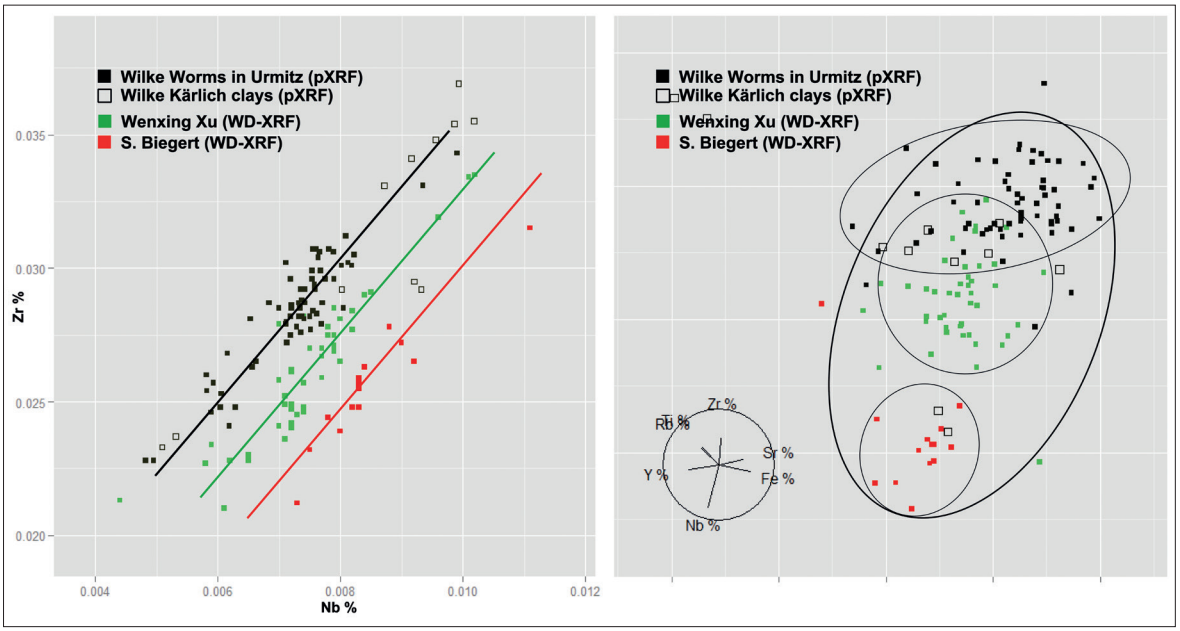


Figure 1: Three sets of Roman sherds from Urmitz-Weißenthurm found in Worms (Wilke) and locally (Wengxing Xu and S. Biegert), Zr/Nb-plot (left) and 8-dimensional rotation in GGobi[14] (right)

points around the regression line forced through zero. Thus, there were more sources of uncertainty than just the calibration factors which impacted the deviating values per sherd obtained with both methods. As observed in similar studies, the slope c=1.0047 and the correlation value R^2=0.9411 for Rb were particularly good, whereas c=1.4099 and R^2=0.6497 for Zr would be insufficient for a mutual use of the obtained results in subsequent statistical evaluations.

Empirical geochemical calibration

When trying to validate the geochemical factory calibration of a Bruker III-SD portable instrument, an empirical calibration based on internal mudrock samples[15], the net count values plotted against the given concentrations, in **Figure 2** (left) shown for Zr, scattered around the regression line. R^2 amounted to 0.95, and the linear regression line did not hit the origin. This, however, is important, since the slope of the net counts plotted versus the given mass fraction values provides the calibration factor, and forcing the regression line through zero is not acceptable. In an attempt to overcome the supposed uncertainties of recommended values in geochemical reference materials with non-identical matrix composition, fired clay blocks spiked with eight discriminative elements have been prepared (Ti, Fe, Ga, Rb, Y, Sr, Zr and Nb, **fig. 3**)[16]. Later on Ca was added as a further spiked element, which is needed for the correction of photon absorption of other elements by Ca

14 Cook, Swayne, Buja 2007.
15. Rowe, Hughes, Robinson 2012.
16. Wilke, Rauch, Rauch 2016.

in Ca-rich clays and loams. The concept of spiking is known as standard addition procedure[17], but except for a few glass standards (NIST 610,612, BAM-S005) has not been systematically applied to produce reliable geochemical calibration sets for relevant minor and trace elements.

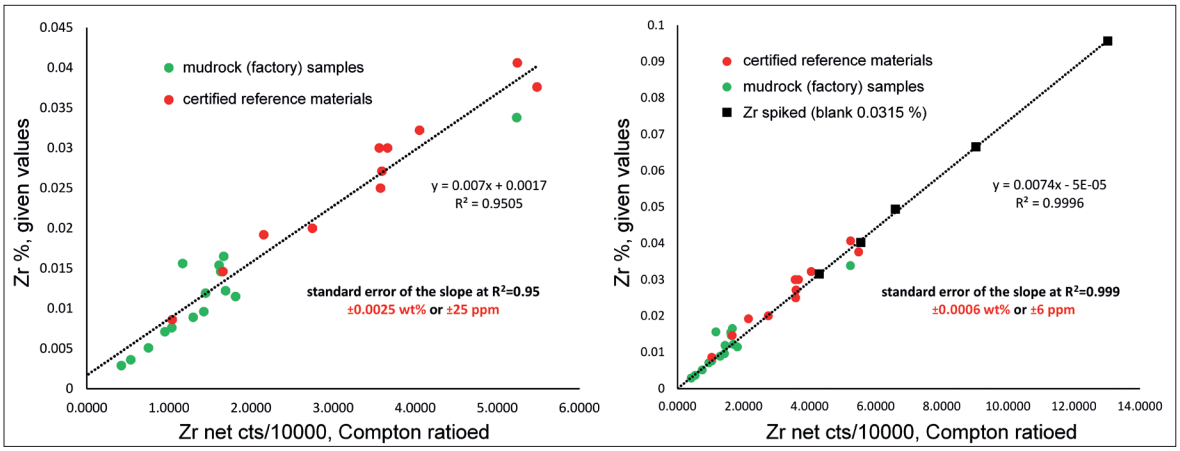


Figure 2: Zr regression line of reference materials (left) and spiked fired clay blocks (right). Net counts obtained with the Bruker deconvolution software ARTAX 7[18]



Figure 3: Blank and fired clay blocks for each 4 concentrations of Ti, Fe, Ga, Rb, Sr, Y, Zr and Nb[19]

17. Cf. Potts, Webb, Watson 1990.
18. Cf. Wilke, Rauch, Rauch 2016 for certified reference materials.
19. The spiking sets of the eight discriminative elements plus Ca are available on request, as is calibration and validation support in ARTAX 7 and Excel.

A total of 200 kg of an industrially processed Westerwald clay powder with particle size smaller than 63 µm was checked randomly for homogeneity. Then, batches of about 1 kg of clay powder each were spiked with four aliquots of the respective discriminative element, resulting in a total of 32 spiked batches plus the blank clay. The element weights were Sigma-Aldrich analytical quality chemicals with 99% purity, which had to be homogenously distributed in the respective 1 kg clay batch. The wetted, carefully worked paste was divided into about 60 small blocks, dried, polished on two opposite sides and fired at 800 to 850 °C for two hours. Perfect distribution of each spiking aliquot in the 1 kg batch was essential. Homogenous distribution in the paste was checked for net count variation of the spiked element in each batch. If outliers were recognised, the batch was discarded.

The Zr baseload in the Westerwald clay blank was calculated to be 315 ppm, which is the crossing of the negative Y axis, when the spiking aliquots are plotted against the measured net counts. The four Zr aliquots cover a total range of up to 1000 ppm. The linear regression line of the total Zr concentrations (spiking aliquots plus blank value) versus net counts properly hits the intersect (fig. 2, right).

The slope of the regression line provides the calibration factor, the multiplier for converting net counts into mass fractions. The quality of the Zr spiking set is obvious. The regression line has a coefficient of determination of 0.999 and a standard error of +/- 6 ppm, reflecting the precision of weighing and mixing of the spiked aliquots, and fitting much better than the individual certified geological reference samples (R^2=0.95, +/- 25 ppm standard error). The spiking set confirms the order of magnitude of the reference materials, but is much more precise. The linear regression line confirms that the lower concentration range of the Bruker mudrock series is reliable, whereas many of the certified reference materials used for validation scatter around the regression line fitted through the four total concentrations, which resulted from the spiking. The differences may be multifactorial, but they explain why calibration discrepancies occur if only a small set of reference materials is used for calibration and validation, respectively.

Inter-laboratory comparison of the spiking sets

The eight spiking sets have been analysed in a collaborative project by Philipp Schulte at Rheinisch-Westfälische Technische Hochschule (RWTH), Aachen, with stationary ED-XRF using pressed pellets of the powdered spiking samples[20]. The instrument had its own independent calibration with a set of certified reference materials. In **Figure 4** the Y-axis provides the values measured with the stationary instrument, the X-axis provides the given or expected values of the respective blank concentration plus the spiking aliquots. All correlation lines confirm the precision of weighing and mixing. Four elements with slopes of the correlation line between 0.95 and 1.01 – Fe, Ga, Y and Zr – exhibit an almost perfect agreement, whereas the remaining four elements somewhat differ: Ti is overreported by 14%, Rb is underreported by 8%, Sr by 10%, and Nb by 11%. The most likely explanation for these modest discrepancies is the selection of certified reference materials in the Aachen laboratory and the resulting calibration factors.

20. Matzerath (ed.) 2022, p. 27.

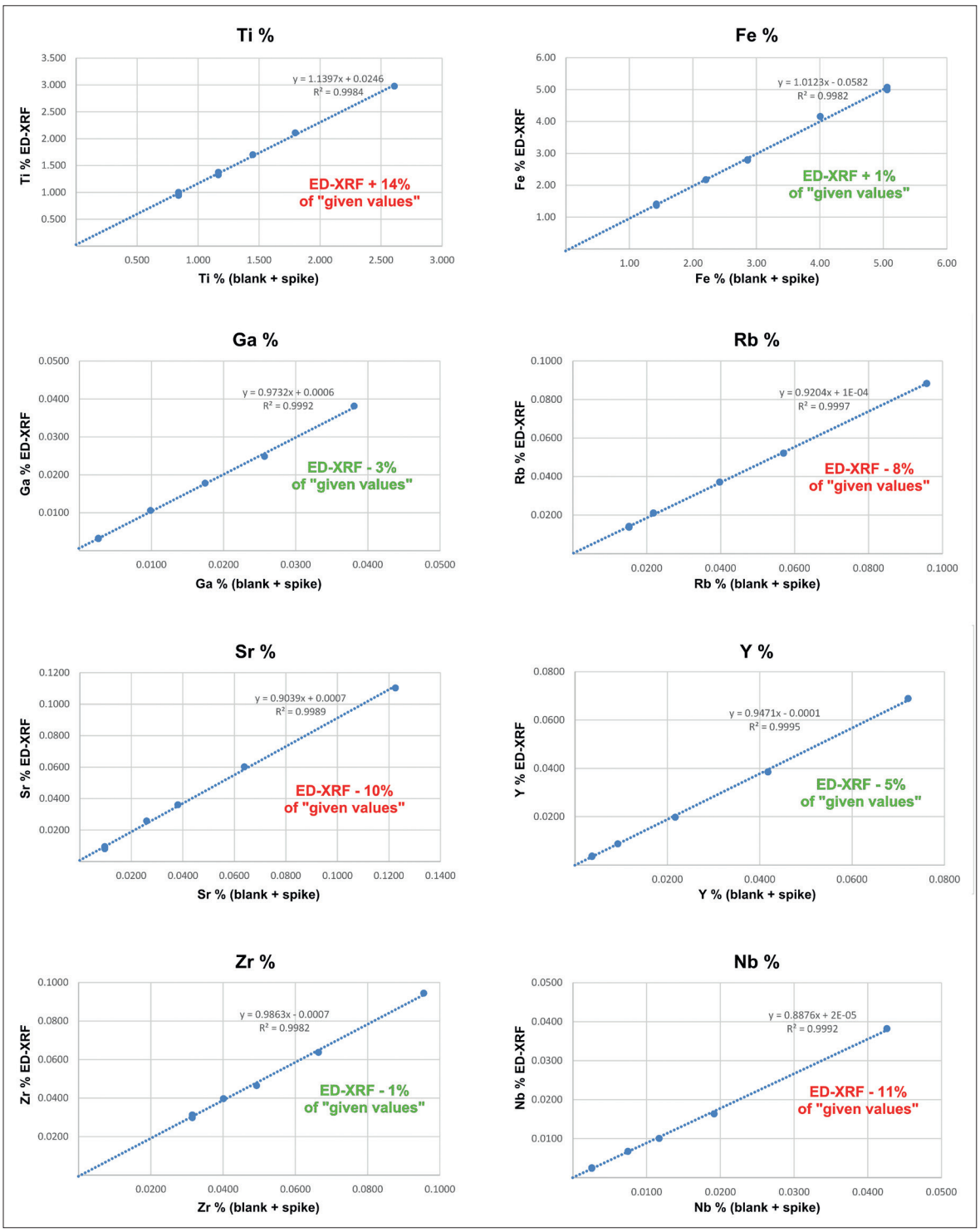


Figure 4: Independent analysis of the spiking sets with stationary ED-XRF (pressed pellets), data by Philipp Schulte, RWTH Aachen[21]

21. *Ibid.*

In the same project, Johannes Sterba at the Atomic Institute of Technical University of Vienna analysed the spiking sets for Sr and Zr with NAA[22]. The Sr correlation line had a slope of 0.88 or minus 12%, but the slope of the Zr line was 0.74, equivalent to 26% underreporting. Despite an intensive search, it was not possible to solve the strong discrepancy of the Zr values found by NAA, deviating from the given Zr aliquots as well as from its confirmation by the Aachen ED-XRF results.

In a collaborative project with University College London (UCL), the calibration of an Olympus Innov-X Delta portable instrument was first checked with the spiked samples, and afterwards pottery sherds were analysed in parallel with a total of three different, but identically calibrated brands[23]. The Olympus instrument provided a factory calibration based on fundamental parameters. Ga and Nb were not covered by the FP software. When quantified with the factory calibration, the Fe series gave slightly lower values than expected, but the correlation line surprisingly was non-linear. Only as a polynomial curve it crossed the intersect (**fig. 5**, upper left graph). The factory calibration did not correct for photon enhancement of Ti by increasing Fe concentrations (fig. 5, lower left graph). The Ti values, however, which means in the presence of a constant Fe background, showed perfect correlation, as well as the Rb and Sr values. Only Rb is shown here (fig. 5, upper right graph). The slope of the correlation line is close to 1.0. By contrast Y was overreported by 16% and Zr by a surprising 35% (fig. 5, lower right graph). In the case of Zr, different instruments and methods, respectively,

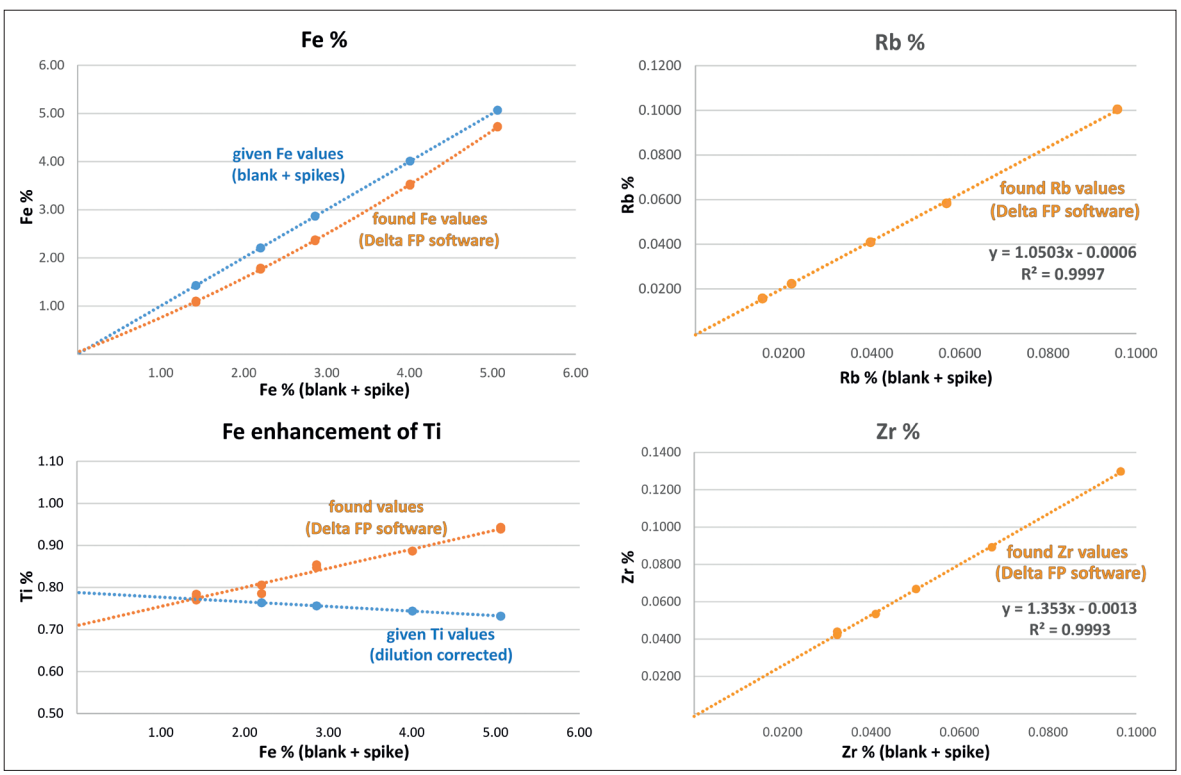


Figure 5: Independent analysis of the spiking sets with an Olympus Innov-X Delta portable instrument, data by Patrick Quinn, UCL[24]

22. Sterba 2022.
23. Wilke *et al.* 2018.
24. *Ibid.*

thus deviated from +35% to -26% when analyzing the same samples. Any inter-laboratory use of Zr figures without proper cross-calibration and validation may therefore be challenging.

It is important to recognise that calibration concerns each individual instrument. Indeed, manufacturers may have improved the software, particularly when launching new models with improved detector performance. Validation checks may then perhaps reveal better correlation values than shown here, but (cross-)validation is anyway mandatory.

Spectral deconvolution

Due to the complexity of XRF spectra, a calibration from scratch needs to start with the raw counts received by the detector, which means a bottom-up approach. The typical format of each raw dataset is a single column of about 2050 lines, the channel numbers, with a header and a tail, either as csv, txt or any proprietary file format of the respective brand manufacturer.

The raw counts plotted against the channel numbers provide the raw spectrum with element-specific peaks, but without peak allocation to the respective element. The raw count files need to be imported into a deconvolution software. The software will fit the channel numbers of the raw count spectrum with the energy lines, which specify the respective element from low to mid and high-Z numbers (for improvements with advanced machine learning approaches cf. Lee Drake in this volume). Additionally, the deconvolution software converts the raw counts into net counts by subtracting the background under the element specific peaks. The absolute numbers per raw count line depend on the acquisition conditions of the spectra, i.e. the X-ray source, geometry of tube vs. detector and sample surface, current, lifetime, beam filter, collimator and window film.

The deconvolution software used here is ARTAX 7. This is a demonstration software distributed by Bruker for free (the actually licensed version is ARTAX 8). The major purpose of peak deconvolution is to integrate the area under the net peak of the respective energy range and provide the element specific net counts. The integration is a complex mathematical operation[25], and the resulting net counts per element can be exported to Excel for further processing.

Matrix correction

The amount of net counts per element recovered by the detector strongly depends on the composition of the sample material, its matrix. The matrix with its dominant major elements exhibits different scales of photon absorption of minor and trace elements. For example, due to absorption by matrix elements the same mass fraction of Zr will result in significantly different numbers of photons/net counts received by the detector in a metal alloy background than in an alumino-silicate or Ca carbonate matrix. Calibration factors for individual elements therefore strongly depend on the matrix which the reference materials are composed of.

25. Cf. Elam *et al.* 2011.

The deconvolution software typically does not specifically correct for matrix effects, but applies a generalised matrix correction by ratioing to the Compton scatter (one of the two scatter peaks elicited by the X-ray tube). In pottery, which means a clay- and sand-based type of ceramics, the elements O, Al and Si contribute more than 85% of the mass, often more than 90%. The three elements together have an almost identical low mass absorption coefficient as compared to the mid-Z trace elements of interest. When using a clay matrix for spiking, the major variable element which still remains, causing matrix effects by absorption or enhancement, is Fe. In calcareous loams and in fabrics that contain shell gravel or have been tempered with calcite, the matrix is also affected, and correction of elements for Ca absorption is necessary.

Correction of Fe absorption and enhancement

With increasing Fe concentration the net counts of the elements with atomic number higher than iron received by the detector decrease, here shown for Zr (**fig. 6**). Since natural clays and pottery cover a broad range of Fe concentrations, the impact of photon absorption by Fe is relevant and needs to be corrected. The Fe spikes can be used to determine empirical influence coefficients

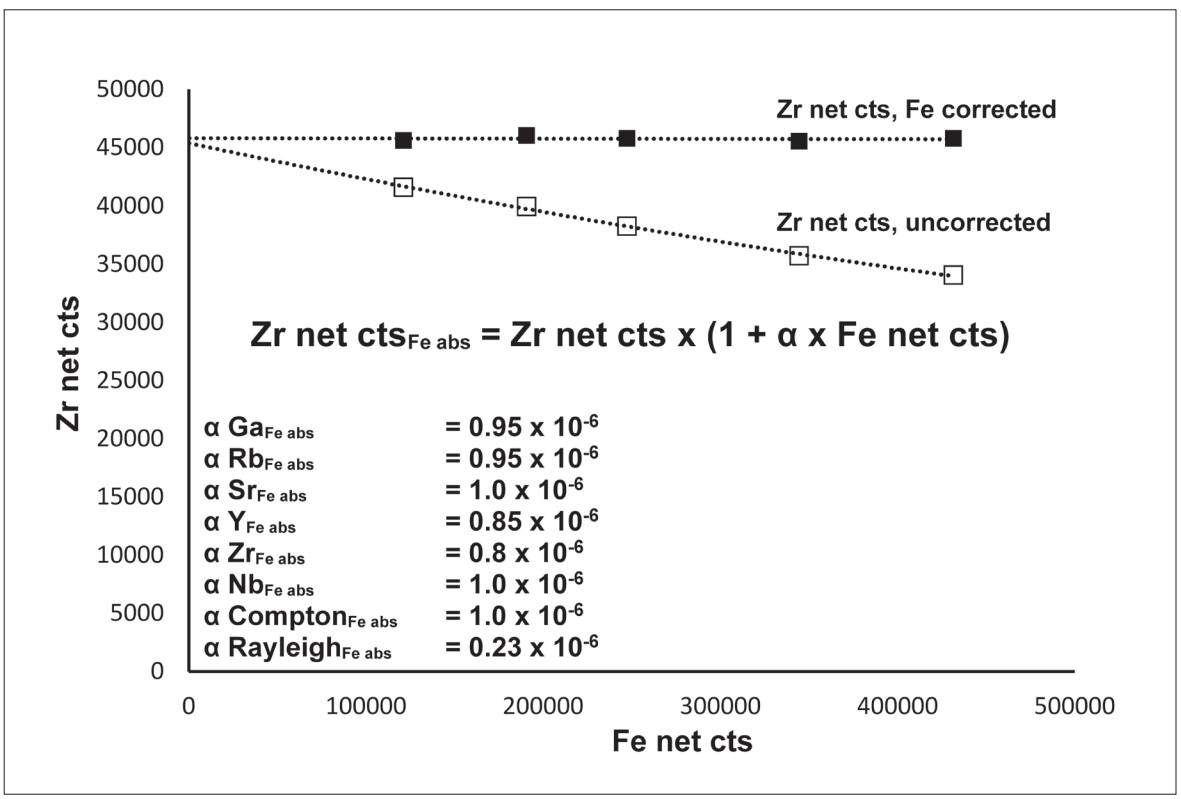


Figure 6: Lachance-Traill type absorption correction of Zr net counts by Fe with an empirically determined influence coefficient α ZrFe abs and further α values (target element concentrations corrected for dilution by the respective Fe spikes)

for Fe absorption of the higher elements of interest. It is state of the art to use Lachance-Traill type correction algorithms[26]. With the algorithm the polynomial Zr net count curve, which exhibits increasing photon absorption with increasing Fe abundance, is converted into a straight line parallel to the x-axis. The numerical value is empirically determined and is setting and software specific. The already mentioned scatter peaks are also impacted. In this case, the influence coefficient of the Compton scatter for Fe absorption is 1.0×10^{-6}, and that of the discriminative trace elements slightly differ from this value, which is an argument to use individual correction terms rather than to rely on a generalised matrix correction by just normalizing with the Compton scatter.

It is evident that the determination of such empirical correction coefficients depends on a concentration series and cannot be performed with normal reference standards, because there are no geochemical standards other than spiked ones which differ in just one element and are constant in all others.

There is one element of interest in pottery analysis, which is enhanced by Fe, namely Ti. The Fe spikes are used to determine an empirical correction term to compensate for enhancement of Ti (**fig.** 7). As shown before, the fundamental parameter software of the Olympus Innov-X Delta instrument did not correct for Fe enhancement of Ti.

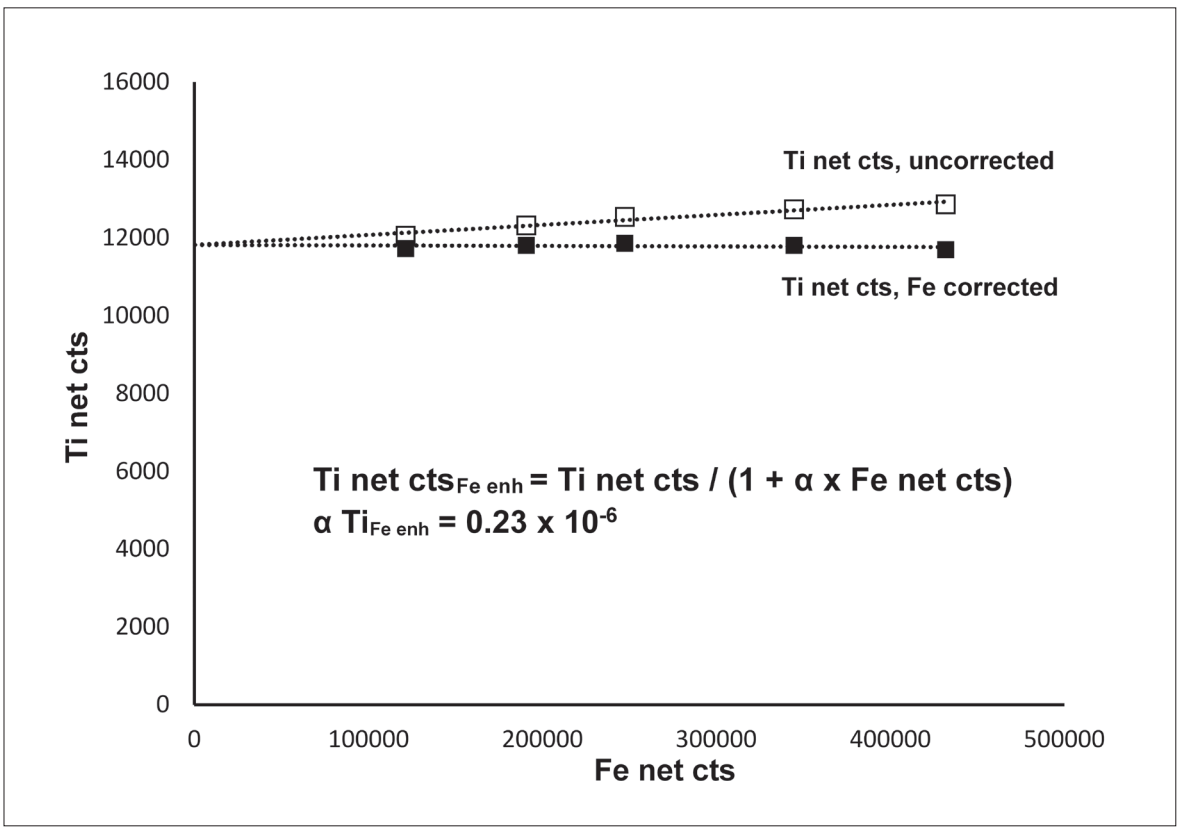


Figure 7: Lachance-Traill type enhancement correction of Ti net counts by Fe with an empirically determined influence coefficient α $Ti_{Fe\ enh}$

26. LACHANCE 1993; CONREY *et al.* 2014.

Spectral interference, Rb Kß over Y Kα

Part of the complexity of XRF spectra is the number of photon peaks with different energy level raised by many elements, in particular the overlap of the Kß peak of one element with the Kα peak of the next but one element, which is called spectral interference. Fundamental parameter calibration typically corrects for the respective overreporting of the next but one element, but not necessarily for all relevant elements under evaluation. The correction is made purely arithmetic based on the physically fixed ratios of the Kα and Kß peaks, but we need to check, whether our elements of interest are included in the interference correction.

Figure 8 provides the example of a missing or false interference correction of the Rb Kß overlap with the Y Kα peak. With increasing Rb concentrations in the spiked samples the reported Y net counts decrease. Above 400 ppm Rb the Y reporting totally collapses. This is not so much a shortcoming of the deconvolution software but a mere consequence of the totally unfavorable ratio of the Rb Kß to the Y Kα peak areas. In the example the correction of the underreported Y net counts is as follows: the Rb Kα and Kß peaks have a fixed ratio, empirically determined as Rb Kß equaling to 18% of the Rb Kα net counts. The net area under the overlapped Y peak can be determined manually as region of interest from 14.6 to 15.3 keV. The subtraction of the respective Rb Kα value times 0.18 from the respective region of interest then provides the interference corrected Y Kα net counts.

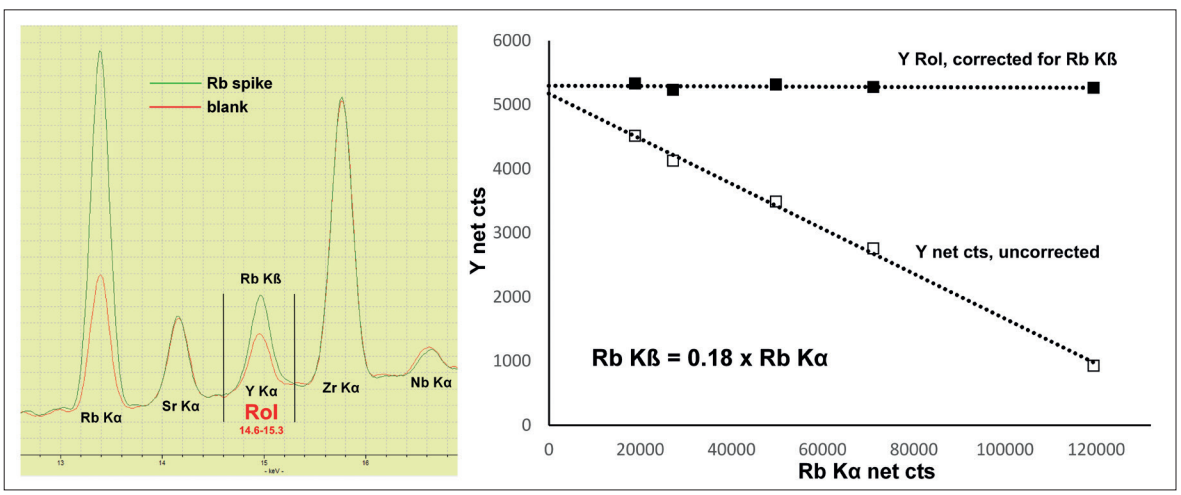


Figure 8: Spectral interference correction of Y Kα by Rb Kß with an empirically determined Rb Kß value

Spectral interference, Y Kß over Nb Kα

Y itself causes peak overlap of Nb, namely by the Y Kß peak on the Nb Kα peak. In this case the deconvolution software overreports the Nb Kα counts with increasing Y Kß counts (**fig. 9**). The Nb Kα net counts can be corrected with a Lachance-Traill type correction algorithm, which, however, is concentration dependent. At Nb concentrations below 50 ppm the interference coefficient α amounts to 0.24. For significantly higher Nb concentrations it needs to be adapted. Alternatively, the Nb Kα net counts overlapped by the Y Kß peak can manually be determined as region of

interest from 16.2 to 17.0 keV. Correction of Y interference on Nb by subtraction of the Y Kß net counts, empirically determined as 0.165 x Y Kα, then provides the interference corrected Nb net count value, which is concentration independent. Furthermore, the Y Kα net counts corrected for Rb interference are used in the equation, which outlines that these complex correction measures can only be performed on the level of net counts, which means, again as a bottom-up approach resulting in a composite calibration term.

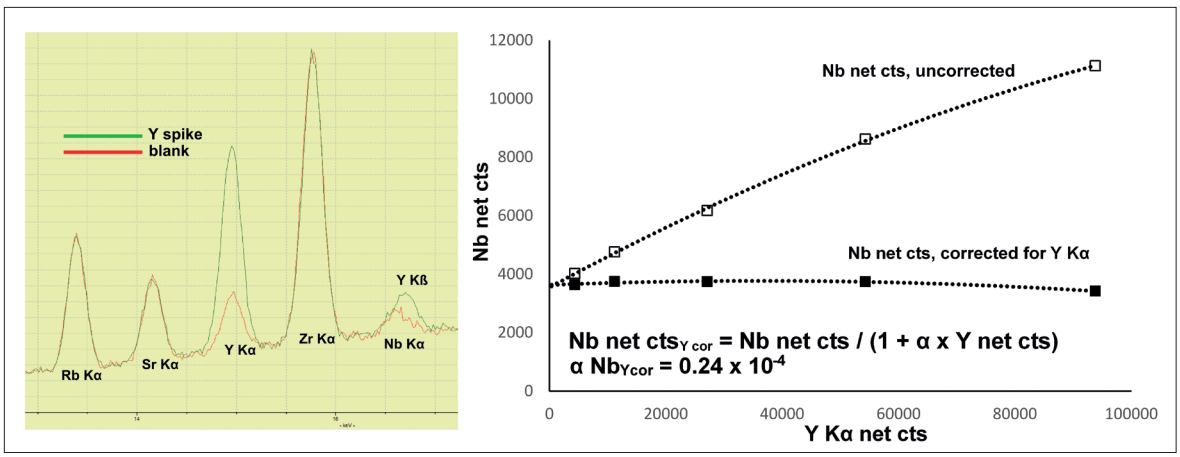


Figure 9: Spectral interference correction of Nb Kα by Y Kß with a concentration dependent Lachance-Traill type influence coefficient α $Nb_{Y\ cor}$

Finally, the Sr Kß peak overlaps with the Zr Kα peak. On an enlarged scale a slight decrease of the Zr Kα net counts with increasing Sr concentrations is detectable, but the overall effect is small, which means that the deconvolution software already applies for some correction. The remaining interference (corrected as Zr net $counts_{Sr\ cor}$ = Zr net counts x (1 + α x Sr net counts), α $Zr_{Sr\ cor}$ = 0.5 x 10^{-6}) was negligible, and since each correction step adds an arithmetic error, perfectionism does not pay off.

Pb absorption and spectral interference

Lead glazed pottery is frequently contaminated with Pb abundances even on the non-glazed surfaces of vessels and fragments. Elevated lead concentrations result in Pb specific matrix absorption and severe spectral interference effects on several discriminative trace elements – Ga, Rb and Y. Empirical Lachance-Traill type correction algorithms have been developed by simulating increasing Pb surface abundances on fired clay samples with lead acetate sprayed on 4.0 µm polypropylene film. For paste surface contaminations with up to approximately 1% w/w elemental Pb concentrations, full compensation could be achieved[27].

27. Forster, Grave 2013; Wilke 2016.

Ratioing with the tube scatter

As already mentioned, the Compton scatter is used in fundamental parameter calibrations for ratioing or normalisation of other net counts. The Compton and the Rayleigh scatter are two instrument specific photon peaks. They are scatter peaks caused by the tube metal in the sample. Thereby the Rayleigh scatter behaves like the element scatter of the tube metal, in many brands a Rhodium tube, and the Rayleigh scatter then looks – so to speak – as if there is Rh in the sample. The Compton scatter photons have lower energy than the tube element and are positioned left of the Rayleigh peak. The Compton peak is rather broad and quite unspecific, whereas the Rayleigh scatter is directly proportional to the current, the lifetime and the window coverage, and is therefore highly appropriate for normalizing spectra.

The Rayleigh peak indeed behaves like a regular element peak and is subject to Fe absorption as well as to matrix and density effects of the sample, very similar to the mid-Z elements. Rh is the preferred tube element, because the Compton and the Rayleigh scatter of Rh do not interfere with the mid-Z elements of interest, but are closest and most similar to them. Before normalizing with the Rayleigh scatter in a clay matrix, the Rayleigh net counts need to be corrected for Fe absorption as well, although the interference coefficient is small (fig. 6).

What, however, is even more important is distance correction with the Rayleigh scatter. Photon intensity decreases by the square of the distance of the sample surface from the detector. In non-destructive XRF of curved vessel sherds, distance differences and surface irregularities are ubiquitous. In **Figure 10** the decrease of the Zr and the Rayleigh (Rh Kα) net counts with increasing distance of the sample from the instrument window is shown. Ratioing the Zr net counts with the Rayleigh net counts corrects the Zr values over a broad distance range. Nevertheless, samples should be positioned as close as possible to the detector, since any arithmetic correction adds additional uncertainty. As mentioned before, the Rayleigh scatter, like any other element photons, is impacted by several parameters, and measurement conditions should therefore be as identical as possible.

Weight % calculation template in Excel

For each discriminative element the respective Lachance-Traill type correction algorithms, normalisation with the Rayleigh scatter and the finally determined calibration factor (slope of the absorption/enhancement and interference corrected as well as tube scatter normalised regression line of the four spiked concentrations plus the blank) were combined into a single term per element, by which the net counts need to be multiplied. A simple template in Excel was built, which relates the net counts, imported from the deconvolution program (here ARTAX 7) with the respective weight calculation term established with the calibration procedure. The conversion of net counts from hundreds of analyses into weight % concentrations is then performed in a single copy and paste step.

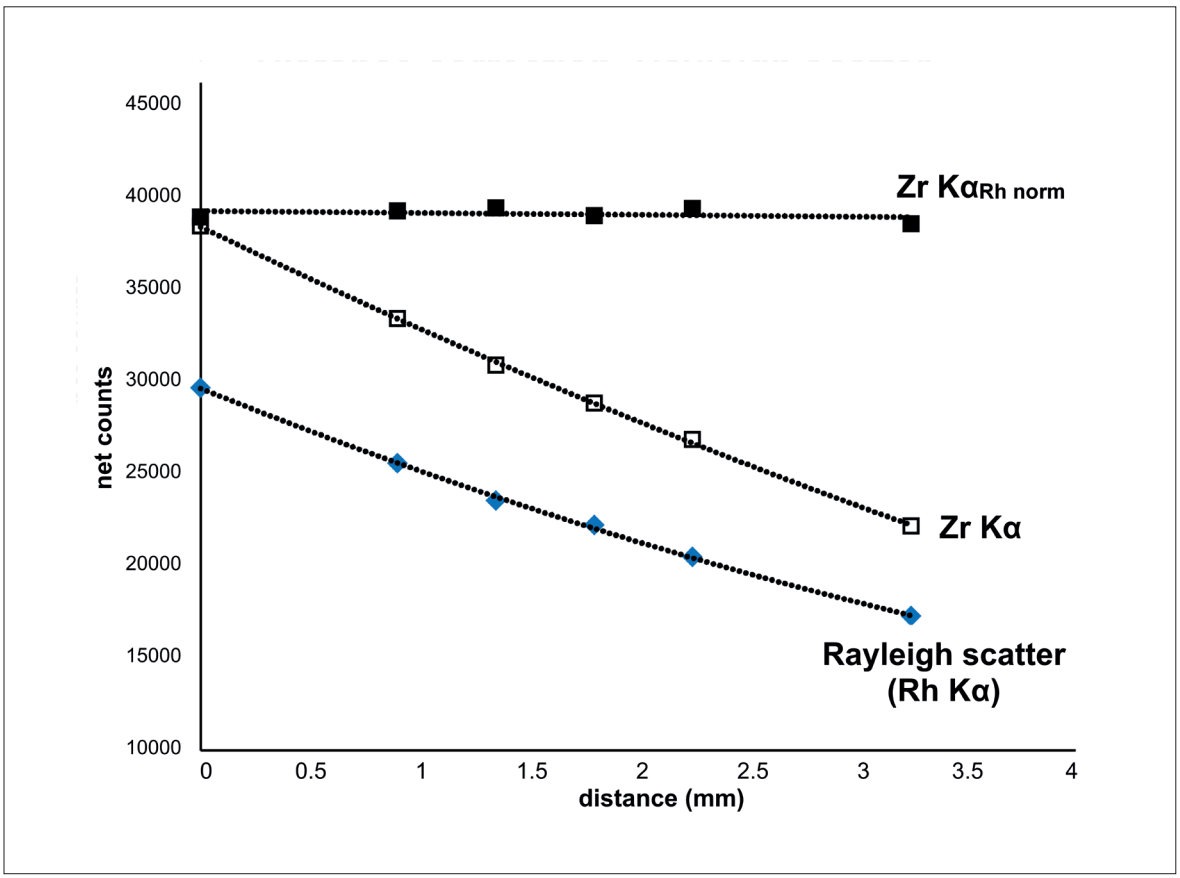


Figure 10: Correction of sample distance from the instrument window in mm by normalisation to the Rayleigh scatter (Zr net counts as an example, Rh as tube metal)

Non-destructive quantification of Al and Si

In alumino-silicate based ceramics, O, Al and Si are the major constituents. In this matrix the measurement depth (also called penetration depth, but of the excited photons) of the low-Z elements up to Cl is in the low µm range. Non-destructive and pressed pellet ED-XRF analysis of low-Z elements is therefore a mere surface measurement, and its accuracy depends on the homogeneity of the sample material. Thus, a reliable non-destructive quantification of Al and Si in ceramics is unrealistic, when even small amounts of quartz sand of whatever size distribution must be expected in the fabric. In these cases an underreporting of the Si values by matrix absorption is inevitable. Furthermore, the low-Z photons are strongly absorbed by ambient air, and measurement under vacuum or Helium flush "between sample and detector" is required.

Since C and O can neither be measured by ED-XRF nor by WDXRF analysis at all, the mass fractions of the major and minor elements are converted into its oxides in geology, and afterwards normalised to 100%. This provides reasonable numbers in weight % for major and minor element concentrations in rocks and sediments, which in geology are often more important than the trace elements in ppm. As vacuum and Helium flush under field conditions is unrealistic, universal geochemical factory calibrations from low-Z to mid-Z elements with automated filter and voltage

change are of limited value, particularly for measurements of heterogenous sample compositions. In ceramic provenancing the discriminative potential of Al and Si as major elements is anyway small, and the mass fractions of Ga as a proxy of Al can be taken as a relative index of the alumino-silicate content and as a marker of the plasticity of the paste before firing. Thus, for ceramic provenancing, similarly to the well established procedure in obsidian analysis, a single constant setting is advantageous, e.g. 40 kV, 10 µA, Al or Ti beam filter, large spot size (collimator) and 60 to 120 sec. lifetime, depending on the detector performance.

Summary and conclusions

The basics of the calibration approach with spiked fired clay blocks have been described before[28]. The empirically established correction terms and the resulting calibration factors are instrument and setting specific. As outlined above, the spiking sets can also be used for validating calibration factors as well as for checking proper absorption, enhancement and spectral interference correction of empirical and fundamental parameter calibrations, regardless of the specific XRF method. Reproducible calibration of instruments is decisive when ceramic provenancing is intended, where the composition of unknown sherds needs to be compared and attributed to a multitude of potential reference groups, established with different instruments through time, and with often very similar geochemical pattern.

However, there is no doubt that many users of portable instruments still rely on the various factory calibrations and restrict themselves to a point-and-shoot approach, where they read and trust the figures on the display. Thus, the concerns expressed by Shackley[29] and Speakman and Shackley[30] are still actual. In 2017, the author published a commentary summarizing the principle obstacles of non-destructive XRF based on limited calibration and validation efforts[31]. The conclusions were: data must be fit for purpose. Many research tasks do not need accuracy, but consistency of semi-quantitative data may be sufficient. This is often the case, if match or distinction of a set of study objects is of concern, and all analyses have been performed with the same instrument under identical conditions. Even comparison based only on net counts may sometimes be sufficient to answer a particular question, thereby abstaining from any instrument calibration and validation.

Other research tasks, however, and ceramic provenancing in particular, definitely depend on accuracy. Due to the peculiarities of the study material, non-destructive XRF analysis of pottery is at present just the best, but by no means an ideal analytical tool. Therefore its intrinsic uncertainties should not be further enhanced by an avoidable lack of calibration and validation diligence.

28. Wilke, Rauch, Rauch 2016.
29. Shackley 2010.
30. Speakman, Shackley 2013.
31. Wilke 2017.

Data availability statement

The data of this study are available upon request from the corresponding author.

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3

Collaborative research: inter-device comparisons and networks

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Intercomparison in pXRF spectrometry: methodological approaches for the study of ceramics

Abstract

The increasing use of portable X-ray fluorescence (pXRF) spectrometry for ceramic elemental analysis has expanded data acquisition but presents challenges in sensitivity, accuracy and precision, and inter-laboratory comparability. Sensitivity remains lower than traditional techniques such as WDXRF, ICP-MS/OES, and NAA, particularly for trace and light elements, underscoring the need for standardised methodologies to ensure reproducibility across instruments and research teams.

The pXRF Ceramic Users Network (pXRF-CUN) programme (2021–2025), led by CEAlex, was established to improve interoperability in pXRF applications through harmonised protocols and inter-laboratory comparisons. As part of this initiative, an intercalibration kit was developed, consisting of 18 ceramic samples and international standards, distributed in both glass bead and powdered forms. Initial results, benchmarked against ICP-MS and WDXRF, highlighted key factors affecting detection sensitivity, resolution, and sample preparation.

A second phase introduced a new ceramic intercalibration kit with 18 fired bricks from clays of known provenance, designed to represent a range of the chemical variability of the clayey resources used for ceramic manufacturing in the Eastern Mediterranean. The intercomparison of ten portable

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XRF systems provides critical insights into data quality and methodological standardisation, supporting ongoing efforts to enhance the reliability and interoperability of pXRF in ceramic studies.

Keywords

Ceramic analysis, clay raw materials, data reproducibility, inter-laboratory comparison, intercalibration kits, methodological standardisation, pXRF spectrometry

Introduction

The issue of equipment interoperability and the subsequent challenges of integrating data from different laboratories is a recurring concern in the study of ancient materials[1]. Over the past decade, the proliferation of pXRF spectrometers has led to a significant increase in publications providing primarily quantitative data. This surge has quickly raised the question of how to effectively compare and reuse this data[2] across different research groups, especially in the context of comparative studies aimed at understanding material composition and provenance.

We will not delve into the well-documented advantages (e.g., ease of use, speed, cost-effectiveness) and disadvantages (e.g., limited element range, precision) of pXRF equipment, as these have been extensively covered in the literature[3]. However, the increasingly complicated export permit requirements for archaeological objects and sherds in some countries, coupled with the need to streamline sampling procedures, have driven the increased adoption of this tool[4].

Intercomparison issues between pXRF and laboratory-based characterisation methods have been addressed across various multidisciplinary approaches encompassing application, including geology, geochemistry[5], and archaeometry (for the study of both homogeneous materials, such as obsidian[6] and glasses or heterogeneous materials[7], such as rocks and ancient ceramics). Most of the research focuses on comparisons of data from Neutron Activation Analysis (NAA), Wavelength Dispersive X-ray Fluorescence (WDXRF) or Inductively Coupled Plasma Mass/Optical Emission Spectrometry (ICP-MS/OES) methods with pXRF[8].

Only a few studies have focused on the intercomparison of portable equipment, and these primarily concern obsidian[9] or other lithic materials[10]. Specialists studying ancient ceramics have adopted a similar approach, comparing laboratory data with data acquired using portable

1. Hein *et al*. 2002.
2. Hunt, Speakman 2015; Shackley (ed.) 2011; Speakman, Shackley 2013.
3. Benech *et al*. (eds.) 2019; Frahm 2019.
4. Hegewisch, Daszkiewicz, Schneider (eds.) 2021.
5. Lemière 2018.
6. Frahm 2019; Goodale *et al*. 2012.
7. Leck *et al*. 2018.
8. Suda *et al*. 2018.
9. Martindale Johnson *et al*. 2021.
10. Da Silva, Triantafyllou, Delmelle 2023; Goodale *et al*. 2012.

equipment[11]. However, no large-scale studies have yet presented results comparing data from different portable devices.

Given these challenges, and with the need for greater consistency and comparability in the field, a network of pXRF users in the field of ceramics (i.e. the pXRF Ceramic Users Network [pXRF-CUN]), supported by the French CNRS International Research Network, was established in 2021. The network currently comprises 14 laboratories from eight countries (**fig. 1**): France (four laboratories: Centre d'Etudes Alexandrines (CEAlex) in Alexandria, Centre Camille Julian (CCJ) and Centre de Recherche et d'Enseignement des Geosciences de l'Environnement (CEREGE), Archeosciences Bordeaux), Great Britain/Greece (The Marc and Ismene Fitch Laboratory, BSA, in Athens), Greece (NCSRD "Demokritos in Athens" and Keramos Research Group in Patras), Cyprus (Science and Technology in Archaeology and Culture Research Center (STARC) and the Archaeological Research Unit of the university of Cyprus [ARU]), Spain (The Archaeological and Archaeometric Research Unit of the University of Barcelona ERAAUB, IAUB, in Barcelona), Lebanon (Lebanese Atomic Energy Commission [LAEC]), Austria (Vienna Institute of Archaeological Sciences [VIAS]), Germany (Munich[12] and Cologne universities). Initially focused on the Mediterranean region, this network project has gradually expanded. Its primary aim is to compare the validity and repeatability of results



Figure 1: Laboratories involved in the pXRF-CUN

11. Quinn *et al*. 2021; Wilke 2017.
12. Munich University was indirectly involved in the project through the affiliation of Michaela Schauer and the data produced within the framework of her post-doctoral position.

obtained using various pXRF devices. The publication of analytical metadata associated with each instrument will ensure that the data produced is robust and shareable and can be used long-term for potential intercalibrations.

Methodology

Ceramics are inherently heterogeneous materials with specific characteristics that can complicate direct X-ray analysis without appropriate sample preparation. The thickness, mass absorption coefficient, and density of the material are key factors influencing X-ray transmission through the sample. These properties affect the penetration depth and intensity of the X-rays interacting with the material. In X-ray fluorescence (XRF) analysis, both the 'matrix effect' – where the composition of the material influences the emission and detection of X-rays – and the grain effects – which arise from the material's internal structure, including particle size and distribution – must be considered. These factors, along with the complex interactions between incoming and outgoing X-rays, impact the quality and accuracy of the analytical results, highlighting the need for meticulous sample preparation and rigorous measurement protocols.

This was one of the key challenges faced by the pXRF-CUN, which led to the development of a common methodology, including the creation of a standardised kit designed to mitigate these issues and ensure consistency across different laboratories. The first step involved developing a common 'kit', based on the archaeological ceramic collections of the participating teams. Initially, a homogeneous preparation through alkaline fusion was carried out from these specimens (see below). However, after further consideration, the approach was revised, and a second kit consisting of ceramic discs made from reference clay materials was produced (see below).

Archaeological ceramics and reference material

To compare the analytical performance of different pXRF analysers and calibrate them accordingly, a first intercalibration kit was developed in 2021. This kit consisted of three international standards (97B, 98B, AN41) and an initial selection of 15 ceramic archaeological samples collected by CEAlex, CCJ, and the Laboratory of Medieval and Modern Archaeology in the Mediterranean (LA3M).

Fused beads preparation

Glass beads, typically used as a support medium for WDXRF analysis, were prepared at the CEREGE by mixing ceramic powders with a flux composed of lithium metaborate (LiM) and tetraborate (LiT). The ceramics were first finely ground using a planetary Micro Mill Pulverizette 6 (Fritsch) with a zircone bowl and seven zircone balls at 400 rpm/min for 2 minutes and one repetition in reverse mode. One gram of powder was mixed with 5 grams of flux prepared to limit the concentration of bromide in the resulting disc (49.9% LiT / 49.9% LiM / 0.2% LiBr). A Claisse LeNeo fusion instrument (MalvernPanalytical) was used to prepare the beads with a protocol consisting of heating the mixture in a Pt crucible at 1065 °C with some steps of crucible rocking at various angles and speeds to achieve the best possible homogenisation of the mixture. This preparation was initially chosen to homogenise the ceramic material and minimise matrix effects during pXRF measurements. This fused beads kit, along with powdered samples, was then distributed to the partners of the network.

Clayey reference raw materials

Given the widespread use of portable analysers for *in situ* analysis, mainly on fresh breaks, a new intercalibration kit was developed to include specimens with a sample matrix more representative of typical ceramic materials analysed.

The reference raw material comprises 18 clayey sediments belonging to the teams' raw material collections. These samples were selected to ensure that their overall compositional range of major chemical elements well covers the variability of the clayey resources used for ceramic manufacturing in the Eastern Mediterranean.

Fired clay disc preparation

Eighteen ceramic discs, each measuring 32 mm in diameter and 7 mm in thickness, were produced from clay raw materials (**Table 1**, **fig. 2**). The selection of sediments, collected by the University of Patras, NCSRD Demokritos, the Fitch Laboratory and CEAlex encompasses part of the most common variability of the clays used for ceramic manufacturing. The clay discs were prepared in the laboratory facilities of the Keramos Research Group of the Department of Geology, University of Patras, Greece, following a slightly modified version of the method described by Allegretta[13]. The selected samples were dry-sieved using a 500-micron sieve. After quartering, an aliquot of 950 g of dried clay was weighed and sprayed with water using a nebuliser until it reached 5% water content by weight. The moistened mixture was then sealed in a plastic bag, shaken thoroughly, and left to mature for 24 hours to achieve uniform moisture distribution. A 15 g portion of the prepared clay was then introduced into a 32 mm evacuable die set and compressed at 15 tonnes using a mechanical press. The die set consists of a base, a body, two pressing pellets (between which the sample is compressed), and a plunger. Also, two O-rings ensure proper sealing and enhance performance. The dies are supplied with an extractor cup or ring to facilitate the easy removal of the pressed sample. The die also includes an evacuation tube, which allows the attachment of a vacuum pump to assist in moisture removal during the pressing process, if required.

The clay discs were then dried at 105 °C overnight. The final step comprised the firing of all prepared discs in a Vulcan 3-550 box laboratory furnace with programmable controls at 950 °C, following a heating ramp of 150 °C/h, with a 1-hour dwell time at the target temperature. A total of ten kits were produced, with one kit allocated to each partner of the network. It should be noted, however, that a single kit was analysed by all research partners, and its results were used for this intercomparison study.

Colour recording

Accurate colour recording is essential for distinguishing and comparing ceramic materials, as it provides valuable insights into their composition and firing conditions. Initially, all samples were characterised in terms of their colour in both unfired and fired states, using the conventional Munsell Soil Chart method under daylight conditions. The recorded colour values are presented in Table 1.

It is acknowledged that this method is inherently subjective, a colour perception can be affected by observer variability and lighting conditions. In contrast, reflectance spectroscopy, a technique

13. Allegretta *et al*. 2017.

Sample	Region	Description	Unfired	Fired
AGS7	Aegina	Aegina white clay	5Y 6/2-7/2 light olive gray-light gray	10YR 8/4 very pale brown
Archangelos	Rhodes	Archangelos potters mix	10YR 5/3 brown	5YR 5/8 yellowish red
C4	Corinthia	Marls	Gley 1 6/1 greenish gray	10YR 7/3 very pale brown
C9	Corinthia	Marls	5YR 4/3-4/4 reddish brown	2.5YR 4/4 reddish brown
CHOM2	Crete	Chomatas	5YR 4/4 reddish brown	2.5YR 4/6-4/8 red
EVGS 15/3	Evia	Styra	10YR 6/3 pale brown	2.5YR 5/6 red
EVGS 15/32	Evia	Kymi	2.5Y 7/2 light gray	7.5YR 6/4 light brown
EVGS 16/3	Evia	Lelas river; Phylla clay pit; Lelantine plain clay pit	2.5Y 7/3 pale yellow	5YR 6/4 light reddish brown
EVGS 16/9	Evia	Manika	7.5YR 3/4 dark brown	2.5YR 4/6 red
HS33	Eastern Achaea	Marls, sandy marls, and sandstones	10YR 7/3 very pale brown	5YR 6/4 light reddish brown
HS45	Eastern Achaea	Marls, sandy marls, and sandstones	2.5Y 7/2-6/2 light gray-light brownish gray	5YR 6/6 reddish yellow
HS62A	Eastern Achaea	Marls, sandy marls, and sandstones	2.5Y 6/3 light yellowish brown	10YR 8/3 very pale brown
KARDA3	Kos	Kardamenia	5Y 5/2 olive gray	5YR 6/6 reddish yellow
NB Egypt	Thasos	Clay sediment – Thasos 2022, one of the sites surveyed by Yvon Garlan	7.5YR 5/4 brown	2.5YR 5/6 red
ND Egypt	Nile Delta Egypt	Silts from the Nile Delta	7.5YR 4/1 dark gray	2.5YR 4/8 red
THRAP5	Crete	Thrapsano	5YR 5/4 reddish brown	2.5YR 5/8 red
TSAMBIKA7	Rhodes	Tsambika	5Y 5/2 olive gray	10YR 7/6 yellow
WA22	Western Achaea	Sandstones, sandy clays and clayey marls	2.5Y 4/4 olive brown	2.5YR 6/8 light red

Table 1: Origin of the clay samples used for the ceramic discs kit; colours of unfired and fired samples at 950 °C, using the Munsell Colour Chart



Figure 2: Clay discs forming the kit in fired state at 950 °C

that uses the excitation energy in the Visible-Near Infrared (350–2500 nm) wavelength range of the electromagnetic spectrum, offers a more accurate and objective approach to colour determination by deriving tristimulus values from the visible region[14]. In this study, colorimetry data were obtained from both unfired and fired clay discs using a SpecTERRA SM-3500 Spectral Evolution portable spectrometer at the Minerals and Rocks Research Laboratory, Department of Geology, University of Patras, in Greece.

The calibration of the instrument was performed using a white reference plate prior to each measurement. The colour of the clay discs was assessed by transforming the visible spectra (350–780 nm) into X, Y, and Z values, following the standards of the International Commission on Illumination (CIE, 1931). These values were then converted to Munsell and CIE L* a * b * notations using the Munsell Conversion Program (Wallkillcolor v. CMC25[15]). The resulting colour palette of the clay discs is illustrated in **Figure 3**.

14. Xanthopoulou, Karountzou, Iliopoulos 2025.
15. Van Aken, H. Munsell Conversion Software (Version CMC25).

Equipment

The network's initial equipment comprised 11 pXRF analysers (**Table 2**), including three Bruker models (Tracer IV, Tracer 5g and Titan S1), two Olympus hand-held analysers (Vanta C and Innov-X Delta), one Hitachi X-MET8000 Expert GEO, and five Thermo-Fisher Niton Xl3t GOLDD+ analysers.

These devices were used in the preliminary intercomparison during the initial trial of creating a pXRF calibration kit, which consisted of archaeological samples and standards prepared in the forms of glass beads, powders, or sherds. However, this "kit" was not analysed in all three forms by every device; nevertheless, each of the 11 analysers measured it in at least one of its forms.

The preparation and measurement of the second kit was conducted a year after the first, with minor variations in the equipment used for the final intercomparison. This difference can be attributed to factors such as the end of the life expectancy of certain devices, including the Bruker Tracer IV and the Olympus Innov-X Delta, or the unavailability of others, including the Bruker Titan S1 analyser. It is worth noting that the only changes in pXRF analysers used during the IRN-pXRF CUN Ceramic Users Network project were this loss of certain models from the study, and that the second phase of the intercomparison saw the addition of a new model, the SciAps Quantum X-200.

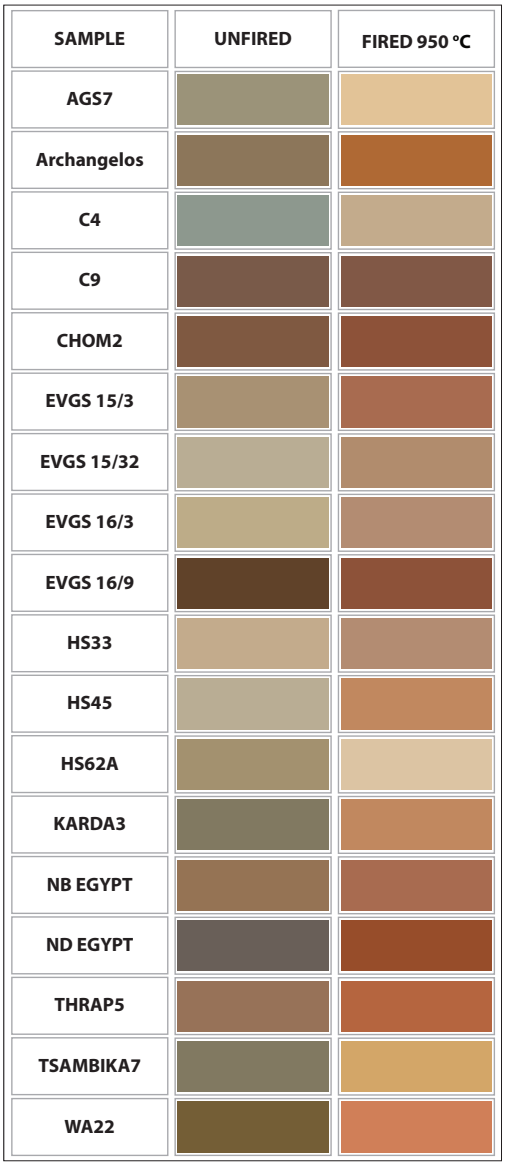


Figure 3: Colour palette of all ceramic disc samples obtained through colourimetry (vis-NIR)

Therefore, the results of our study are presented here as an intercomparison of a total of 10 hand-held analysers, belonging to five different models: one Bruker Tracer V, one SciAps X-200, two Hitachi XMET8000, one Olympus Vanta C; and five Thermo-Fisher Niton Xl3t GOLDD+ analysers (Table 2). During the meeting of the Network in Cyprus in 2023, all the partners of the network met with their pXRF analysers to analyse the same prepared set of ceramic discs. It was deemed essential for all devices to analyse the same set in order to minimise variability in the resulting dataset, thereby enabling a more accurate and consistent comparison of their performance.

These devices have different features (Table 2): for example, all of the Niton analysers have a silver anode, while the Vanta, Hitachi, SciAps and Tracer devices are equipped with rhodium anodes. Each device was used with its specific measurement mode: mining mode for four Niton, Hitachi and SciAps; TestAll Geo for the fifth Niton; Geochem for the Vanta; and Mudrock Dual for the Tracer. Each disc was measured three times on different locations: for 6 minutes using two of the

	NITON XL3t GOLDD+			
Tube	Anode Ag, 50kV, 200 μA	Anode Ag, 50kV, 200 μA	Anode Ag, 50kV, 200 μA	Anode Ag, 50kV, 100 μA
Detector	High performance, semiconductor	High performance, semiconductor	Geometrically optimised large area drift detector	Geometrically optimised large area drift detector
Analysis mode	Mining	Mining	Mining/Soil	TestAllGeo
Analysis time	90s, 90s, 60s, 120s	180s	120s	60s, 60s, 60s, 120s
Filter type	Cu, Ti, Al	Cu, Ti, Al	Cu, Ti, Al	Cu, Ti, Al
Spot diameter	8 mm	8 mm	8 mm	8 mm
Name of the laboratory	CEAlex (2 devices)	LAEC	Demokritos	Munich
	Olympus VANTA C	**HITACHI X-MET8000 Range**	**SciAps x200**	**Bruker Tracer 5g**
Tube	Anode Rh, 4W, 40 kV, 200μA	Anode Rh, 4W, 50kV, 200μA	Anode Rh, 5W, 40kV, 200 μA	Anode Rh, 4W, 50kV, 195μA
Detector	SDD 13 mm2	25 mm2 high resolution silicon-driftSDD	SDD 20 mm2	SSD 20 mm2
Analysis mode	Geochem	Mining	Mining	Mudrock Dual
Analysis time	60s, 90s	120s	30s, 90s	150s, 150s
Filter type	Cu, Ti, Al	Automatic 6-position filter changer		Cu, Ti, Al
Spot diameter	10 mm	8 mm	4 mm	8 mm
Name of the laboratory	Archeosciences Bordeaux	ARU, STARC	CEREGE	Vienna

Table 2: Characteristics of the pXRF devices involved in the pXRF-CUN for the analysis of the ceramic discs kit

Niton analysers, 5 minutes for the third Niton and the Tracer, 3 minutes for the fourth Niton, 2.5 minutes for the Vanta, and 2 minutes for the fifth Niton, Hitachi, and SciAps.

Each laboratory employed its own methodology (calibration, standard monitoring) and carried out the analyses using its own measurement conditions and parameters (mode/algorithm inherent in the equipment, analysis duration, and filters). However, all laboratories followed a common approach by performing three measurements on three different areas of each sample. The averages of these three measurements per sample was then used for the intercomparison of the obtained results. In parallel two other techniques were used to provide elemental composition: ICPS-MS

(Perkin Elmer Nexlon 300X) for trace elements and ICP-OES (Agilent 5800 VDV) for major elements and WDXRF[16] for both major and trace elements.

Results

All the quantitative results were further processed by considering 21 elements common across almost all the devices (Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba and Pb). Although we typically work with compositional data for ceramics expressed as oxides, in this study we chose to compare elemental results.

For the comparison of the compositional data acquired using individual pXRF devices and different quantification methods the data were not further processed but regarded as original. A normalisation of the data or alignment according to a hypothetical complete composition of 100 wt% was not considered as the quantification methods provided by the different system manufacturers are expected to imply too many unknown parameters and prerequisites. Apart from this, compositional data provided in literature commonly are based on these quantification methods unless a calibration is explicitly confirmed.

Comparable devices

The results collected using the two types of kits (beads and ceramic discs) indicated that the portable devices were comparable to each other, although differences were observed in terms of the limits of detection, analytical precision, and the absolute total amount quantified (**fig. 4**). Nevertheless, the main problem with the first kit ("fused beads") concerned the dilution of the ceramic material in the flux used to make the glass bead, which impaired the limit of detection for certain elements, such as V, Mn, Ni and Cu, depending on the hand-held model and the protocol of data acquisition. Furthermore, the high lead content of two ceramic samples in the glass-beads kit interfered with the detection of rubidium, rendering this kit ineffective.

In order to investigate sample preparation and matrix effects, and to further expand on the methodological question, the results of a single ceramic sample prepared in three forms (bead, powder, and sherd) and analysed by the same laboratory (CEAlex) are presented in **Figure 5**. Across the three examples (XLYN0308, XLYN1163, and XLYN1583), elements such as Al, Fe, Mg, Ca, and, to a lesser extent, K are detected at lower levels in the glass bead than in the sherd or even the powder. This is also the case for V, Cr, Cu, Zn and Sr. As a result, the deviation from the expected value is notably higher in the glass beads confirming that this sample support type is unsuitable for our study of intercomparison and leading the different partners to focus the pXRF intercomparison on the ceramic disc samples.

The results presented below will focus solely on the second 'ceramic discs' kit prepared by selected clayey raw material.

16. Georgakopoulou *et al*. 2017.

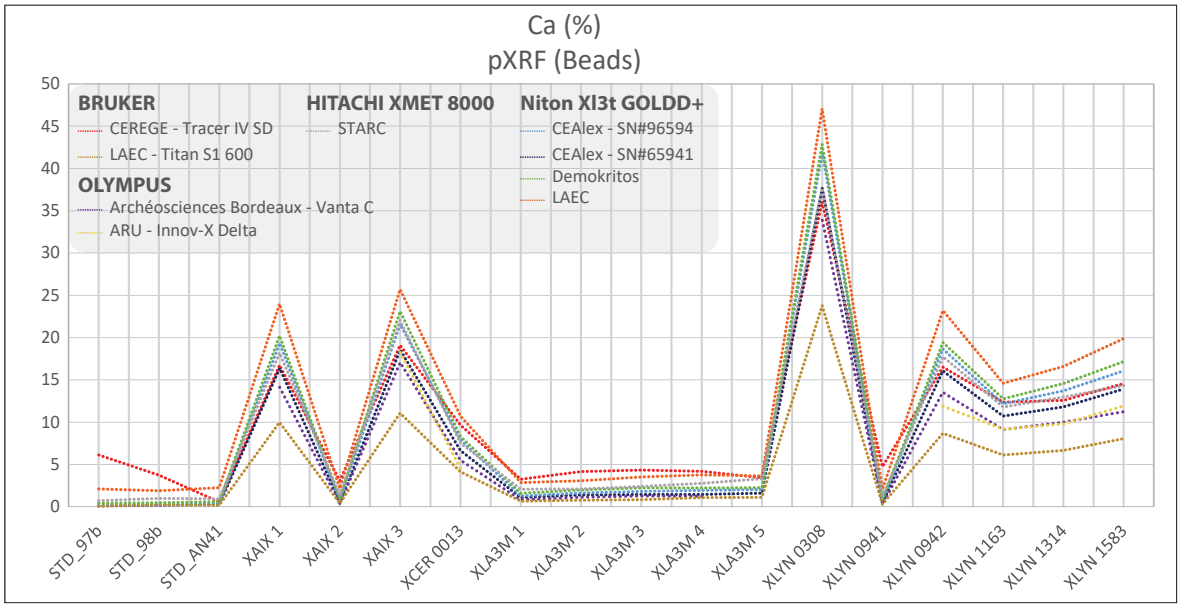


Figure 4: Behaviour of pXRF equipment with samples prepared as glass beads – example of Ca content (%)

Accuracy: comparison with robust methods (WDXRF and ICP-MS and OES)

Two comparable robust methods

Firstly, both types of robust analysis produced comparable results, aligning consistently with international standards (**Table 3**) and the ceramic kit samples (**Table 4**).

The content measured by the two types of equipment are therefore reliable and comparable with the data produced by portable equipment. However, some differences were observed (Table 4). Specifically, significant discrepancies between the two measurement methods were noted only for silicon, with WDXRF values consistently higher than those of ICP-OES, and for potassium, where ICP-OES values were significantly higher than those obtained by WDXRF. For all the other elements, whether major or trace, the measurements obtained by both methods were closely aligned.

Sodium was not detected by the portable equipment and is therefore excluded from the following comparison. As for Nb, its values were only detected through mass spectrometry (ICP-MS) and will be used for comparison with the data obtained by the portable equipment. Considering the above-mentioned deviations, the measurements obtained by these two analytical methods are considered as our reference values for the intercomparison with the pXRF data produced through the analysis of the ceramic discs of the second kit.

Accuracy of portable XRF devices

Before discussing the accuracy of the pXRF analysers used, two key definitions must be clarified when evaluating the performance of an equipment concerning the quality of the results: accuracy and precision. Accuracy refers to the closeness of the results obtained by the pXRF analysers to reference values measured using more precise laboratory methods, such as WDXRF or ICP-MS/

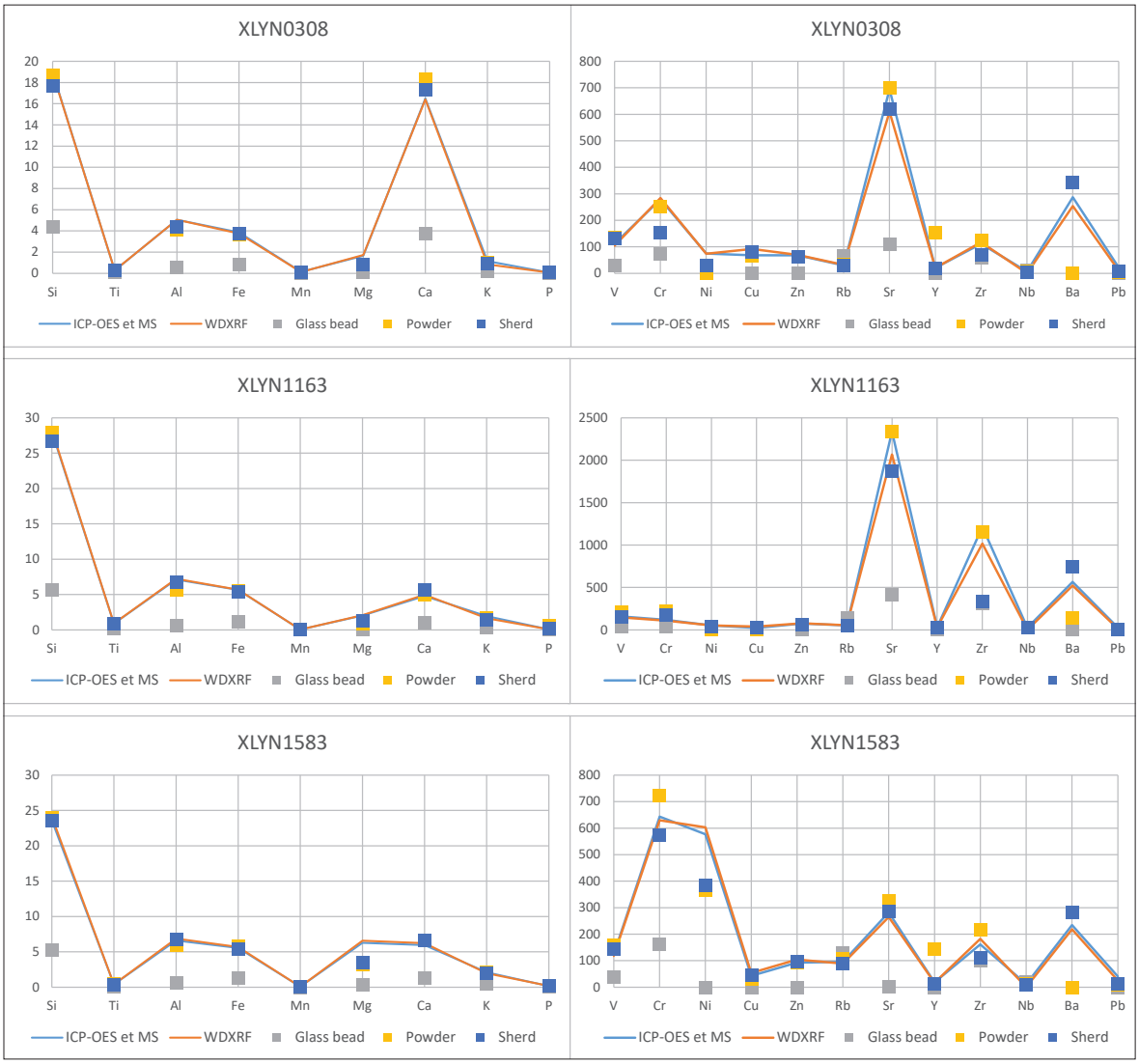


Figure 5: Effect of sample preparation on concentration measurement – example of three ceramics samples prepared as beads, powders, and fresh broken sherds

OES. However, precision refers to the repeatability of the pXRF measurements, regardless of their closeness to the reference value.

Almost all of the 21 elements presented above were detected by all the equipment, with the exception of Y, Zn, Nb and Pb, which were not detected by some of the Niton and Hitachi devices. However, their accuracy varies across the different hand-held models. To evaluate the performance of pXRF instruments regarding the accuracy parameter, two methods have been applied. The first approach was using the linear regression models with correlation coefficients (R^2) to show the relationship between the measured and expected reference values (**Table 5**). The second approach was the calculation of the root mean square error (RMSE) and the mean absolute error (MAE) for each element obtained by portable analysers with respect to WDXRF results (**Table 6**) which allows an easier readability of intercomparison and accuracy of the equipment used.

97b				98b			AN41		
%	NIST 2018 catalogue	WDXRF	ICP-OES	NIST 2018 catalogue	WDXRF	ICP-OES	Brammer Std FLUXANA DB	WDXRF	ICP-OES
Na	0.05	0.08	0.06	0.15	0.17	0.13	0.07	0.11	0.08
Mg	0.11	0.13	0.11	0.36	0.40	0.36	0.21	0.23	0.20
Al	20.76	21.33	20.87	14.30	14.65	14.31	19.27	19.61	19.16
Si	19.81	19.98	19.99	26.65	26.80	26.66	22.67	22.61	22.51
P	0.02	0.03	0.02	0.03	0.03	0.02	0.06	0.06	0.06
K	0.51	0.52	0.51	2.81	2.80	2.80	1.32	1.28	1.50
Ca	0.02	0.03	0.02	0.08	0.08	0.07	0.06	0.08	0.07
Fe	0.83	0.93	0.83	1.18	1.34	1.17	0.43	0.49	0.43
Ti	1.43	1.44	1.43	0.81	0.81	0.82	0.02	0.02	0.02
ppm	NIST 2018 catalogue	WDXRF	ICP-MS	NIST 2018 catalogue	WDXRF	ICP-MS	Brammer Std FLUXANA DB	WDXRF	ICP-MS
Mn	47	59	45	116	128	116	N/A	64	63
V	N/A	251	264	N/A	171	191	N/A	7	4
Cr	227	214	233	119	114	122	N/A	4	4
Ni	N/A	32	32	N/A	64	65	N/A	8	8
Cu	N/A	9	11	N/A	44	42	N/A	25	34
Zn	87	72	60	110	98	84	80	101	141
Rb	33	27	32	180	153	179	N/A	181	202
Sr	84	87	83	189	177	184	85	145	150
Y	N/A	41	38	N/A	31	32	N/A	24	25
Zr	500	478	475	220	234	242	N/A	63	59
Ba	180	161	187	700	641	708	179	187	196
Co	3.8	5	4	16.3	17	16	N/A	2	2
Ce	N/A	43	48	N/A	99	121	N/A	47	49
Pb	N/A	39	71	N/A	50	50	N/A	20	61
Sb	2.2	N/A	2	1.6	N/A	2	N/A	N/A	1
Cs	3.4	N/A	3	16.5	N/A	15	N/A	N/A	16
Hf	13	N/A	17	7.2	N/A	8	N/A	N/A	3
Sc	22	N/A	23	22	N/A	25	N/A	N/A	4
Th	36	34	N/A	21	18	N/A	N/A	19	N/A
L.O.I	13.3	13.58	--	7.5	8.04	--	12.3	12.37	--

Table 3: Elemental concentrations of three international standards (97B, 98B, AN41) analysed by WDXRF and ICP-MS/OES; data expressed in % for major and minor elements, and in ppm for trace elements

SAMPLE	WDXRF	ICP-OES	WDXRF	ICP-OES	WDXRF	ICP-OES	WDXRF	ICP-OES	WDXRF	ICP-OES
Element	Na		Si		Ti		Al		Fe	
	%									
AGS7	0.82	1.31	22.33	17.86	0.35	0.32	5.90	5.64	4.12	3.39
ARCHANGELOS	0.68	1.08	25.57	20.19	0.46	0.46	8.51	8.13	5.87	5.87
C4	0.92	1.31	22.37	19.30	0.36	0.32	6.01	4.97	3.48	2.95
C9	0.40	0.55	31.07	25.71	0.46	0.41	8.85	7.37	5.29	4.49
CHOM2	0.33	0.51	27.94	22.02	0.76	0.76	12.11	11.53	7.30	7.34
EVGS_15/03	0.92	1.48	34.63	27.51	0.38	0.38	6.88	6.53	4.68	4.27
EVGS_15/32	1.24	2.03	25.23	20.44	0.52	0.53	9.05	8.75	5.02	4.71
EVGS_16/03	1.28	2.05	35.43	28.32	0.40	0.40	5.95	5.69	2.88	2.65
EVGS_16/09	1.97	3.19	27.41	21.77	0.46	0.46	7.02	6.71	9.36	9.48
HS33	0.83	1.33	23.98	18.42	0.34	0.34	5.85	5.46	3.61	3.31
HS45	1.06	1.48	29.52	23.82	0.42	0.38	6.85	5.66	3.94	3.31
HS62A	0.48	0.84	12.77	9.88	0.22	0.21	4.11	3.75	2.23	2.01
KARDA3	1.28	2.13	25.56	20.21	0.41	0.42	8.59	8.30	4.29	4.04
NB EGYPT	1.38	2.19	32.76	26.44	0.39	0.37	8.96	8.78	3.51	2.93
ND EGYPT	1.17	1.84	27.99	21.73	1.16	1.13	9.61	8.95	8.15	8.04
THRAP5	0.88	1.39	27.13	21.26	0.68	0.68	11.72	11.06	6.34	6.28
TSAMBIKA7	0.44	0.76	19.36	15.33	0.21	0.21	3.18	2.99	5.01	4.60
WA22	0.73	1.20	26.07	20.90	0.41	0.42	7.39	7.12	4.45	4.19

Element	Mg		Ca		K		P	
	%							
AGS7	4.28	3.22	15.10	14.98	1.61	3.16	0.04	0.04
ARCHANGELOS	5.76	5.41	5.72	5.71	2.08	4.21	0.05	0.05
C4	1.93	1.46	20.21	17.17	1.34	2.31	0.05	0.04
C9	1.40	1.08	2.69	2.86	2.25	3.89	0.02	0.02
CHOM2	1.06	0.92	1.34	1.52	1.67	3.47	0.03	0.03
EVGS_15/03	1.66	1.46	0.63	0.72	1.63	3.35	0.02	0.02
EVGS_15/32	2.96	2.58	8.32	8.44	2.61	5.33	0.05	0.05
EVGS_16/03	1.07	0.94	2.95	3.51	1.68	3.46	0.04	0.04
EVGS_16/09	4.41	3.81	1.97	2.28	1.69	3.44	0.04	0.03
HS33	1.88	1.58	16.43	15.64	1.61	3.28	0.05	0.05
HS45	1.71	1.31	7.53	6.44	1.70	2.81	0.05	0.04
HS62A	2.29	1.85	32.09	30.55	0.72	1.63	0.03	0.03
KARDA3	2.97	2.61	7.03	7.07	2.99	6.12	0.07	0.07
NB EGYPT	1.20	0.94	1.27	1.42	2.66	5.16	0.05	0.04
ND EGYPT	2.02	1.71	2.38	2.65	1.03	2.03	0.09	0.09
THRAP5	1.82	1.59	1.84	2.09	3.13	6.27	0.04	0.04
TSAMBIKA7	13.51	12.08	15.24	14.83	0.64	1.34	0.04	0.03
WA22	1.82	1.59	11.91	11.91	1.98	4.23	0.06	0.06

SAMPLE	WDXRF	ICP-MS	WDXRF	ICP-MS	WDXRF	ICP-MS	WDXRF	ICP-MS	WDXRF	ICP-MS	WDXRF	ICP-MS
Element	Mn		V		Cr		Ni		Cu		Zn	
	ppm											
AGS7	649	626	101	107	489	518	389	355	52	41	113	97
ARCHANGELOS	757	739	148	165	593	659	578	548	91	83	150	123
C4	1187	1139	101	110	186	216	141	138	73	69	87	76
C9	2119	2102	135	148	285	323	233	224	66	62	106	90
CHOM2	1646	1585	244	269	173	199	122	120	43	42	110	94
EVGS_15/03	816	760	113	118	378	420	353	328	83	74	94	85
EVGS_15/32	806	812	143	164	211	257	127	129	55	50	128	113
EVGS_16/03	543	499	73	81	152	171	57	59	20	23	65	60
EVGS_16/09	2490	2467	125	137	1482	1680	2376	2304	62	63	89	77
HS33	1206	1230	104	110	205	249	148	148	79	68	86	74
5.081 mm	1139	1107	106	120	239	273	141	135	68	60	90	80
HS62A	599	569	68	71	105	104	95	81	68	44	59	51
KARDA3	405	399	104	115	255	286	241	226	42	39	87	77
NB EGYPT	892	916	89	96	46	67	29	43	19	20	65	58
ND EGYPT	1346	1251	211	218	149	164	91	89	80	68	113	97
THRAP5	1193	1169	174	191	125	139	86	78	54	52	140	115
TSAMBIKA7	992	955	82	91	1057	1157	1220	1127	45	32	59	50
WA22	1109	1115	126	139	226	252	171	163	115	105	113	105
Element	Rb		Sr		Y		Zr		Ba		Pb	
	ppm											
AGS7	74	65	476	513	22	21	113	117	215	212	13	9
ARCHANGELOS	113	96	182	158	32	31	150	153	319	322	69	44
C4	69	60	531	557	24	23	121	129	217	223	18	12
C9	130	118	130	124	32	31	189	211	361	352	30	22
CHOM2	121	108	104	87	43	40	363	382	430	440	46	33
EVGS_15/03	82	72	44	41	41	40	125	131	387	388	27	15
EVGS_15/32	128	105	125	127	29	29	184	200	480	520	29	20
EVGS_16/03	73	62	75	73	27	29	242	282	349	358	19	12
EVGS_16/09	77	66	67	66	20	18	115	122	150	172	16	10
HS33	81	69	382	405	24	24	124	141	241	262	22	15
HS45	92	74	219	217	27	26	185	205	289	306	23	15
HS62A	29	27	944	955	14	14	80	80	223	223	12	8
KARDA3	153	131	431	433	33	30	237	244	579	570	46	35
NB EGYPT	113	96	183	181	26	27	170	191	637	639	30	20
ND EGYPT	53	41	261	260	37	34	275	278	469	430	15	8
THRAP5	15 4	130	104	90	34	32	250	263	556	529	28	18
TSAMBIKA7	28	23	504	509	13	11	60	62	82	91	11	4
WA22	108	102	197	191	29	28	135	145	281	283	28	21

Table 4: Elemental concentrations of the ceramic discs kit; data obtained by WDXRF and ICP- MS/OES analyses

Some results are considered "satisfactory", meaning they correlate well with only slight deviations from the reference values and a R2 coefficient ranging between 0.9 and 1. This is particularly true for Mg, Ca, Ti, Mn, Sr, Ni.

While magnesium was found to be overestimated by all equipment except for three Niton analysers, this study highlighted the relatively good quantitative detection of this light element, which is important for the discrimination of ceramic assemblages.

Calcium exhibited excellent accuracy compared to the expected results. Similarly, titanium demonstrated very good accuracy, except for the Hitachi model and one Niton analyser, both of which showed an underestimation for this element. For manganese, the SciAps and Tracer devices produced optimal results, while the other equipment showed minor deviations, either over- or underestimating this element. Notably, one Niton analyser reported consistently higher concentration. Strontium demonstrated satisfactory results, except at higher concentrations (over 1000 ppm), where overestimation was observed with the Tracer 5g and one Hitachi analyser. Similarly, nickel exhibited accurate results, except for the sample with a higher concentration of around 4000 ppm, which resulted in overestimation by certain analysers, particularly the Tracer.

The following elements exhibit good R^2 values across most equipment, with a few exceptions: Cr (except for one Hitachi and Tracer 5g), Fe (except for one Hitachi and Tracer 5g), Zr (except for SciAps and Tracer 5g), and Nb (except for SciAps and one Niton). Iron displays negligible deviation from the reference data across all equipment. For chromium, all equipment, except for one Niton analyser, the SciAps, and the Tracer, tend to overestimate its concentration. Zirconium shows slightly higher variation compared to the expected results, with R2 values falling below 0.9 for SciAps and below 0.8 for the Tracer devices.

Aluminium demonstrates satisfactory results for four out of five Niton analysers ($0.91<R2<0.94$) and one SciAps device ($R^2 = 0.91$) but is less consistent across the other devices ($0.73<R2<0.88$). All portable analysers exhibit the same behaviour concerning this element, apart from one Niton analyser, which demonstrated a higher concentration (**figs. 6**–7).

The second class of elements were those showing a slightly higher deviation from the reference results ($0.8 <R2<0.9$) such as Si and K. Except for the Hitachi, silicon showed underestimation across all equipment, despite minor deviations from the reference line. The results for potassium showed significant heterogeneity across all equipment: some analysers overestimated the element (Hitachi, Vanta), while others underestimated it (three out of five Niton devices).

Finally, the last category includes elements that were detected and accurately measured by only some of the devices; these are Y, V and Zn. Yttrium was only detected by four of the instruments used; two Niton devices, the Vanta, the SciAps, and the Tracer. The data for this element provide qualitative rather than quantitative information. Vanadium was only detected to a satisfactory extent by three Niton devices. The results obtained with the Hitachi model are notably higher than those obtained by other hand-held models. Zinc showed variable results with over- and underestimation relative to the reference across almost all portable equipment. However, the coefficients of determination for this element remained above 0.9.

Although lead could show significant variation from the expected value, its detection with Vanta and Niton devices is good and could be used for ceramic composition interpretation. It should therefore remain in the list of detected elements for these instruments.

Finally, certain elements could not be compared to the reference values when using portable equipment. However, these elements are still important for the characterisation of ceramic materials in terms of alteration and/or contamination; such elements include phosphorous, and copper.

Discussion

Based on these results, one might be inclined to assign greater value to certain devices over others. This often mirrors the inquiries received from colleagues, such as, "Which device do you recommend we purchase?". However, it is important to acknowledge that each device has undergone calibration by its operators, and specific operating procedures have been implemented for each model. These differences in calibration and procedures can significantly affect the inter-comparison of devices, as variations in calibration standards, measurement techniques, and operational settings may lead to discrepancies in accuracy and precision across different instruments, even when measuring the same elements.

A positive finding from our analysis is that the Mg results are consistently good across nearly all equipment. Only four elements, i.e. Ca, Ti, Sr and Ni, were satisfactorily measured by all devices. While there is some variability in the accuracy of measurements between devices, we have been able to show that the equipment follows the same trend. Moving forward, it will be essential to address these discrepancies to facilitate more effective cross-comparisons.

Certain patterns are observable with specific device models (Table 5). For instance, the Niton analysers demonstrated a distinct advantage in the detection of Al, V, and Ba. Barium measurements are only reliable with the Niton and Hitachi models. For vanadium, accurate measurements were achieved by the Niton and SciAps devices. The data on yttrium are acceptable when detected by some pXRF analysers, such as the Vanta and two out of the five Niton devices.

However, we are confident that elements such as P and Cu should be excluded, while Nb can be used. Elements such as Si and K are very important for the characterisation of ceramics and may show a slightly greater deviation from laboratory values on conventional equipment than might be expected.

The results and differences in accuracy with the Tracer 5g raise questions regarding the post-processing of the data.

Conclusion

In conclusion, despite differences in measurement protocols, the portable equipment demonstrated its ability to detect most elements within the same concentration range, including light elements such as magnesium. Although precision may not match that of the WDXRF, the portable devices still provide reliable detection across a broad range of elements.

Despite the lower degree of precision of the hand-held analysers compared to the laboratory-based models, the results obtained demonstrated comparable concentrations for most elements. However, the deviations in elemental compositions should be carefully considered when using different analysers for different case studies.

Laboratory	CEAlex						Archéosciences Bordeaux			ARU Cyprus			CEREGE			Demokritos		
pXRF Model	Niton Xl3t GOLDD+ SN#65941			Niton Xl3t GOLDD+ SN#96594			Olympus Vanta C			HITACHI X-MET 8000			SciAps Quantum X-200			Niton Xl3t GOLDD+		
Element	Slope	Intercept	R2	Slope	Intercept	R2	Slope	Intercept	R2	Slope	Intercept	R2	Slope	Intercept	R2	Slope	Intercept	R2
Mg	1.5	-0.3	0.99	1.3	-0.4	0.99	1.1	-0.4	0.99	0.9	-0.9	0.98	0.8	-0.2	0.92	2.2	-0.8	0.91
Al	0.8	0.1	0.94	1.1	0.1	0.94	0.9	1.3	0.86	0.9	0.4	0.84	0.7	0.9	0.91	1.2	0.5	0.93
Si	1.1	-4.3	0.88	1.1	-2.4	0.87	1.3	-0.8	0.88	1.4	-7.7	0.93	0.8	4.6	0.58	1.3	-1.6	0.88
P	0.1	0.0	0.26	3.3	-0.2	1	X	X	X	0.3	0.0	0.2	0.5	0.0	0.46	0.6	0.0	0.43
K	0.6	0.6	0.82	0.9	0.4	0.83	0.6	0.7	0.79	0.7	0.6	0.79	0.6	0.5	0.75	0.8	0.4	0.71
Ca	0.9	0.0	0.99	0.8	-0.1	1	0.9	0.4	0.99	1.2	-0.1	0.99	0.8	1.0	0.95	0.9	-0.0	1
Ti	0.8	0.0	0.99	1.0	0.0	0.99	1.0	0.0	0.98	1.2	0.0	0.98	1.1	-0.0	0.93	1.0	0.0	0.99
V	0.9	-17.0	0.95	0.6	9.0	0.95	0.9	-7.0	0.7	0.2	-139.8	0.5	1.0	-25.5	0.88	0.6	-2.3	0.96
Cr	1.3	-199.6	0.98	1.3	-192.8	0.96	1.2	-105.1	0.99	1.4	-321.8	0.92	1.0	-68.0	0.9	1.2	-150.9	0.97
Mn	0.9	0.0	0.99	0.9	0.0	0.99	1.0	0.0	0.98	1.1	0.0	0.97	1.0	0.0	0.97	1.0	0.0	0.99
Fe	1.0	0.1	1	1.0	0.1	0.99	1.1	-0.3	1	1.2	-0.5	0.85	1.1	-0.4	0.97	1.0	0.1	0.99
Ni	1.4	-8.0	1	1.1	22.6	1	93.0	-1.3	1	1.1	9.2	0.99	0.9	-64.5	0.97	1.2	-22.4	1
Cu	0.7	29.7	0.28	0.8	6.9	0.64	0.9	16.2	0.59	0.6	35.4	0.31	0.9	21.1	0.38	0.4	19.0	0.11
Zn	0.9	2.9	0.97	0.8	11.0	0.81	0.9	1.6	0.97	1.3	-9.3	0.89	1.0	-0.8	0.83	1.1	-3.9	0.97
Rb	0.8	11.6	0.97	1.4	3.3	0.97	0.8	11.4	0.97	0.9	8.3	0.95	0.9	6.9	0.82	2.3	2.9	0.82
Sr	0.8	19.8	0.99	1.1	18.6	1	0.9	11.2	1	1.0	27.2	0.99	0.8	42.2	0.99	1.3	18.3	1
Y	0.1	0.6	0.91	X	X	X	0.9	1.7	0.97	X	X	X	0.8	1.9	0.84	X	X	X
Zr	0.9	0.2	0.99	1.2	3.4	0.99	1.0	0.5	0.99	1.2	-14.1	0.97	1.0	4.1	0.88	X	X	X
Nb*	1.0	1.2	0.96	1.0	2.7	0.98	1.1	-0.6	0.97	0.7	11.1	0.91	-5.1	1455.3	0.19	0.9	1.0	0.88
Ba	0.9	-151.6	0.94	1.1	-252.7	0.95	0.4	184.4	0.26	1.8	-264.1	0.92	0.5	-181.6	0.72	1.1	-147.8	0.93
Pb	0.9	-4.7	0.91	0.9	-6.7	0.91	0.9	-6.8	0.98	0.9	5.6	0.89	1.1	-2.0	0.9	0.9	-6.5	0.9

Laboratory	LAEC			Munich University			STARC			VIAS		
pXRF Model	Niton Xl3t GOLDD+			Niton Xl3t GOLDD+			HITACHI X-MET 8000			Bruker Tracer 5g		
Element	Slope	Intercept	R2	Slope	Intercept	R2	Slope	Intercept	R2	Slope	Intercept	R2
Mg	X	X	X	0.4	-0.3	0.98	0.9	-1.1	0.97	1.0	-0.0	0.94
Al	1.1	1.3	0.88	0.6	0.7	0.91	0.9	0.6	0.82	0.8	2.4	0.73
Si	1.5	-1.6	0.9	1.0	-4.4	0.88	1.4	-6.0	0.94	1.1	6.6	0.61
P	0.0	0.0	0.12	0.6	0.0	0.35	1.0	-0.0	0.72	0.0	0.0	0.15
K	0.6	0.8	0.84	0.6	0.6	0.83	0.7	0.6	0.81	0.6	0.9	0.71
Ca	0.9	-0.3	1	0.9	0.1	1	1.1	-0.1	0.99	1.3	-0.5	0.92
Ti	1.3	0.0	0.93	0.8	0.1	0.97	1.2	0.0	0.97	1.1	0.1	0.95
V	0.5	-0.3	0.89	0.7	26.8	0.91	0.2	-177.8	0.48	0.6	60.9	0.22
Cr	1.4	-188.6	0.96	1.4	-39.2	0.93	1.1	-322.1	0.86	2.4	-67.6	0.81
Mn	0.8	0.0	0.95	0.9	0.0	0.93	0.8	0.0	0.93	1.2	0.0	0.89
Fe	1.0	0.1	0.99	1.0	0.1	0.99	1.0	-0.4	0.97	1.4	-0.7	0.79
Ni	1.1	-1.5	1	1.3	-100.5	1	0.9	2.5	1	0.9	7.5	0.98
Cu	0.7	12.3	0.49	0.7	25.2	0.65	0.8	30.4	0.57	0.6	14.8	0.37
Zn	1.0	8.9	0.96	1.1	-5.2	0.98	1.1	-14.5	0.92	0.6	34.5	0.55
Rb	1.0	16.4	0.98	0.9	9.8	0.97	0.7	10.4	0.93	0.9	24.7	0.77
Sr	0.2	14.9	1	0.9	18.6	0.99	0.8	20.2	0.99	0.9	22.5	0.98
Y	X	X	X	1.1	0.7	0.94	X	X	X	0.8	5.2	0.72
Zr	1.1	10.2	0.98	1.0	24.4	1	0.9	-14.2	0.97	1.4	29.7	0.73
Nb*	X	X	X	0.9	0.2	0.97	0.8	11.5	0.98	0.6	0.4	0.95
Ba	1.3	-229.1	0.9	1.4	-424.0	0.91	1.0	-89.0	0.8	0.5	259.7	0.32
Pb	X	X	X	1.0	-4.6	0.97	0.8	13.9	0.85	0.4	6.5	0.31

WDXRF=Slope*pXRF+intercept	
* Values calculated against ICP-MS results	
●	0.9 → 1
●	0.8 → 0.9
●	0.75 → 0.8
●	<0.75

Table 5: Linear regression results from all the pXRF devices compared to WDXRF (except *Nb compared to ICP-MS references); colour code: green (0.9<R2<1), yellow (0.8<R2<0.9), orange (0.75<R2<0.8), red (0.75<R2)

Laboratory		CEAlex		Archéosciences Bordeaux	ARU Cyprus	CEREGE	Demokritos	LAEC	Munich University	STARC	VIAS
pXRF Model		NITON Xl3t GOLDD+ SN#65941	Niton Xl3t GOLDD+ SN#96594	Vanta	HITACHI X-MET 8000	SciAps Quantum X-200	Niton Xl3t GOLDD+	Niton Xl3t GOLDD+	Niton Xl3t GOLDD+	HITACHI X-MET 8000	Bruker Tracer 5g
Si (%)	MAE	2.33	1.39	6.20	2.26	3.24	4.18	7.93	3.36	3.43	7.92
	RMSE	3.09	2.08	6.60	2.92	3.64	4.69	8.30	3.71	3.97	8.21
Ti (%)	MAE	0.05	0.04	0.02	0.12	0.03	0.02	0.12	0.06	0.12	0.09
	RMSE	0.07	0.04	0.03	0.13	0.03	0.02	0.13	0.07	0.14	0.10
Al (%)	MAE	1.58	0.80	0.93	0.66	1.52	1.82	2.00	6.16	0.71	1.61
	RMSE	1.85	0.92	1.00	0.96	1.86	1.96	2.17	6.35	1.19	1.68
Ca (%)	MAE	1.71	1.71	0.86	1.60	1.70	1.22	1.07	0.75	1.19	1.51
	RMSE	2.76	2.37	1.62	2.22	2.57	1.74	1.40	1.24	1.62	2.46
Fe (%)	MAE	0.33	0.11	0.11	0.60	0.20	0.11	0.13	0.11	0.48	1.02
	RMSE	0.68	0.17	0.15	0.80	0.33	0.14	0.16	0.15	0.53	1.27
Mn (%)	MAE	0.01	0.01	0.01	0.01	0.01	0.00	0.03	0.01	0.02	0.03
	RMSE	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.02	0.03	0.03
Mg (%)	MAE	0.87	0.46	0.25	1.40	1.28	1.38	ND	4.53	1.68	0.40
	RMSE	1.34	0.79	0.41	1.51	1.71	2.17	ND	5.87	1.81	0.53
K (%)	MAE	0.44	0.38	0.43	0.38	0.44	0.36	0.47	0.40	0.37	0.54
	RMSE	0.56	0.40	0.48	0.43	0.66	0.40	0.51	0.55	0.41	0.59
P (%)	MAE	0.14	0.01	ND	0.03	0.01	0.04	0.47	0.04	0.03	0.02
	RMSE	0.17	0.02	ND	0.03	0.01	0.05	0.49	0.04	0.03	0.03
V (ppm)	MAE	40	56	39	2048	40	108	150	22	1167	33
	RMSE	44	62	42	3993	38	115	159	29	1172	42
Cr (ppm)	MAE	109	110	60	171	81	102	94	99	261	185
	RMSE	142	126	73	185	106	113	133	162	295	305

Laboratory		CEAlex		Archéosciences Bordeaux	ARU Cyprus	CEREGE	Demokritos	LAEC	Munich University	STARC	VIAS
pXRF Model		NITON Xl3t GOLDD+ SN#65941	Niton Xl3t GOLDD+ SN#96594	Vanta	HITACHI X-MET 8000	SciAps Quantum X-200	Niton Xl3t GOLDD+	Niton Xl3t GOLDD+	Niton Xl3t GOLDD+	HITACHI X-MET 8000	Bruker Tracer 5g
Ni (ppm)	MAE	122	60	31	52	93	48	50	85	41	31
	RMSE	200	84	54	89	134	113	90	148	80	61
Cu (ppm)	MAE	18	11	15	17	20	32	13	12	17	22
	RMSE	28	15	19	21	30	34	19	15	22	25
Zn (ppm)	MAE	13	8	13	14	9	6	9	5	7	6
	RMSE	20	14	13	17	10	7	10	5	9	7
Sr (ppm)	MAE	62	37	14	34	34	82	1428	16	40	23
	RMSE	90	42	25	41	67	101	1931	29	72	47
Zr (ppm)	MAE	37	30	4	24	13	ND	18	18	26	74
	RMSE	46	33	6	30	21	ND	21	19	30	81
Rb (ppm)	MAE	20	27	8	7	12	58	13	6	30	19
	RMSE	26	29	11	9	18	61	15	8	35	22
Nb (ppm)*	MAE	1	3	1	4	7	3	ND	2	8	7
	RMSE	2	3	2	5	7	3	ND	2	8	8
Y (ppm)	MAE	177	ND	1	ND	4	ND	ND	4	ND	2
	RMSE	185	ND	1	ND	4	ND	ND	4	ND	2
Pb (ppm)	MAE	7	9	9	3	4	10	ND	5	8	13
	RMSE	8	10	9	5	5	11	ND	6	9	15
Ba (ppm)	MAE	186	179	227	60	802	96	113	215	111	173
	RMSE	196	183	246	75	804	104	125	223	127	197

Table 6: Intercomparison of accuracy across devices, using Mean Absolute Error (MAE) and Root Mean Square Error (RMSE); results calculated by comparing expected values (WDXRF) to measured values (pXRF). (*Nb values compared to the ICP-MS results)

It is important to acknowledge that the obtained results from each device are closely linked to the data acquisition protocol, the analytical conditions employed, and the specific features of each instrument, particularly in terms of measurement sensitivity and accuracy.

This stage in the intercomparison of ten pXRF analysers provides a valuable opportunity to engage in a constructive discussion regarding data quality, including detection limits and the potential for other teams to use this kit to better understand the performance of their hand-held equipment. However, the task of intercalibrating devices specifically for the analysis of ceramic materials remains complex and challenging to implement.

Following this initial comparison of the quantitative results produced by the equipment, a new approach is being adopted: returning to the results concerning the physical measurement obtained by the equipment and the comparative analysis of spectra using software such as PymCA[17] or CloudCal[18].

Currently, the network has established a viable kit that has enabled the intercomparison of results among the participating laboratories working specifically on ceramic materials. The laboratories which have recently joined the research network will soon contribute their findings, further strengthening the intercomparison, not only between portable equipment but also between portable equipment and laboratory-based methods, such as WDXRF and ICP-MS/OES.

A variety of tools are available for studying archaeological ceramics and conducting material analysis. X-ray fluorescence analysis, for instance, provides valuable insights into elemental composition. However, it is essential to acknowledge that such data are often inseparable from other sources of information, including mineralogical, molecular, and microstructural analyses. These complementary datasets are equally important for addressing archaeological questions related to the production, distribution and consumption of ceramic materials.

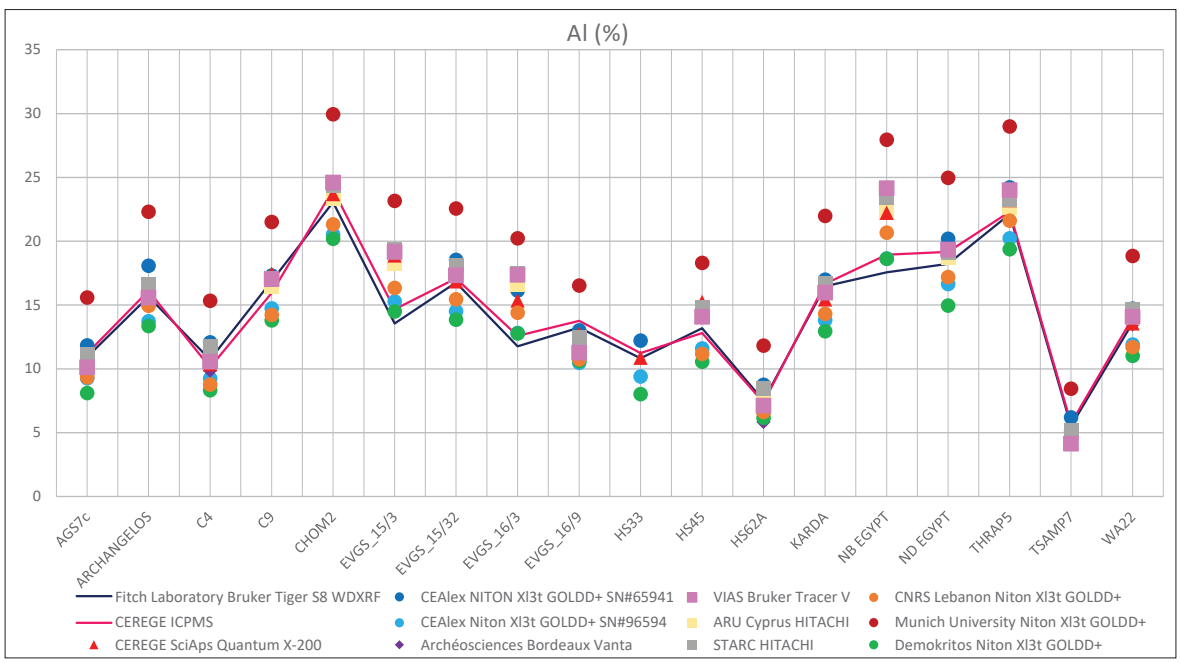


Figure 6: Example of measured aluminium concentrations, showing differences in accuracy across hand-held models

17. https://www.silx.org/doc/PyMca/dev/index.html.
18. https://www.xrf.guru/Apps/CloudCal/index.html.

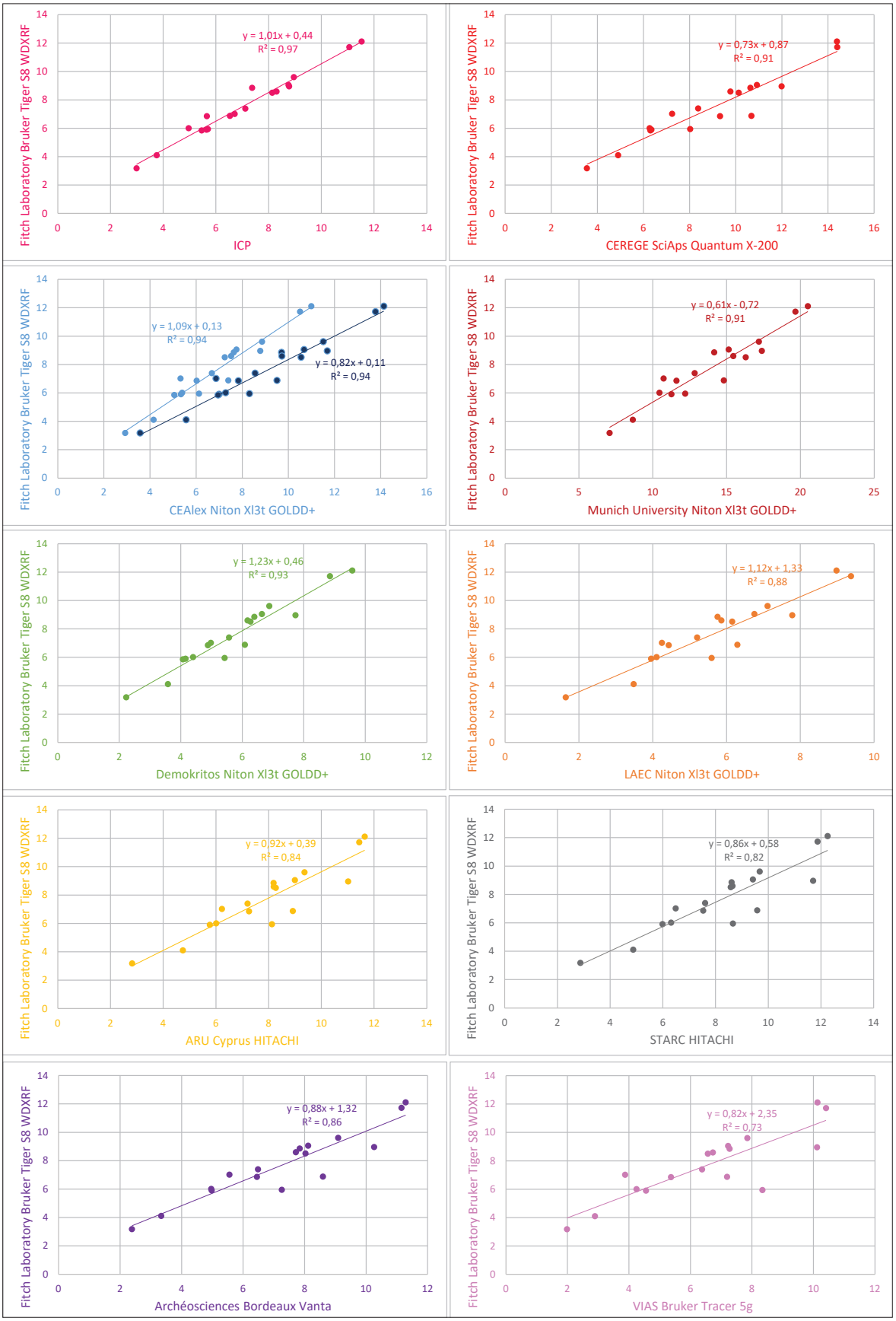


Figure 7: Example of measured aluminium concentrations, showing differences in accuracy across hand-held models

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Author contribution

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Michaela Schauer: methodology, investigation, validation, review and editing;

Vayia Xanthopoulou: methodology, investigation, validation, visualisation, writing original draft, review and editing.

Data availability statement

The supplementary data are available at https://api.nakala.fr/data/10.34847/nkl.5db5ug01/72a38a0a9e87477427c9658ff4a77cbb22ad4c3c.

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Michelle J. Richards, Andrew McAlister

Inter-instrument calibrations for archaeological research: an Australasian archaeological researchers pXRF collective pilot study

Abstract

We present the results of an inter-instrument calibration experiment conducted as a pilot study for an Australasian Portable X-ray Fluorescence (pXRF) Archaeological Research Collective. This is a first step in addressing common issues faced by archaeological and First Nations researchers wanting to use pXRF, a preferred technique for chemical characterisations of artefacts because it is non-destructive. Portable or hand-held EDXRF instruments are often marketed as 'out-of-the-box-ready-to-go', however the practical realities for research are not always straightforward. This extends to training communities on these instruments for use in the field and in collections. Key issues include custom calibrations, radiation safety, realistic field applications and data quality. The solution requires much more collaboration between researchers and institutions in Australasia. Importantly, our current research must now confront how archaeologists curate databases for Open Science to meet the UNESCO FAIR and CARE principles especially when working with Indigenous communities. Work towards solutions is being achieved through this project by connecting multiple archaeology departments in different institutions across Australia and New Zealand to establish a network of accessible research-ready instruments across Australasia. During our pilot study we tested six instruments from three manufacturers (Bruker, Niton and Olympus) and found that, although their default factory calibrations varied widely, all were able to provide accurate and compatible results either by applying correction factors to the factory calibrations or by calibrating their raw spectrum data with suitable silicate rock reference standards.

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Keywords

Reliability, reproducibility, spectra processing, FAIR (Findable, Accessible, Interoperable, and Reusable) and CARE (Collective Benefit, Authority to Control, Responsibility, and Ethics)

Introduction

Researchers in archaeological science frequently employ and adapt methods from the hard sciences to answer questions about the past. The benefits of such approaches are also appreciated by First Nations communities seeking to reclaim ownership of information and gather their own data from cultural materials often held in museums or other institutions[1]. Portable X-ray fluorescence (pXRF) analysis is a preferred technique for chemical characterisations of such artefacts because it is non-destructive. Debates about the reliability and reproducibility of elemental data have existed since the emergence of pXRF use in archaeological studies particularly in the 1990s and they continue today[2]. We briefly review this history here to highlight the advancements pXRF has had in archaeometry and how this applies to training communities on these instruments to produce data in accordance with the FAIR (Findable, Accessible, Interoperable, and Reusable) and CARE (Collective Benefit, Authority to Control, Responsibility, and Ethics) principles[3]. Many issues emerge when archaeologists wish to use pXRF with communities. These include local and federal government radiation safety legislation, realistic field applications and data quality. We focus here on the latter by demonstrating the importance of accurate calibrations for processing pXRF raw spectra data to achieve the research quality results required to contribute to regional databases and answer archaeological questions.

The potential to use different brands and models of pXRF instruments at a research level standard through a collective network is advantageous to archaeologists and First Nations communities, as it allows researchers and communities to work more easily across state and territory borders, include museum and other institutional collections in comparative research and produce high-quality, archive-standard regional databases for future research. In Oceania, one such database includes Pofatu which aspires to the FAIR principles[4]. FAIR data allows the improved application of multivariate statistical advancements, for instance, SourceXplorer for geochemically matching stone tools to raw source material locations across landscapes[5]. While several previous studies have evaluated the performance of different calibration procedures for pXRF instruments, none have explicitly investigated compatibility between multiple instruments from different manufacturers for fine-grained rock analyses (e.g. basalt, andesite, meta-basalt)[6]. We designed this pilot study to determine whether a network of researchers at different institutions can establish standard methods and

1. Allen 2021.
2. E.g. Frahm 2024; Speakman, Shackley 2013.
3. Carroll *et al.* 2020.
4. Hermann *et al.* 2020; Hermann, Forkel 2023.
5. Mcmillan *et al.* 2022.
6. See Johnson *et al.* 2021 for results of obsidian analyses on Bruker and Olympus instruments.

baseline custom calibrations for the use of multiple pXRF instruments in archaeological research. This pilot study is intended to be replicable on a large scale and form a best practice protocol for the use of pXRF in archaeological research.

pXRF in archaeology

Energy Dispersive X-ray Fluorescence (EDXRF) spectrometers started being used for archaeological studies in the late 1960s, but usage was generally restricted to lab-based instruments operated by specialist technicians. Portable self-contained EDXRF instruments became commercially available in the late 1990s. These instruments were not intended specifically for archaeology but rather for commercial activities, such as the presence/absence of toxic materials and identifying metallic alloys. As such, "off-the-shelf" instruments were not necessarily suitably calibrated for collecting accurate quantitative concentration data for archaeological materials, such as various types of stone, ceramics, glasses and metals[7]. In the first decade of the 21st century, there was considerable debate over the usefulness of potentially inaccurate but "internally consistent" data[8]. These debates remain current in archaeometry today, however, most all agree that standard reference materials (SRM) are required to improve pXRF data to research quality, whether custom calibrations or data corrections are being used[9].

Key problems

We asked whether it is possible to obtain the same quantitative results from the measurements taken on stone artefacts with various pXRF instruments available to archaeologists and First Nations communities in Australasia. The results allow us to consider the appropriateness of "rapid vs reliability" in relation to (1) research design; (2) FAIR data for inclusion in First Nations cultural heritage enduring databases to which CARE protocols apply, and; (3) what data should be archived from pXRF analyses in publications and databases.

Rapid vs reliable

The "rapid and cost-effective" reputation of pXRF is appealing to many archaeologists. The rapid approach, however, comes at a cost to the reliability of the data produced. The best research quality data must be reliable to be reuseable. What is rapid pXRF data? The "rapid" results are those produced by an instrument and its factory-set calibration, often a fundamental parameter (FP) calibration[10]. As Frahm points out, the factory settings on various instruments have seen many recent improvements and corrections can be applied to ameliorate the data quality. Our results here show that custom calibrations produce superior results, although achieving this requires some additional time to be spent post-processing data. Needless to say that the avoidance of sample preparation in non-destructive XRF analysis provides the foremost time efficiency advantage compared to any destructive laboratory method.

Certainly, we do agree to an extent with Frahm that depending on the archaeological research questions and research design rapid results can be extremely useful. We do however, advocate for

7. Shackley 2011.
8. Goodale *et al.* 2012.
9. Lundblad, Mills, Hon 2008; Frahm 2019; Glascock 2020; Frahm *et al.* 2022; Fedeli, Di Lella, Loppi 2024.
10. Frahm 2024, p. 15–16.

reliable data to be the archival standard for regional cultural heritage databases. Further, archiving the raw spectra measurements for artefacts and standard reference materials as well as the procedures used to quantify the results would all contribute to curating FAIR data for future research. Archaeologists have a moral and ethical obligation to produce the best quality data when working on Indigenous-led projects where First Nations communities wish to CARE for their data (see below). Although pXRF is non-destructive, First Nations communities may not wish their cultural objects to be repeatedly treated as scientific specimens and might ask why this analysis is being done again and why it was not done properly the first time – and consequently, may not aid in building positive relationships.

Admittedly, both the data correction-based approach and custom calibration-based approach require more specialist and expert knowledge – neither is rapid. Propriety software and file formats are the main limitation in the FP corrections-based approach for achieving the 'I' interoperable and the 'R' reusable in FAIR. Solutions for this are the use of open-source software such as R-code CloudCal or Python-code PyMca for custom calibrations using the raw spectra data[11]. There are several advantages to working with and archiving raw spectra data, not least increased opportunities in future research including the ability to re-process raw spectra data with new innovate methods such as machine learning or AI applications for advanced multivariate statistical analyses[12].

CARE: Indigenous data sovereignty

The impetus for this research collective in Australasia came from working on First Nations-led research projects. First Nations communities have often worked collaboratively with researchers, but it has not always been beneficial for Indigenous people[13]. More recently, meaningful approaches to collaborative research have included Indigenous intellectual cultural property rights and Indigenous data sovereignty and the incorporation of Indigenous knowledge into archaeological research[14]. Portable XRF analysis is a non-destructive technique that is accessible to First Nations communities through such collaborative research, and with the appropriate training, communities can build capability and capacity to conduct their own pXRF analyses of their cultural objects. The relative ease of using pXRF instruments in archaeological fieldwork, for instance, in cultural resource management, may inform on the scientific value and cultural significance of a site, which, in turn, can aid in Indigenous cultural heritage protection in sustainable development contexts. In museum collections, pXRF analysis is an excellent non-destructive tool which can assist Indigenous peoples to re-connect to their cultural patrimony[15].

Beyond academic publications and supplementary material, opportunities exist for pXRF data to be archived in several data repositories managed by government departments, museums or universities with the appropriate cultural permissions, but most relevant are the cultural heritage databases owned and curated by First Nations communities. Given that these databases are curated for the benefit of future generations, it is imperative that both the FAIR and CARE principles are met.

11. Drake 2025; Sole *et al.* 2007.
12. E.g. Drake in this volume.
13. Langton, Corn 2023, p. 15.
14. Walter *et al.* 2021; Caroll *et al.* 2020; Mcniven 2024; Fletcher, Romano 2026.
15. Allen 2021.

Future research between different First Nations groups, for example, might investigate the long-distance exchange of ground edge axes across multiple cultural boundaries[16]. Reliable pXRF data from cultural heritage databases would make such studies plausible and rapid. This aligns with the ethical approach by minimizing harm, maximizing benefits and creating data for future use[17].

Methods

The broader aim of this project is to establish a network of "research-ready" pXRF instruments for First Nations community-led archaeological research and capacity building that will produce data that meets the FAIR & CARE principles. However, it is first necessary to test whether the various instruments included in this network are capable of producing compatible data, and if not, find methods of achieving this goal. A survey of 12 archaeology departments in different institutions across Australia and New Zealand found that a variety of instruments from three manufacturers, Bruker, Olympus and Niton, were routinely used for archaeological research (**fig. 1**). We selected six instruments from these manufacturers to test; three current production models (the Bruker Tracer 5g, the Niton XL5 and the Olympus Vanta,) and three, older, previous generation instruments that are still in service (the Bruker Tracer III-SD, the Olympus Delta, and the Niton XL3t). These instruments share similar specifications (**Table 1**). All are equipped with Silicon Drift Detectors (SDD) and, with the exception of the Tracer III-SD, internal carousels for automatic selection of different filters. The main hardware differences between the older and newer generation instruments are improvements in tube power and detector sensitivity, but all are capable of developing sufficient accelerating voltages at currents suitable for analysis of the elements of interest for most archaeological materials. For this study, we included 15 elements in the range from K – Nb (see **Table 2**).

	Bruker Tracer III-SD	Bruker Tracer 5i/g	Olympus Delta	Olympus Vanta	Niton XL3	Niton XL5
Anode material	Rh or Ag	Rh	Rh, Ag, Au or Ta	Rh or Ag	Ag or Au	Ag
Tube power	4W	4W	4W	4W	2W	5W
keV (max)	40	50	40 or 50	40 or 50	50	50
Current (max)	60μA	200μA	200μA	200μA	100μA	500μA
Detector	10mm^2 SDD	20mm^2 SDD	SDD	SDD	SDD	SDD
Spot size	4 x 3 mm	3 & 8 mm	unknown	3 & 8 mm	3 & 8 mm	3 & 8 mm
Filter positions	5 (manual)	5	up to 8	8	6	6
# of channels	2048	2048	2048	2048	4000	4000
Channel spacing (eV)	20	20	20	20	15	15

Table 1: Overview of the instruments' specifications

16. E.g. Ford, Hiscock 2021; Mcbyrde 1984; Mcbyrde, Watchman 1976.
17. Caroll *et al.* 2021.

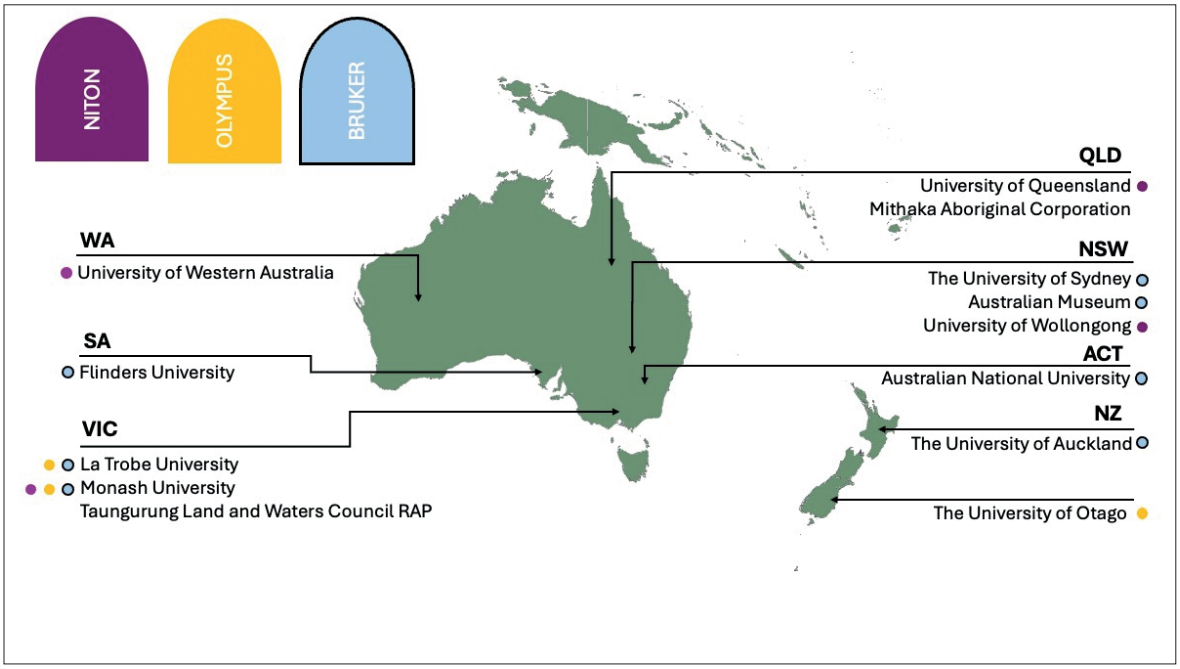


Figure 1: Map showing the pXRF instruments available to archaeologists at universities in Australasia used in this pilot study

The instruments were tested with a set of 19 reference samples that included 11 standard reference materials (SRM) and eight silicate rock specimens previously analysed using Wavelength Dispersive X-ray Fluorescence (WDXRF) at the University of Auckland (Table 2)[18]. The samples were selected to cover a broad range of igneous rock types that included the common stone tool materials used on the Australian mainland, Papua New Guinea and New Zealand. The intention behind this selection was to evaluate instrument performance over the expected range of elemental concentrations, rather than targeted calibrations for specific rock types, such as basalts and obsidians, and also non-igneous rock[19]. All reference samples were analysed in pressed powder disc form, and the GeoReM values were used for the SRM samples[20]. Because one of the aims of our study was to determine the extent to which instrument settings impacted data quality, the instruments were operated according to each lab's usual internal protocols and settings for stone artefact analysis (see Table 4).

18. McAlister 2011.
19. Nutman *et al.* 2025; e.g. McAlister, Richards (eds.) 2019.
20. GeoReM Database http://georem.mpch-mainz.gwdg.de/.

Sample	Material	K_2O	CaO	TiO_2	MnO	Fe_2O_3	V	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb
		%					ppm									
9.5	Obsidian	4.54	0.20	0.23	0.09	4.64	7	12	1	1	204	143	5	124	1067	82
BIR-1	Basalt	0.03	13.30	0.96	0.18	11.30	310	370	170	125	70	0	110	16	18	1
DNC-1a	Diabase	0.23	11.49	0.48	0.15	9.88	147	270	247	100	70	5	144	19	39	3
JB-1b	Basalt	1.40	9.31	1.28	0.15	9.05	205	392	139	57	82	39	442	24	144	27
JB-2	Basalt	0.42	9.82	1.19	0.22	14.25	575	28	17	225	108	7	178	25	51	2
JB-3	Basalt	0.78	9.79	1.44	0.18	11.82	372	58	36	194	100	15	403	27	98	3
JG-3	Granodi-orite	2.64	3.69	0.48	0.07	3.69	70	22	14	7	47	67	379	17	144	6
JR-2	Rhyolite	4.45	0.50	0.07	0.11	0.77	3	3	2	1	28	303	8	51	96	19
JR-3	Rhyolite	4.29	0.09	0.21	0.08	4.72	4	4	2	3	209	453	10	166	1494	510
MQ-001	Basalt	1.93	6.25	3.79	0.12	11.31	275	100	96	50	104	57	676	38	369	51
MQ-007	Phono-lite	6.23	1.41	0.27	0.23	3.99	3	1	3	1	134	280	72	37	686	183
MQ-1529	Basalt	0.70	10.27	3.16	0.16	12.98	302	324	130	101	114	13	367	33	216	20
MQ-5296	Basalt	1.10	10.82	4.13	0.17	14.06	349	105	115	64	131	15	627	35	339	37
MQ-5337	Basalt	0.81	11.46	3.61	0.17	12.41	354	115	117	82	112	15	456	34	259	26
MQ-5567	Basalt	1.09	10.82	3.94	0.16	12.77	361	56	80	95	113	32	551	37	294	32
MQ-5875	Basalt	1.62	11.13	3.56	0.17	12.65	355	53	69	117	118	41	676	34	258	44
NIST-278	Obsidian	4.16	0.98	0.25	0.05	2.04	15	6	4	6	54	128	64	39	295	16
NIST-688	Basalt	0.19	12.70	1.17	0.17	10.35	250	332	150	96	58	2	174	21	56	4
SARM-1	Granite	4.99	0.78	0.09	0.02	2.02	2	12	8	11	50	320	10	143	300	53

Table 2: Reference samples used in the calibration

Two sets of data were collected for each instrument – the calibrated data from factory-supplied calibration and the uncalibrated raw spectrum data taken from the same analyses. The Bruker Tracer III-SD was originally supplied with a calibration spreadsheet (S1calprocess). However, this software depended on an Excel spreadsheet macro that was rendered obsolete by a Microsoft software update several years ago and can no longer be used. For this reason, we could only use the raw spectrum data for Tracer III-SD. The Bruker Tracer 5g was supplied with a factory calibration (GeoExploration) and also another program for creating custom calibrations (EasyCal), and we made an additional calibration for this instrument using that software. EasyCal uses Bruker's proprietary PDZ file format so cannot be used with other manufacturers' file formats (except when transformed into txt files).

Although most current instruments are supplied with factory calibrations, it is widely acknowledged by manufacturers and users alike that these calibrations are not usually suitable for analyses of specific materials (e.g. silicate rock, ceramics or soil) "out-of-the-box". Consequently, most manufacturers provide some means of applying linear regression to improve accuracy for the targeted material and allow uploading the slope and intercept coefficients (termed "User Factors" by Olympus and "Calfactors" by Niton) to the instrument to make custom calibrations. It is also possible to perform

these calculations externally using standard spreadsheet software [21], and this can be preferable, particularly if the instrument is hired or borrowed from another lab, as it is less intrusive.

On evaluation of the "out-of-the-box" factory calibrations, it was found that many elements had large errors. However, the coefficients of determination (R^2) for most elements were greater than 0.90, suggesting that linear regression would be a viable means of correcting these errors. Ideally, calibrations are evaluated using two sets of reference samples, one to build the calibration and the other to test its validity[22]. Because we did not have enough reference samples for two complete sets, we used a simple three-fold cross-validation method. The 19 samples were randomly grouped into three approximately equal portions (n = 6, 6 & 7). One portion was removed from the set, linear regression was performed using the two remaining portions and the resulting slope and intercept coefficients were applied to the omitted portion. The same procedure was then repeated for the other two portions. This ensured that the calibrated values for each specimen were independent of the coefficients used to determine those values. In practice, this method lowered the overall accuracy slightly (approximately 1–10% relative) compared to including all standards simultaneously but provided a more robust measure of performance. We refer to this dataset as the "corrected" factory calibration, following Frahm[23], who advocates similar methods.

pXRF spectrum processing

In addition to the "out-of-the-box" and "corrected" factory calibrations, we used the raw spectrum data to generate empirical calibrations independent of the manufacturers' software. We used simple spreadsheet calculations which involved common procedures:

1. The background was removed from the spectra using 50 iterations of the SNIP (Statistic-sensitive Non-linear Iterative Peak clipping) algorithm[24];
2. the net areas under the characteristic element peaks were calculated by interpolating between fixed bandwidths[25];
3. peak areas were normalised to time for the three lightest elements included in this study (i.e. K, Ca and Ti) and to the Compton scatter for all other elements;
4. regression was used to calibrate the peak areas to the known concentrations. Elemental interferences were accounted for by adding coefficients to the regression slope and/or intercept terms to the regression using a variation of the Lucas-Tooth and Pyne algorithm[26]. Corrections were kept as simple as possible and limited to known interferences (**Table 3**).

All of the instruments tested here generated multiple spectra per analysis (variously called "beams", "illuminations" or "phases" by different manufacturers) with different combinations of analysis time, tube voltage and current and filtering to optimise fluorescence for ranges of elements of differing atomic weight. The spectrum metadata for the Olympus and Bruker instruments

21. Hnila *et al.* 2025, p. 28.
22. Da Silva, Triantafyllou, Delmelle 2023; Frahm 2024.
23. Frahm 2019; Frahm 2024; Frahm *et al.* 2022.
24. Ryan *et al.* 1988.
25. Van Espen 2002, p. 265.
26. Lucas-Tooth, Pyne 1964.

included details of these settings but the Niton spectra only identified the four spectra used by name (light, main, high, low) (**Table 4**). Because it is uncertain which of the spectra settings were used to calibrate which elements in the factory calibrations, we made separate calibrations for each setting and report the most accurate result for each element. The same three-fold cross-validation method as described above was used to generate the spectra calibrations and calculate performance. Microsoft Excel spreadsheets were used to process the spectrum data reported here but several open-source calibration applications are available, including CloudCal and PyMca[27]. We note that calibrations based on spectra are specific to the instrument on which they are developed. Small differences in the filters, tubes and geometry of the detector and target can result in variations in spectra, even for instruments of the same make and model.

Element	Normalisation	Element peak	Peak overlap	Compton tail	Escape peak	Sum peak
K	time	K Kα1		Ca Kα1		
Ca	time	Ca Kα1	K Kβ1			
Ti	time	Ti Kα1			Fe Kα1	
Mn	Compton	Mn Kα1		Fe Kα1		
Fe	Compton	Fe Kα1				
V	Compton	V Kα1	Ti Kβ1		Fe Kα1	
Cr	Compton	Cr Kα1	V Kβ1			
Ni	Compton	Ni Kα1				
Cu	Compton	Cu Kα1				
Zn	Compton	Zn Kα1				
Rb	Compton	Rb Kα1				Fe Kα1
Sr	Compton	Sr Kα1				
Y	Compton	Y Kα1	Rb Kβ1			
Zr	Compton	Zr Kα1	Sr Kβ1			
Nb	Compton	Nb Kα1	Y Kβ1			

Table 3: Element overlap corrections used in the spectra calibrations

27. Drake 2025; Sole *et al.* 2007.

Instrument	Spectrum label	Voltage (kV)	Current (μA)	Filter (μm)	Analysis time (s)
Niton XL3t & XL5	light	unknown	unknown	unknown	60
	main	unknown	unknown	unknown	60
	low	unknown	unknown	unknown	60
	high	unknown	unknown	unknown	60
Olympus	Exposure 1	40	55	2000* Al	60
Vanta	Exposure 2	10	71	none	60
	Exposure 3	50	56	350* Cu	60
Olympus	Exposure 1	40	73	"3"	60
Delta	Exposure 2	40	78	"1"	60
	Exposure 3	15	158	"5"	60
Bruker Tracer 5g	Exploration_15	15	13	none	60
Geoexploration	Exploration_30	30	13.85	25 Ti; 300 Al	60
mode	Exploration_50	50	5.75	75 Cu; 25 Ti; 200 Al	60
Bruker Tracer III-SD	Spectrum 1	40	25	25 Ti; 300 Al	60
	Spectrum 2	15	30	none	60
*Filter thickness units are not reported for the Olympus Vanta					

Table 4: Instrument settings for the spectra

Results

The results for all the calibrations were compared using the root mean square error (RMSE) as a simple measure of the calibrations' goodness of fit (**Table 5**). As was expected, the "out-of-the-box" factory calibrations showed large deviations for several elements across most instruments. However, these calibrations are not intended to provide highly accurate quantitative data for all materials without first making adjustments for the particular material of interest. As Frahm[28] has recently noted, fundamental parameters algorithms have improved greatly over the last 20 years or so, and there is no reason to doubt that they are capable of producing accurate material-specific calibrations if used in conjunction with suitable standards[29].

Indeed, once we applied slope and intercept corrections based on our reference samples, the accuracy of the factory calibrations for all instruments increased markedly. This is illustrated by the calibration curves for two typical elements, CaO and Sr, shown in **Figures 2** and **3**. As mentioned

28 Frahm 2024.
29. Frahm 2019, Frahm *et al.* 2022.

above, the high coefficients of determination for these elements indicate that the "out-of-the-box" calibrations are primarily systematic rather than random and, as such, adding slope and intercept corrections was very effective.

Our calibration of the raw spectra data also performed well, as did the EasyCal calibration for the Bruker 5g. Although no formal significance tests were undertaken for this pilot study, the data suggest that, with a few exceptions discussed below, there is no notable difference in accuracy between the corrected factory and spectra calibrations. Overall, our tests indicate that all six of the instruments tested are capable of generating accurate and, importantly, compatible data.

Instrument	Calibration	K_2O	CaO	TiO_2	MnO	Fe_2O_3	V	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb
		%					ppm									
Bruker Tracer III-SD	Spectra	0.13	0.27	0.07	0.01	0.31	41	32	8	7	8	3	8	3	11	4
Bruker Tracer 5i	Factory	0.55	1.98	0.56	0.03	2.29	175	88	17	9	17	22	62	10	89	194*
	Corrected	0.27	0.26	0.08	0.02	0.29	80	70	9	7	10	5	26	7	62	2*
	Easycal	0.11	0.15	0.04	0.01	0.21	21	16	7	5	11	6	10	2	15	5
	Spectra	0.12	0.25	0.03	0.01	0.31	34	19	8	5	7	4	10	3	14	4
Olympus Delta	Factory	0.58	1.09	0.24	0.01	0.63	163	27	16	17	12	10	9	6	14	12
	Corrected	0.18	0.23	0.07	0.01	0.37	83	25	8	9	9	5	9	3	11	3
	Spectra	0.15	0.23	0.05	0.01	0.31	32	22	7	5	8	4	8	2	12	3
Olympus Vanta	Factory	0.24	0.42	0.08	0.02	0.42	32	37	10	15	13	6	13	4	20	8
	Corrected	0.16	0.25	0.06	0.01	0.34	29	28	6	10	8	4	10	3	11	4
	Spectra	0.15	0.25	0.04	0.01	0.29	29	16	7	7	8	3	10	1	13	3
Niton XL3t	Factory	0.48	4.27	1.1	0.04	1.39	78	98	33	19	20	18	24	†	248	†
	Corrected	0.31	0.98	0.18	0.02	0.53	47	48	27	12	10	6	11	†	19	†
	Spectra	0.23	0.26	0.04	0.01	0.38	21	11	16	7	10	7	10	2	15	3
Niton XL5	Factory	0.38	1.67	0.08	0.03	1.04	71	35	32	8	10	8	12	8	25	3
	Corrected	0.23	0.25	0.06	0.01	0.34	51	21	12	7	9	8	10	5	22	3
	Spectra	0.12	0.25	0.04	0.01	0.39	27	15	7	5	9	8	9	2	18	3

* The majority of results for Nb were reported as <LOD. See text for further details.

† Element not calibrated.

Table 5: Comparison of the calibrated results reported as Root Mean Square Error (RMSE)

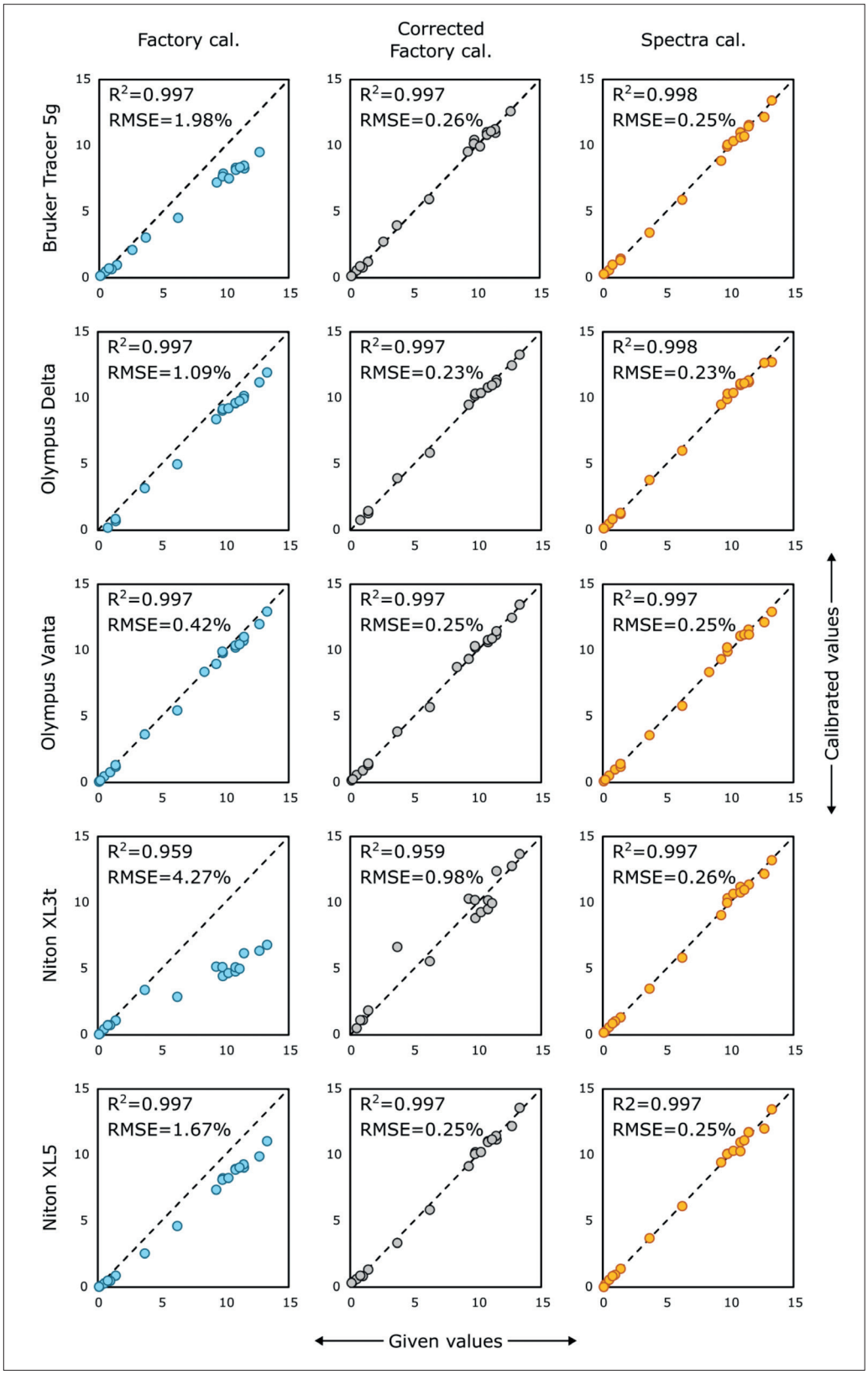


Figure 2: Calibration curves for CaO. The dashed lines show the ideal 1:1 calibration line

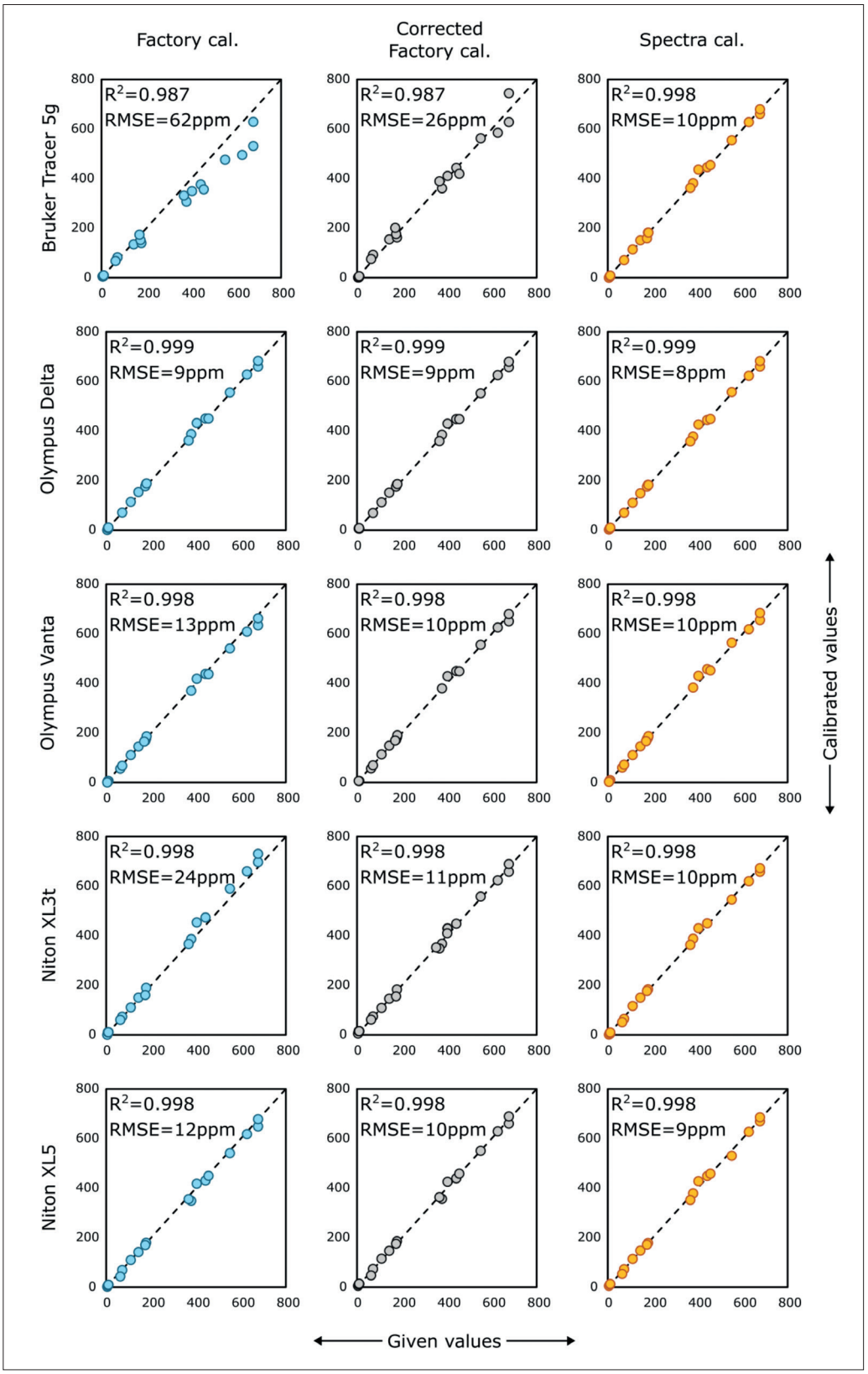


Figure 3: Calibration curves for Sr. The dashed lines show the ideal 1:1 calibration line

Discussion

Once corrected, the factory calibrations for all instruments were much more accurate and similar to one another, despite variations in hardware, tube settings, filtering and analysis times. Extraction and processing of the raw spectra data also produced almost identical results across the instruments. Although accurate results are obtainable from both calibration methods, there are several advantages to saving and post-processing raw spectral data.

First, manufacturers often use proprietary file formats (e.g. Bruker's *.pdz; Niton's *.ntd), which can be difficult to read without access to the manufacturers' proprietary software. Furthermore, there may be issues with software obsolescence and back-compatibility. As noted above Bruker's Tracer III series calibration software used an Excel spreadsheet macro that was suddenly rendered obsolete by a Microsoft update sometime around 2016.

Second, adjusting instrument-specific calibrations may require access to the manufacturers' software and, in some cases, the instrument may need to be sent to a service agent for modification. For example, the factory calibration installed on the Niton XL3t we examined did not include the trace elements Y or Nb and, to the best of our knowledge, these elements cannot be added by the user. The peaks for these elements were, however, clearly visible and easily calibrated using the spectra. Additionally, the same Niton instrument reported results in percentages to three decimal places, which is equivalent to a resolution of 10ppm, and coarser than necessary for some trace elements.

Third, examining spectra data allows the overall pattern of element peaks to be evaluated. This is not only a valuable check on the instrument's energy calibration but also can be used to identify potential issues. For instance, the GeoExploration calibration used with the Bruker Tracer 5g reported that all but five samples had levels of Nb below the level of detection (<LOD), including one specimen with a given concentration of 82ppm, which should be well above the noise floor for that element. Again, examination of these spectra showed that the peaks for Nb were clearly visible and easily calibrated.

Lastly, archiving the spectrum files allows the data to be accessed by third-party software and makes research truly open source, in keeping with CARE and FAIR principles.

Building upon suggestions from Johnson[30] and Frahm[31], and at the risk of producing yet another "laundry list" of dos and don'ts, we recommend the following best practice procedures for data analysis, publication and archiving data to FAIR and CARE principles in archaeometry:

1. Routinely run an appropriate set of standard reference materials on pXRF instrument (with the same settings used to analyse specimens);
2. record the time (seconds) used for the measurements;
3. record the settings used (filter/beam, keV and μA);
4. save the raw spectra data. At a minimum, spectra files need the analysis time (preferably livetime if possible) and the channel spacing;
5. save the processed data output from factory calibration, including the software version used;
6. save all files in open formats e.g. *.csv;

30. Johnson *et al.* 2024.
31. Frahm 2024.

7. record information about any data post-processing procedures (e.g. correction coefficients from factory calibrations);
8. create a READ ME .txt file explaining the contents of the folder;
9. save in multiple locations (as appropriate).

Conclusion

Although the "out-of-the-box" performance varied widely across instruments, applying corrections to the factory calibrations improved accuracy greatly and rendered all instruments comparable to one another. Generating custom calibrations from the raw spectra produced similar results to the corrected factory data in terms of accuracy but also has several advantages. These include permitting material-specific calibrations to be made after data has been collected, adding elements that are not included in factory calibrations, and not being reliant on the availability of proprietary software. These features help improve pXRF data accessibility, allowing contributions to and comparison with larger regional and global archaeological and geochemical databases and including data from other techniques, such as WDXRF or Inductively Coupled Plasma Mass Spectrometry (ICP-MS), in future research.

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Author contribution

Michelle J. Richards: responsible for the project conceptualisation, funding acquisition, investigation, methodology, project administration and writing – reviewing and editing;
Andrew McAlister: contributed to the conceptualisation, data curation, formal analysis, resources, software, validation, visualisation and writing – reviewing and editing.

Statement on the use of artificial intelligence

AI was not used in this research or publication.

Data availability statement

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Launching the global portable X-ray fluorescence network (GopXRF.net)

Abstract

This paper introduces the Global Portable X-ray Fluorescence Network (*GopXRF.net*), a newly established initiative aimed at creating a scientific home for the pXRF community in archaeology and heritage sciences. pXRF has become a valuable tool for chemical analysis, but its use has been hindered by issues of limited access to expertise. The network addresses this by providing a collaborative platform for sharing knowledge, fostering innovation, and promoting standardised practices. Launched during the 2024 conference on Methodological Innovations in pXRF Studies in Vienna, the network is volunteer-led by experts in the field. It aims to connect specialists and novices, host teaching and mentoring opportunities, support the development of best practices, and centralise resources such as standards and reference materials. Initial activities are focused on creating a website to host key information, a colloquium series, pXRF research forums, and the formation of task forces to develop guidelines for material-specific applications, starting with soils and ceramics. The network also plans to publish a beginner's guide to pXRF and maintain a directory of experts and standards. By creating an inclusive and egalitarian community, GopXRF.net seeks to enhance the credibility, accessibility, and application of pXRF in diverse research contexts, ultimately driving methodological advancements and bridging gaps between cultural and natural sciences.

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Keywords

pXRF, standardisation, archaeometery, interdisciplinary, provenance studies, cultural resource management

Introduction

Portable X-ray fluorescence (pXRF) studies have featured in archaeometry and heritage conservation sciences since the 1990s[1]. Hand-held pXRF analysers were initially embraced by these scientific and archaeological communities which saw the potential of this mobile, quick, cost-effective and minimally invasive to non-destructive method of chemical analysis to investigate art works, archaeological finds and sites[2]. However, it quickly fell out of favour due to the critique of insufficient precision and accuracy noted by laboratory specialists, and also the application by untrained researchers unaware of the limits and pitfalls of the method[3]. Now, in recent years, the method is experiencing a revival: specialists of the method have emerged, bridging the gap between natural and cultural sciences and doing their best to (re)establish transparent applications, data procedures and interpretations, including teaching and training[4]. Specialists are still few and far between, and it is not straightforward to connect with someone specialised in the same research area. Additionally, internationally agreed standard procedures for pXRF in archaeological research are not yet well established and require development and discussion among scholars.

Today, there is a huge body of published literature on pXRF in archaeometry, including some contradictory information, which a novice must grapple with. Several barriers exist between the novice and experts. Students, especially, are often required to produce results long before they are sure about what they are doing. Many current specialists have failed more than once, realizing mistakes much too late, wasting precious money and time. This could have been avoided if there had been someone to learn from and to establish a professional baseline to build upon. Learning from these experiences, the newly established Global Portable X-ray Fluorescence Network (*GopXRF.net*) aims to address such issues by creating a scientific home for the archaeometry and heritage science pXRF community, sharing contacts and knowledge, providing a platform for discussion and teaching, as well as fostering innovation and collaboration in pXRF studies.

Establishing the network

The real need for a global network of specialists to provide guidance has been discussed and agreed upon by the archaeological and heritage community and those involved in pXRF studies. Discussions with pXRF users in archaeometry almost always uncover common issues and experiences related to connecting with a specialist researcher with appropriate knowledge about the method, its best application, the limitations, data procurement and processing as well as data

1. Shackley 2011; Frahm 2024.
2. Shackley 2011.
3. E.g. see Speakman, Shackley 2013; Frahm 2013; Frahm 2024.
4. E.g. Johnson *et al.* 2024; Frahm 2024.

interpretation. It is also accepted that current leading experts and specialists themselves faced steep learning curves at the beginning of their research careers with pXRF, often devoting a considerable portion of their PhD or postgraduate work to learning the technique to an appropriate level of expertise to produce research quality data in answer to archaeological questions.

This shared sentiment was a key reason for launching the ESPRIT Project ESP-476, *Standardising Portable X-ray Fluorescence Analysis* funded by the Austrian Science Fund (FWF) in September 2023[5]. In practical terms, the value of such a network became even more evident through the *Mediterranean pXRF Ceramic User Network* (pXRF CUN), where meetings fostered the development of improved methodologies in ceramic analysis and inspired innovative thought processes. The session *From Lab to Field, from Vertical to Horizontal. New Approaches to the Use of Portable X-ray Fluorescence (pXRF) in Archaeology*, organised at the European Archaeologists Association (EAA) 2024 conference in Rome, then provided the ideal opportunity to gauge the interest and needs of the community for establishing a Global pXRF Network. Likewise, on the other side of the world, work towards an Australasian Archaeological Researchers pXRF Collective had begun[6]. The idea gained substantial support, and as a result, *GopXRF.net* was initiated during the conference on *Methodological Innovations in pXRF Studies* in Vienna in September 2024.

Aims and Objectives of the Network

GopXRF.net is designed to address the issues discussed while being volunteer-led, independent, self-sustaining and egalitarian. The network first and foremost is a scientific home for the pXRF community, a hub for the exchange of knowledge, skills and support across the archaeology and heritage pXRF community. Second, but no less important, the network aims to host and provide necessary key information and materials as well as leading discussions on best practice and foster innovation.

The four key objectives of the network are to:

- **Facilitate connections** – maintain and share a directory of specialists, laboratories, and pXRF community members to enhance visibility, accessibility, and communication both within and beyond the pXRF network;
- **promote knowledge exchange and mentoring** – organise teaching, mentoring and learning opportunities to share ideas, encourage innovation, and strengthen collaboration within the community;
- **support best practices** – collaboratively develop, review, and disseminate globally recognised guidelines for materials analysis and methodologies in archaeology and heritage studies to uphold best practices;
- **centralise resources** – provide comprehensive information on standards and reference materials, including guidance on their use and availability.

Since the initiation of the network in late September 2024, the first steps to bring the network to life and address the key objective have been undertaken. The network's preliminary website is taking

5. Schauer 2023a.
6. Richards, McAlister in this volume.

shape with the primary goal to host and disseminate information[7], while the final website needs some time to be set up properly in terms of GDPR and backend opperationality (**Objectives 1–4**). An online colloquium series on pXRF as well as the pXRF research forum have been launched and international conference sessions and workshops were provided in 2025 (**Objectives 1–3**). Several task forces are planned to develop standards and guidelines for specific materials and applications in archaeometry; the soils task force is currently underway with a ceramics/pottery task force to follow. Also, a Cambridge Elements booklet providing a basic introduction to the method is in preparation (**Objective 3**). A monthly newsletter sharing information on events, publications and the network activities is sent by email to the rapidly growing pXRF community. The use of an open email-list is an intermediary way to share who is in the network until the website is up and running. Finally, a survey is planned to identify which protocols are used in the different pXRF applications to form the basis of the directory of standards hosted on the network's website (**Objective 4**).

Core team members and their contributions

Since the 2024 meeting in Vienna, the core team of the Global pXRF Network meets once a month via video conference and is in regular contact through written and oral communication. The core team brings together expertise from different parts of Europe, Australasia, the Americas and the UK. Our core team members, their research expertise and current contributions to the network are:

Michaela Schauer is a European prehistorian and Near Eastern archaeologist who is currently working as senior scientist on her first personal research project *Standardising portable X-ray fluorescence analysis for archaeometry*[8] at the Vienna Institute for Archaeological Science (VIAS) of the University of Vienna. She is a member of the research network Human Evolution and Archaeological Sciences (HEAS). Since July 2025, she holds a permanent position as scientific researcher and curator at the renowned research institution, the Natural History Museum Vienna (NHMW).

She has worked on a range of projects and sites in Europe and the Near East. Schauer has performed pXRF analyses on a variety of materials ranging from metals, glass, slags to obsidian, but enjoys most working with fired and non-fired clay materials and sediments. The use of geochemical data to explore social structures, contacts and processes of transformation, whether cultural, technological, economic or social in nature, is central to her work on archaeological case studies[9]. More recently she has focused on methodological studies and is at the forefront of developing new methods and pXRF routines for data quality control and data processing. She is also very interested in the definition of protocols, benchmarks and guidelines[10].

Schauer is the initiator and, due to the opportunity to invest some work time in her project, the organisational coordinator of the network and responsible for its newsletter. She generally supports the other core team members in their endeavours and keeps in touch with the pXRF community. As an informal means of discussion and information exchange, she has developed the online pXRF Research Forum, as an explicitly closed community format of the pXRF network with a strict privacy

7. https://vias.univie.ac.at/projekte/standardising-portable-x-ray-flourescence-for-archaeometry/the-global-p-xrf-network/.
8. Schauer 2023a.
9. Schauer 2020; Daszkiewicz *et al.* 2020; Schauer, Amicone 2024.
10. Schauer 2023b; Schauer 2024a; Schauer 2024b; Schauer 2024c; Schauer *et al*. 2024; Schauer, Truntschnig, Almstädter 2025; Schauer *this volume*.

policy. The pXRF research forums are designed to be a safe space to discuss unpublished data, draft ideas for papers, projects, field work and experiments. They are particularly aimed at emerging researchers and provide a unique opportunity to receive feedback on studies, results and approaches from specialists and novices in a protected environment. The forum consists of a 15 minute presentation of the research question followed by 45 to 60 minutes of feedback and discussion.

Michelle Richards is an archaeologist and postdoctoral research fellow at the University of Melbourne in Australia. Richards' research combines archaeological and earth science approaches with heritage and museum studies. She has been working at the forefront of the development and application of non-destructive pXRF geochemical analysis to identify and characterise the origin of archaeological stone tools to explore exchange systems, historical complexities and interactions among First Nations and early settler communities in Australia and the Pacific[11]. Richards and Andrew McAlister have worked across the Pacific with pXRF in archaeology and have been leading the pilot research project *An Australasian pXRF Archaeological Researchers Collective* to standardise pXRF use for First Nations communities conducting archaeological research[12].

Richards is highly active, together with Schauer and McAlister, in editing and writing the network publications, especially the Cambridge Elements on pXRF as a beginner's introduction to the method. This book is meant to be a resource for novices and lecturers alike. She also led and coordinated the workshop "How to Calibrate pXRF Data for Archaeological Research: A Workshop Hosted by the Global pXRF Network" at the 10th World Archaeological Congress (WAC-10) in Darwin 2025 in cooperation with Drake, Schauer, McAlister and Bruce Kaiser.

Lee Drake is an archaeologist who specialises in scientific instrumentation, principally X-ray fluorescence (XRF) for applications in art conservation, archaeology, geology, and agronomy. His research interests include geochemistry and how past climate change has affected human societies.

Drake and Brandi L. MacDonald recently edited *Advances in portable X-ray fluorescence spectrometry: instrumentation, application and interpretation*, a comprehensive volume which includes several examples of how pXRF can be used qualitatively in archaeology, cultural heritage objects, geologic profiles and spatial mapping[13]. Drake's archaeological research includes improving the validity of geochemically sourcing obsidian and other stone tools with pXRF in archaeometry[14]. He is also researching climate environment applications for pXRF in soils and plants as well as machine learning processes for the analysis of pXRF data[15].

Drake has built and currently maintains an XRF users website, which includes animated tutorials, online videos, and multiple manuals, documents, CloudCal and other materials (www.xrf.guru). This will be adopted, revitalised and further developed by Drake to become part of the network's website. He is leading the development of the latter supported by Richards and Schauer.

Roger Doonan is an archaeologist whose research interests lie in Eurasian prehistory with an emphasis on craft practice as understood through innovative field methods, including pXRF. He and

11. Richards 2019a; Richards 2019b.; Richards 2021; Richards 2023; Hayes, Fullagar, Richards 2023.
12. McAlister, Richards (eds.) 2019; Richards, McAlister in this volume.
13. Drake, Macdonald (eds.) 2023.
14. Nazaroff, Prufer, Drake 2010; Johnson *et al.* 2021.
15. Lillios *et al.* 2016; Towett, Shepherd, Drake 2016; Sapkota *et al.* 2019; Shugar, Drake, Kelley 2021; Sapkota *et al.* 2020; Drake in this volume.

colleagues are engaged in debates on the analytical performance of pXRF and are working to develop the technique for greater *in situ* analyses in archaeology especially for soils and metals[16]. He encourages the routine pXRF use for cultural resource management and archaeological prospection[17].

Luisa Dallai is an archaeologist at the University of Siena in the Department of Historical Sciences and Cultural Heritage. Her research includes landscape archaeology, with particular emphasis on the interpretation of settlement patterns in relation to exploitation of economic resources, the analysis of production cycles and by-products, especially metallurgical, and the study of archaeo-mining contexts using pXRF.

Dallai and colleagues have been employing pXRF as part of multidisciplinary archaeological and geochemical surveys to reconstruct historical anthropogenic landscapes[18]. Her research combines geographical information systems (GIS), quantitative data from pXRF analyses and multivariate statistical analyses to map variability in soils and ceramics across landscapes through time[19].

Dallai, together with Doonan, is developing standard methodological procedures for soil analyses with pXRF in cultural resource management[20]. This stems from a productive session on pXRF: *From Lab to Field, from Vertical to Horizontal. New Approaches to the Use of Portable X-ray Fluorescence (pXRF) in Archaeology*, at EAA conference in 2024 and has been continued together with Schauer and others at the EAA 2025 with the session, *Recent developments in HH-pXRF studies and the Global pXRF Network (GopXRF.net)*.

Doonan and Dallai are leading the networks first pXRF task force to develop, discuss and agree on standards for soil analysis in scientific and commercial contexts. The pXRF Soil Standards Task Force learning experience will pave the way for other task forces, which will focus on standards and guidelines for other materials, such as ceramics, metals, obsidian and stone.

Mai Abdelgawad is a chemical engineer with long-standing experience in pXRF studies working at the Materials Characterisation Laboratory of the Centre d'Études Alexandrines. With a background in the natural sciences, she offers a unique perspective on the method and its applications, enriched by close collaboration with earth science specialists and archaeologists in diverse settings. Her primary focus is on ceramic/pottery studies and pXRF methodology.

Abdelgawad's research projects include leading, with Nadia Cantin, the *Mediterranean pXRF Ceramic User Network* (pXRF CUN) funded by the Centre National de la Recherche Scientifique (CNRS) International Research Networks (IRN) programme[21].

After launching the soil task force and gaining valuable insights from that experience, Abdelgawad will be prepared to take on the ceramic/pottery task force.

Ioannis Liritzis is a specialist in natural sciences in archaeology. He has worked with colleagues to enhance the application of pXRF for the study of archaeological artefacts from field excavations and museum collections[22]. He has worked on developing statistical approaches for the chemical

16. Frahm, Doonan 2013; Doonan, Craver, Waddington 2021; Thompson, Doonan 2019; Doonan, Dungworth 2013; Doonan *et al.* 2014.
17. Craver *et al.* 2021; Boyd *et al.* 2021.
18. Dallai, Carli, Volpi 2020; Dallai, Donati, Volpi 2018; Dallai *et al.* 2018.
19. Dallai, Donati, Volpi 2018.
20. Doonan, Dallai in this volume.
21. Abdelgawad *et al.* in this volume.
22. Liritzis, Zacharias 2011; Liritzis *et al.* 2018; Ganetsos *et al.* 2019.

characterisation of ceramics with pXRF[23]. Liritzis has also worked on inter-instrument calibrations to increase compatibility between different techniques used in archaeometry, such as XRF, Flame Atomic Absorption Spectroscopy (FAAS) or Scanning Electron Microscope (SEM)[24].

Liritzis is coordinating, supported by Schauer and Keelie Rix, a series of colloquia on portable X-ray fluorescence endorsed by the European Academy of Sciences and Arts and STEMAC Expert Group[25]. The colloquia aim to provide a platform for knowledge exchange, featuring expert presentations from both the natural sciences and the humanities. Each session includes 30-minute talks by specialists from archaeology and natural sciences, followed by a 30-minute discussion. Topics include resources and guidance for the XRF community, case studies and exemplary applications and the colloquia provide opportunities for the exchange of knowledge.

Long term vision

The core team believes in the network's potential to bring a community together and that sharing knowledge is the most inspiring thing to witness and participate in. We have many more ideas that will emerge in the near future. For now, we are starting by creating online lectures to set the next pXRF generation up for success. We also envision a mentoring programme where young researchers will be paired with a specialist willing to provide individualised support and training, thus providing a solid background for new, exciting research. We look forward to supporting the network in hosting summer schools and to create focused opportunities to develop innovative ideas and collaborations.

We also wish to support the personal development of those already familiar with the method to enhance their own approaches. We want to involve already well-established specialists to provide advice. In particular, we envision specialists advancing practices and participating in our lecture series and our discussion forums. The network aims to create an atmosphere where everyone can learn from each other – a network of support and flourishing ideas. We are looking forward to developing new ways of communication and sharing knowledge together with specialists to make the method as transparent and approachable as possible.

We are dreaming big, and we are aware of that. Therefore, we also acknowledge that we can only do so much as the small, yet ambitious, group that we are. We can already see a steady growth in our membership. More expertise will not only affect what topics we are taking up but also, over time, grow and develop the core team. Fresh minds and new ideas are needed to keep the network going and help it prosper.

We have designed the network specifically to be community driven which also means that the community must be involved and engaged to make things happen. The future of GopXRF.net is bright and we are very excited to be part of the journey!

23. Liritzis *et al.* 2020; Papageorgiou, Liritzis 2007.
24. Liritzis *et al.* 2011.
25. https://euro-acad.eu/events?id=258.

Get involved!

Getting involved is easy – just get in touch with the core team and let us know about your vision, your ideas. Have an idea for a workshop? Let's hear it! Want to have a pXRF Research Forum or give a lecture on your specific topic? No problem. A colleague is struggling and needs help and advice. Let us know! We won't be able to save the world on our own but that's what the network is for – we can always give a shout and count on the community. If you want to be part of the community and receive the newsletter, just write to the Core Team and we will support you to become (an active) part of the network.

Acknowledgements

We would like to extend our heartfelt thanks to the community for your unwavering support and enthusiasm. Your commitment in spreading the network's activities, helping to carry them out, and fostering growth is invaluable. We are deeply grateful for your continued involvement, as it plays a crucial role in the success and expansion of the network.

Author contribution

Michaela Schauer: conceptualisation, funding acquisition, project administration, writing – original draft, writing – review and editing;
Michelle Richards: conceptualisation, writing – original draft, writing – review and editing;
Mai Abdelgawad: writing – review and editing;
Luisa Dallai: writing – review and editing;
Roger Doonan: writing – review and editing;
B. Lee Drake: writing – review and editing;
Ioannis Liritzis: writing – review and editing.

Statement on the use of artificial intelligence

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4

Integrating machine learning in pXRF studies

Katharina Streit, Brandon Lee Drake

Comparative analysis of dark faced burnished ware from Tel Kurdu and Ein el-Jarba (6th millennium BC): typology, pXRF characterisation, and deep learning of ceramic assemblages

Abstract

A connection between the 6th millennium BC dark faced burnished ware (DFBW) of the northern Levant and the Wadi Rabah ware of the southern Levant has been suggested based on typological comparison and the shared decoration with red and black slip and burnish, but not explored in detail. This study offers a direct comparison between a ceramic assemblages of the northern (Tell Kurdu) and the southern Levant (Ein el-Jarba). The typology and surface finish indicate greater similarity than distinction between the assemblages. Portable energy dispersive X-ray fluorescence (pXRF) characterisation of 20 sherds from Tell Kurdu and 40 from Ein el-Jarba with deep convolutional neural networks indicate that both assemblages can be clearly distinguished geochemically. No specialisation of the raw material selection for the recipe of the slip for preparation of red or black burnish can be discerned, and the distinct colouration appears to have been produced *ad hoc* during the firing process. The use of a CNN model to address the low sample size (n=60) of these sherds is itself notable – suggesting that small data sets are not prohibitive to the use of neural networks and machine learning in archaeology.

Keywords

Levant, Neolithic, ceramics, typology, pXRF, machine learning

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Introduction

The ceramic tradition of the Levant in the 6th millennium BC

The Pottery Neolithic of the northern Levant in the late 7th and early 6th millennium BC is characterised by the advent of a burnished ceramic tradition, so called dark faced burnished ware (DFBW), which continued until the early 5th millennium, when it was gradually replaced by a painted decoration[1]. Around 5800 BC, burnished ware appears for the first time also in the southern Levant and becomes the hallmark of the Wadi Rabah culture[2] (**fig. 1**). The new ceramic industry shows a clear break with the previous Pottery Neolithic, with the introduction of new typological shapes, as well as intensive slip and burnish, resembling the DFBW of the northern Levant. This shift in ceramic tradition occurred embedded in an intensive network of transregional interaction between the three dominant cultural entities, the Halaf culture in northern Mesopotamia, the Amuq C phase of the northern Levant and the Wadi Rabah of the southern Levant formed between *circa* 5800 and 5300/5200 BC[3]. Almost without exception all that remains of these cultures is their material culture, thus research focuses on physical artefacts of which ceramics are one part. However useful these material remains are, they are only part of a larger dynamic cultural process. Additionally, raw materials such as obsidian[4] and chlorite[5], finished products such as stamp seals[6], but also aesthetic concepts of ceramic shapes[7] and figurine style[8] were exchanged[9]. The extent to which these ceramic traditions correspond to distinct cultural entities remains uncertain. The simplistic equation of "pots = people" is widely regarded as problematic, and ceramics should not be treated as direct indicators of specific human groups. Nevertheless, stylistic and technological influences in pottery can often be traced across regions, potentially reflecting broader patterns of cultural interaction and exchange.

The new ceramic tradition necessarily entailed technological innovations to achieve the high-quality slip and burnish characteristic of this period. In order to achieve the glossy finish, the vessel was formed and then covered with a layer of well-levigated clay, rich in iron oxides, which was applied and left to dry until it reached a hard leathery state. Then the vessel was burnished with a smooth object to achieve the fine, glossy finish[10]. The iron content of the slip converted to magnetite or hematite, turning black or red, depending on whether the vessel was fired in an oxidizing or reducing atmosphere[11]. The dark glossy finish may also be caused by graphite formation which can occur even at relatively low temperatures[12]. Kilns may have been used in the process, but

1. Braidwood, Braidwood 1960, p. 501–512; Yener *et al.* 2000, p. 65.
2. Garfinkel 1999, p. 104–153; Gopher, Gophna 1993, p. 328–332.
3. Garfinkel 1999, p. 5–7.
4. E.g. Schechter *et al.* 2013; Delerue *et al.* 2012; Garfinkel 2011; Gopher, Marder, Barkai 2011; Prausnitz 1969.
5. Rosenberg, Getzov, Assaf 2010.
6. Getzov 2011.
7. Garfinkel 1999, p. 150–151.
8. Streit 2018; Milevski 2016; Streit, Garfinkel 2015.
9. For a recent summary, see Streit 2020.
10. For a detailed reconstruction of the production process, see Goren 1992.
11. Goren, Gopher, Goldberg 1993, p. 36.
12. Noll, Heimann 2016, p. 141.

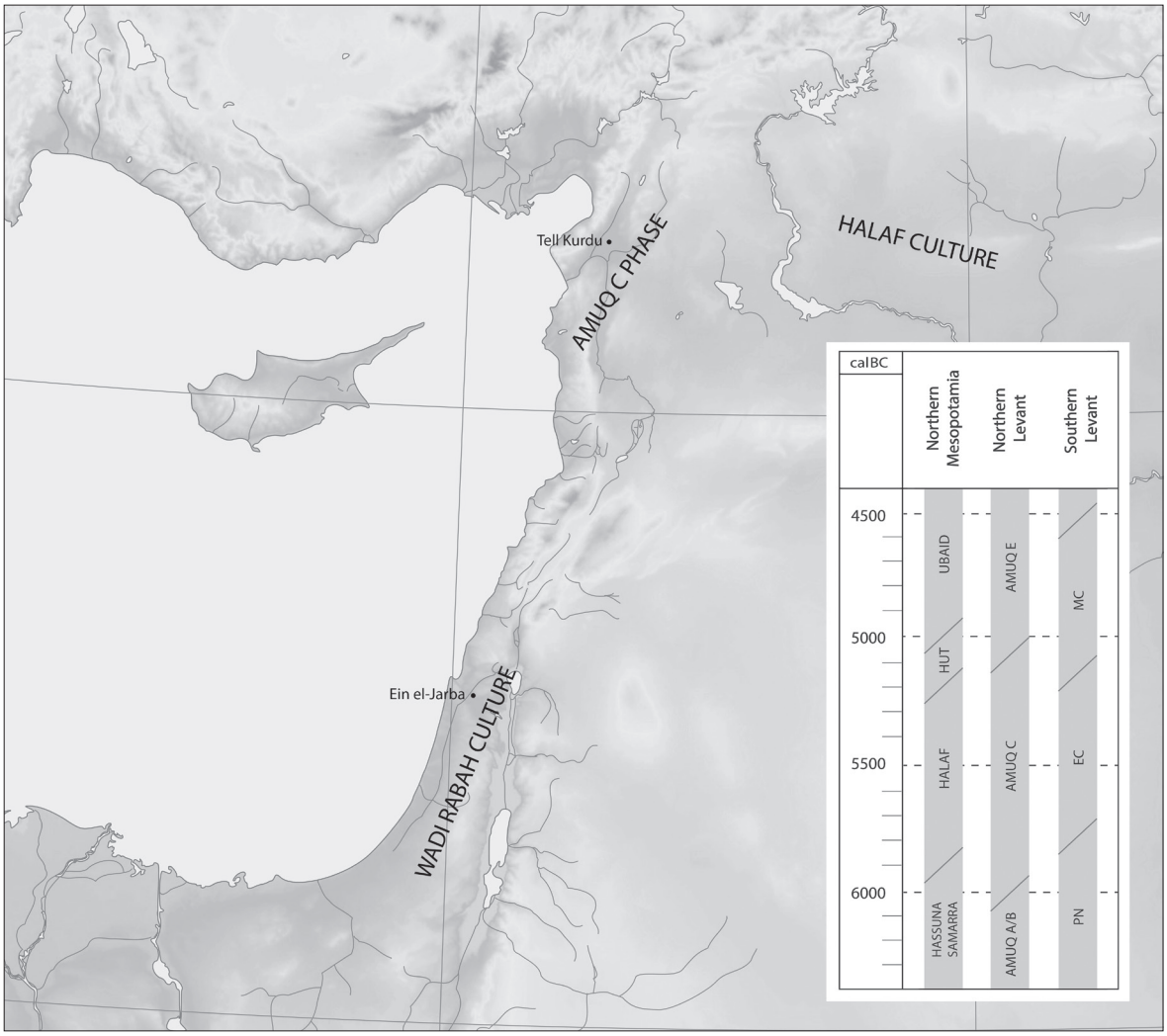


Figure 1: Geographic and chronological overview of cultural entities of the Near East in the 6th millennium BC and the sites of Ein el-Jarba and Tell Kurdu marked

these results can also be achieved in open fires[13]. Micromorphology data would be needed to confirm these possible processes. The earliest preserved pottery kilns have been uncovered in northern Mesopotamia at sites ascribed to the Hassuna culture, dating to the late–7th to early–6th millennium BC[14]. In the southern Levant, the earliest pottery kilns date to the Early Bronze Age[15]. The vessels themselves frequently show irregular transitions between red and black, with various shades of brown in between (**fig. 2**), which would rather contradict any highly controlled firing environment. The appearance of red and black burnish in the southern Levant thus implies the transmission of stylistic preferences, but also technological knowledge. However, the connection of

13. THÉR 2014.
14. HANSEN STREILY 2000.
15. PAZ 2006, p. 63–67; FIACCAVENTO 2013, p. 81.

the burnished ceramic tradition between northern and southern Levant has so far only been studied in terms of typology and not with regard to technological aspects of its production, such as raw material selection and craft specialisation.

While some technological stages of the production process have been reconstructed, a more nuanced understanding of raw material choice, clay preparation and particularly of the production of the characteristic glossy finish of these wares is lacking. It has been argued[16] that the visual effect of red and black burnish is created solely by absolute control of the firing atmosphere. This implies that the raw material for both colours was identical and the colouring was decided ad hoc in the course of the firing process. However, specialised slip recipes for ceramic decoration have been observed in elite ceramic assemblages of later periods in the Mediterranean region[17]. Considering the proposed high status of the burnished ware of the 6th millennium[18], similar production specialisations can be envisaged already in prehistoric times. Furthermore, while typological comparisons of the ceramic assemblages of northern and southern Levant were proposed shortly after the initial discovery of these cultural entities[19], a comparison of the fabric has been hampered by the present-day political geography of the region. The accessibility of finds curated at the Oriental Institute collections and the export policy for research purposes of the Israel Antiquities Authority provide a unique chance to directly compare and characterise the fabric and technological aspects of both assemblages.

X-ray fluorescence characterisation of ceramics

Over the last decade, portable energy dispersive X-ray fluorescence (pXRF) has gained popularity in the analysis of archaeological materials. As a non-destructive analytical method, material characterisation is possible in a range of finds, which could not be sampled with destructive methods[20]. A main application of the method constituted raw material characterisation and subsequent source discrimination. The fast, flexible and inexpensive sampling of archaeological materials with a pXRF further permitted the analysis of large numbers of samples in reasonably short study periods. The validity of pXRF analysis for ceramic sourcing purposes has been recently subject to a vivid debate[21]. Comparative studies of pXRF vis-à-vis other analytical methods, such as WDXRF[22], ICP-OES[23] and NAA[24], however, showed that raw material source discrimination of pXRF could be confirmed with other methods. Other studies stressed the limitations of the method[25], emphasizing however that while the resolution gained with destructive methods remains higher, pXRF sampling obtained data from objects otherwise inaccessible to chemical characterisation.

XRF studies aiming to discriminate raw material sources in pottery and other ceramic material dating from the Neolithic to the Iron Age have been conducted on material from the Eastern

16. Goren, Gopher, Goldberg 1993, p. 36.
17. Klesner *et al.* 2017.
18. Özbal, Gerritsen 2013.
19. Kaplan 1960; Kirkbride 1969.
20. Tykot 2016; Shugar, Mass (eds.) 2012.
21. Emmitt *et al.* 2018; Wilke, Rauch, Rauch 2016; Hunt, Speakman 2015.
22. Rowe, Hughes, Robinson 2012.
23. Bonizzoni, Galli, Milazzo 2010.
24. Karacic, Osborne 2016; Goren, Mommsen, Klinger 2011.
25. Speakman *et al.* 2011.

Mediterranean and adjacent regions[26]. While the general validity of the method has been confirmed, interfering factors must be taken into account. The primary challenge when sampling ceramic material, unlike obsidian, is the heterogenous nature of the clay matrix. Clay can contain mineral inclusions which were added as temper or occurred naturally in the clay deposit. As the detecting window of most pXRF equipment is but a few millimeters in diameter, single minerals could significantly impact the reading. This problem can be bypassed with pretreatment protocols which include the pulverisation of the sample and subsequent pressing into a pellet[27]. While this method is doubtlessly efficient, this destructive pretreatment method is often excluded. The preferred method is therefore the selection of flat and homogenous sampling surfaces and the measurement of usually two to four different sampling locations per sherd[28]. Methodological studies have stressed that while the quantification of lighter elements such as Si, Ca and Ti could be inaccurate, particularly on uneven target surfaces, heavier elements such as Fe, Rb, Sr and Zr were not impacted[29].

Deep neural networks

Considerable advances have been made in the field of artificial intelligence and its subfield of machine learning. Machine learning itself is based on the idea that patterns in data can be recognised algorithmically through multiple iterations. Deep learning, a subset of machine learning, relies on neural networks to generate abstractions of data capable of forming generalisable methods. And of these, convolutional neural networks (CNNs) have the capability of retaining spatial information about the input data. They are based on mathematical models of the human visual cortex, with convolution layers representing spatial connections between data[30] with a max-pooling step to condense this information[31]. Each layer in a neural network enhances the model's capacity to extract and build abstractions from the data, with the aim that, given a sufficient number of layers and a suitable architecture, the network can approximate the classifications required by a specific archaeological question (e.g. determining whether a ceramic artefact belongs to one cultural group or another).

The ultimate goal of current-generation machine learning models is to abstract data to match cultural classifications. The present study simply adopts this to meet archaeological definitions of material culture.

pXRF, while traditionally an analytical technique, produces an X-ray spectrum containing a variety of photon-electron interactions producing a variety of fluorescence and scattering effects along the electromagnetic continuum. The nature of this data can be represented by a single dimensional CNN to identify patterns in fluorescence by site using the spectrum as the primary input. By using a 1-dimensional (1D) CNN to interpret the spectra directly, the first steps toward generating an artificial intelligence classifier can be made. Single dimensional CNN models have been used with

26. Aloupi-Siotis, Kalogirou 2024; Emmitt *et al.* 2018; Karacic, Osborne 2016; Gajić-Kvaščev *et al.* 2012; Frankel, Webb 2012; Goren, Mommsen, Klinger 2011; Forster *et al.* 2011; Papargeorgious, Liritzis 2007; Morgenstein, Redmount 2005.
27. Hunt, Speakman 2015; Shackley 2011.
28. Emmitt *et al.* 2018, p. 423; Wilke, Rauch, Rauch 2016, p. 142.
29. Forster *et al.* 2011; Hunt, Speakman 2015.
30. Fukushima 1980.
31. Weng, Ahuja, Huang 1993.

spectra from medical equipment to make diagnoses[32]; their utility comes from preserving the positional placement of counts in the spectra.

Comparative typology of the ceramic assemblages of northern and southern Levant in the 6th millennium BC

The ceramics of the Wadi Rabah culture and Amuq C culture share many distinct features (fig. A–1). Both assemblages feature a large variety of deep bowls (A1/2), with their height exceeding their diameter, usually with a simple sharpened rim, and a slightly S-shaped wall. Bases can be flat or occasionally ring shaped. Carinated bowls (A4) are also present in both assemblages and were likely inspired by Halafian shapes[33]. The vessels are marked by a carination in their upper half and an elegantly flaring rim. These shapes are frequently rather thin-walled and intensely decorated with burnish or a painted decoration. Spouts represent an unusual shape (A3) and they are predominantly found detached from the rest of the vessel. Based on the proportions of the preserved body shape, they most likely belong to deep bowls. Spouts are found in both assemblages. Shallow bowls (B), with their diameter exceeding their height, have been further subdivided into more generic incurving (B1), rounded (B2) and carinated (B3) shapes and basins (B4). So-called lids (B5) form a very peculiar typological group. Similarly to the deep carinated bowls (A4), they are a clear influence of the Halaf culture[34]. Additionally, large platers (B7), shallow flaring rim bowls (B8) and so-called 'Cream Bowls' (B9) are only present in the Amuq C assemblage and are lacking from the Wadi Rabah tradition.

Very rare and distinct to the Amuq C and Wadi Rabah assemblages are footed bowls or chalices (C1), as well as fenestrated stands (C2). The latter group has been seen as a rare typological influence from the southern Levant on the northern Levant[35]. Pithoi (D) form a constant in the ceramic assemblages over most periods and it is therefore not surprising that they are found in both the northern and the southern Levant alike.

Holemouth jars (E) make up more than one third of the assemblage in the southern Levant[36], and occur with a variety of sizes and rim shapes. It should be noted that they largely disappear after the Amuq C and Wadi Rabah phase at the end of the 6th millennium BC. Among the necked jars (F), the so-called bow-rim jar (F1) should be again considered an influence of the Halaf culture[37] and appears in both assemblages. Other shapes such as the everted neck jar (F2/3) are less diagnostic but also common to both assemblages, while the straight-necked jar (F4) is present only in the northern Levant.

The dominant decoration practice in both assemblages is slip and burnish. Colours in burnished ware can range from black through different brown shades to bright red (**fig. 2**). Burnish accounts

32. Kiranyaz, Ince, Gannouj 2017.
33. Garfinkel 1999, 111, fig. 69, 150–151.
34. Garfinkel 1999, 119, fig. 75, 150–151.
35. Özbal, Gerritsen 2013.
36. Streit, Favis, Garfinkel 2017, p. 532–534; Garfinkel 1999, p. 131.
37. Garfinkel 1999, 133, fig. 84.

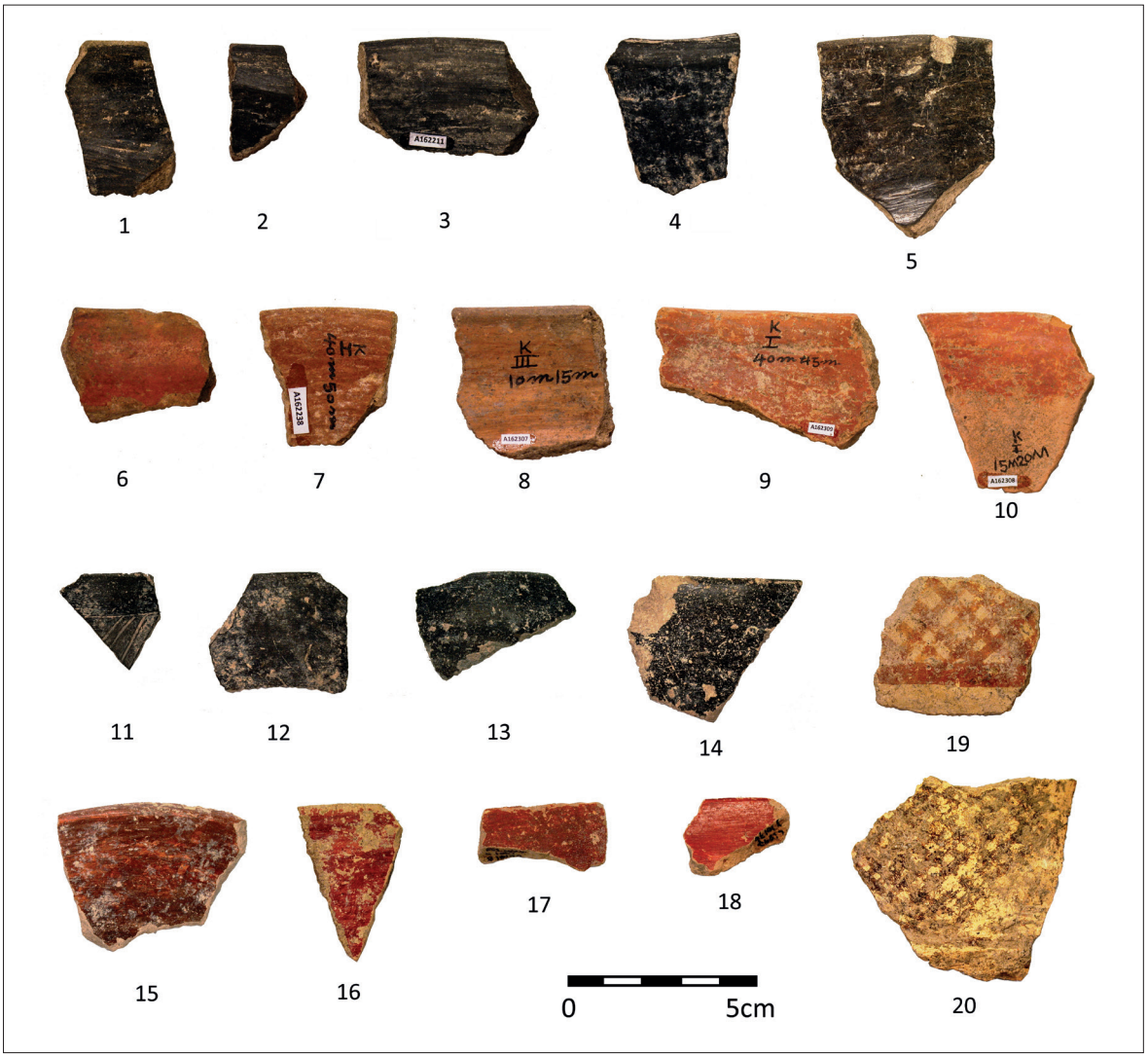


Figure 2: Colour plate of representative decorated black burnish, red burnish and painted ware from Tell Kurdu (Reg. no.: 1: A162195; 2: A162197; 3: A162211; 4: A162226; 5: A162310; 6: A162237; 7: A162238; 8: A162307; 9: A162309; 10: A162308) and Ein el-Jarba (Reg. no.: 11: L1091, B10408; 12: L1091, B10408; 13: L1080, B10378; 14: L1084, B10389; 15: L1020, B10306; 16: L1047, B10190; 17: L1047, B10170; 18: L1047, B10170; 19: L1099, B30378; 20: L1099, B10447)

for 35-40% of the assemblage in the Amuq C phase of Tell Kurdu[38], and ranges from 37.74% and 71%[39] in the southern Levant.

It can be concluded that the two assemblages are more similar than they are different. The vast majority of typological shapes is represented both in the northern and southern Levant, and slip and burnishing is the preferred mode of decoration in both areas. The typological analysis thus suggests

38. Braidwood, Braidwood 1960, p. 138.
39. Streit 2020, table 95.

that these two assemblages appear to have developed independently of each other. It remains to be determined to what extent this also applies to raw material selection and production technology.

Materials and methods

The assemblage

Two ceramic assemblages from two key sites dating to the 6th millennium BC were chosen for this study: Tell Kurdu in the northern and Ein el-Jarba in the southern Levant.

The ceramic assemblage of Tell Kurdu (Turkey) was formed by the Oriental Institute of the University of Chicago expedition to the site under the directorship of Robert Braidwood in 1938[40]. A portion of the ceramic assemblage is currently stored in the Oriental Institute collections of the same institution and was analysed for this study (fig. 2; fig. A–2; Table A–1). Permission for non-destructive examination was provided by the Oriental Institute in the framework of the Oriental Institute Collections Research Grant. Destructive sampling (e.g. for petrography) was not permitted. Altogether 20 sherds were selected based on the criteria outlined below from the Amuq C[41] layers of the site. Unfortunately, the excavation methodology employed in the 1930s did not reach a sufficient stratigraphic resolution to verify the context of every find.

The site of Ein el-Jarba (Israel) was excavated by Katharina Streit on behalf of the Hebrew University in five season between 2012 and 2016[42]. Material culture uncovered at the site included large numbers of obsidian pieces imported from Cappadocia, the southern Caucasus and the Lake Van region[43], but also small finds with iconographic features with distinct ties to the north[44]. At the time of sampling, ceramic material from Area A was available for analysis. The samples were exported to Chicago as part of the Israel Antiquities Authority loan scheme (export approval No. 14052) for the duration of the study and were subsequently returned to Israel. Altogether 40 sherds were selected from the Early Chalcolithic (Wadi Rabah) strata A5 and A6. Sherds with unclear stratigraphic ascription were not included (fig. 2; fig. A–3, Table A–2).

Ceramic sherds from both sites were selected for this study based on the following criteria:

1. Sherds were to be of sufficient size (thickness and surface) to permit sampling at multiple locations at the section and surface;
2. a sufficient portion of the profile of the vessel had to be preserved to allow secure reconstruction and categorisation of the typology. Diagnostic body parts such as rims and bases were preferred for this purpose;
3. the assemblages were selected so as to represent the full range of typological shapes (open and closed vessels), as well as surface treatments (black and red burnish, painting, plain wared);
4. well-preserved sherds were preferred and sherds showing encrustations were avoided to reduce the risk of contamination of samples;

40. Braidwood, Braidwood 1960.
41. Braidwood, Braidwood 1960, p. 135–156.
42. Streit 2015a; Streit 2016a; Streit 2016b.
43. Carter, Campeau, Streit 2020.
44. Streit 2015b; Streit 2016a.

5. sherds from reliable and well documented stratigraphic context were preferred.

Instrumentation and analytic settings

The samples were analysed with the pXRF Bruker Tracer III-SD (T3S2581) with a rhodium anode and silicon-drift detector at the Conservation Laboratory of the Oriental Institute of the University of Chicago. In this study we have applied analytical settings similar to those used in previously performed successful studies on comparable material[45].

Major element analysis (Si, Ti, Ca) was conducted using 15 kV and 25 µA with 60 sec assays and without a filter in the X-ray beam path leading to the sample. A vacuum pump was used for light element analysis to reduce air attenuation and thus ensure optimal efficiency at these lower energy settings at < 17 torr. Trace elements (Fe, Th, Rb, Sr, Y, Zr, Nb) were analysed at 40 kV and 11.5 µA with 120 second assays in air with a Ti (25 µm) and Al (1 µm) filter.

Each sherd was sampled both in its section and its surface. Encrustations were carefully removed mechanically using a scalpel, and the sherds were additionally cleaned with compressed air. For each sherd, the section was sampled at up to four locations, depending on the size of the sherd (fig. A–4). Particularly flat portions of the section were preferred and visual inclusions, such as mineral temper, were avoided as much as possible. Additionally, one or two measurements were taken on the decorated surface (paint or slip) of the vessel. The sampling locations were marked in the photo documentation of each sampled sherd. Raw data in the form of individual spectra were generated with S1PXRF software.

For descriptive analysis, data were aggregated into intensities using CloudCal software[46]. For CNN analysis, data was normalised and presented to the model by normalizing to 0.7–1.0 keV for light (e.g. 15 keV) data and normalised to total counts for trace (e.g. 40 keV) data. A parallel data set of quantified data was provided for replication purposes. The instrument was calibrated using 26 reference standards following procedures recommended by Rowe[47]; data available in Table A–3.

Statistical processing

All data analysis was done using R (3.6.1). CNN analysis was conducted using Keras (2.2.4) with tensorflow as a back end (1.3) through PlaidML (0.6.4) for processing on an AMD Vega Pro 64 graphics card. Only clay data (e.g. Locations 1–3) were used to train and test the CNN. The CNN was constructed using three 1D convolutional layers, the first having filters matching the number of energy channels inputted (rounded to 0.1 keV), 0.7–15 keV or 0.7–40 keV, the second having 128 filters, and the third having 64. Each of these had a 3 × 3 kernel size. The last 1D CNN layer was then passed to a 1D max pooling with a pool size of 2. This was followed by a dropout layer with a rate of 25%, followed by a flattening layer. A dense layer with 64 hidden units was followed by a 30% dropout, then a dense layer of 32 hidden units, followed by a dropout of 30%, followed by a dense layer of 16 hidden units, followed by a dropout layer of 30%, and finally a dense layer of 12 hidden units. All layers used a rectified linear unit (ReLU) for activation, except

45. E.g. Forster *et al.* 2011.
46. Drake 2025.
47. Rowe, Hughes, Robinson 2012.

for the final layer which outputted one of two classes activated by softmax: Tell Kurdu or Ein el Jarba. This CNN model was compiled using categorical cross-entropy as a loss function, an Adam optimiser, and accuracy as a metric[48]. While typically a binary cross-entropy loss function would be used for dual-category data, this particular model was built to be scaled to multi-category use cases. This model was run using a batch size of 4 over 250 epochs, or forward and backward propagation of the entire data set through the network. To test generalisability of this CNN, 20% of data was withheld from training for validation testing (fig. A–5).

Results

The results of the trace element protocol measurements (40 keV and 11.5 µA; 120 second assaults; in air; Ti (25 µm) and Al (1 µm) filters) of the Tell Kurdu and Ein el-Jarba datasets were examined using principal component analysis (PCA), which has been successfully used for other clay provenance studies[49]. The results revealed two distinct geochemical groups (**fig. 3A**), which correlate to two geographic origins for the clay in most of the sherds studied here. A similar pattern was observed with the major element protocol. The two clusters correlate with the geographic origin of the samples. However, one sample from Tell Kurdu (A162285: B1, red burnished, three repetitions on different locations) displays a chemical signature similar to the examples from Ein el-Jarba, which otherwise form a very coherent group. As three measurements were taken from different locations on the section of this sherd, the deviation cannot be ascribed to measurement distortion caused by the heterogenous nature of the clay.

The dataset of trace element protocol measurements was further plotted as a triangular scattergram (fig. 3B) of Rb, Fe, and Sr. These three elements have been found as particularly indicative of geochemical composition of different sediments in earlier publications[50]. It is thus expected that the clusters will reflect different lithic sources of the clay material. Indeed, these elements have proved to be highly diagnostic for characteristic northern and southern Levantine fabrics. Sample A162285 is shown on the scattergram, where it shares the southern Levantine geochemical signature, as indicated by the PCA of the same dataset.

A PCA of the decorated ceramic surfaces of red and black burnished ware was generated for the Tell Kurdu (**fig. 4A**) and Ein el-Jarba (**fig. 4B**) datasets. In this case, no distinctive clusters were evident, so the burnish does not follow any specific geochemical pattern that might suggest different recipes for each geographical area. An Rb-Fe-Sr scattergram of the burnish showed similar results.

Titanium-potassium (Ti-K) tests have been found to be particularly indicative for certain geographic regions in the Near East[51]. This should be ascribed to a range of highly distinctive geological environments, which are marked by volcanic activity in the northern Levant[52] and alluvial activity

48. These parameters are the most commonly used in neural networks; categorical cross entropy quantifies the difference between reference (i.e. given) and predicted values during training. The Adam optimiser (short for adaptive moment estimation) exponentially weights past movements of gradient descent, estimating both mean and variance for updating weights.
49. Goren, Mommsen, Klinger 2011.
50. Morgenstein, Redmount 2005, p. 1618.
51. Goren, Mommsen, Klinger 2011, p. 691–692.
52. Morgenstein, Redmount 2005, p. 1621.

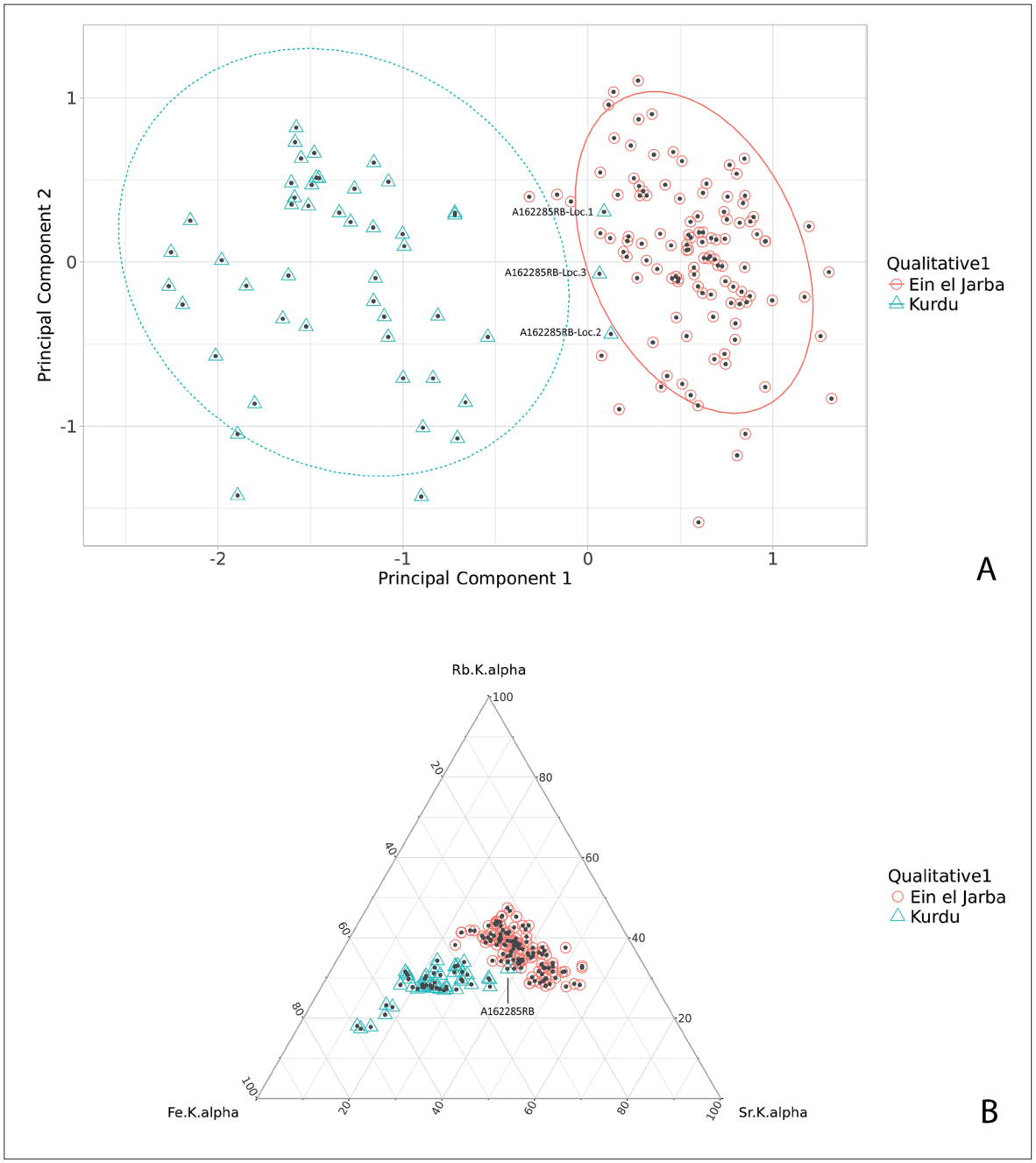


Figure 3: **A**: Principal component analysis (PCA) of fabric measurements of both assemblages conducted with the trace element protocol (40 keV and 11.5 μA; 120 second assaults; in air; Ti (25 μm) and Al (1 μm) filter), **B**: Scattergram plotting Rb, Fe, and Sr values of fabric measurements of both assemblages conducted with the trace element protocol (40 keV and 11.5 μA; 120 second assaults; in air; Ti (25 μm) and Al (1 μm) filter)

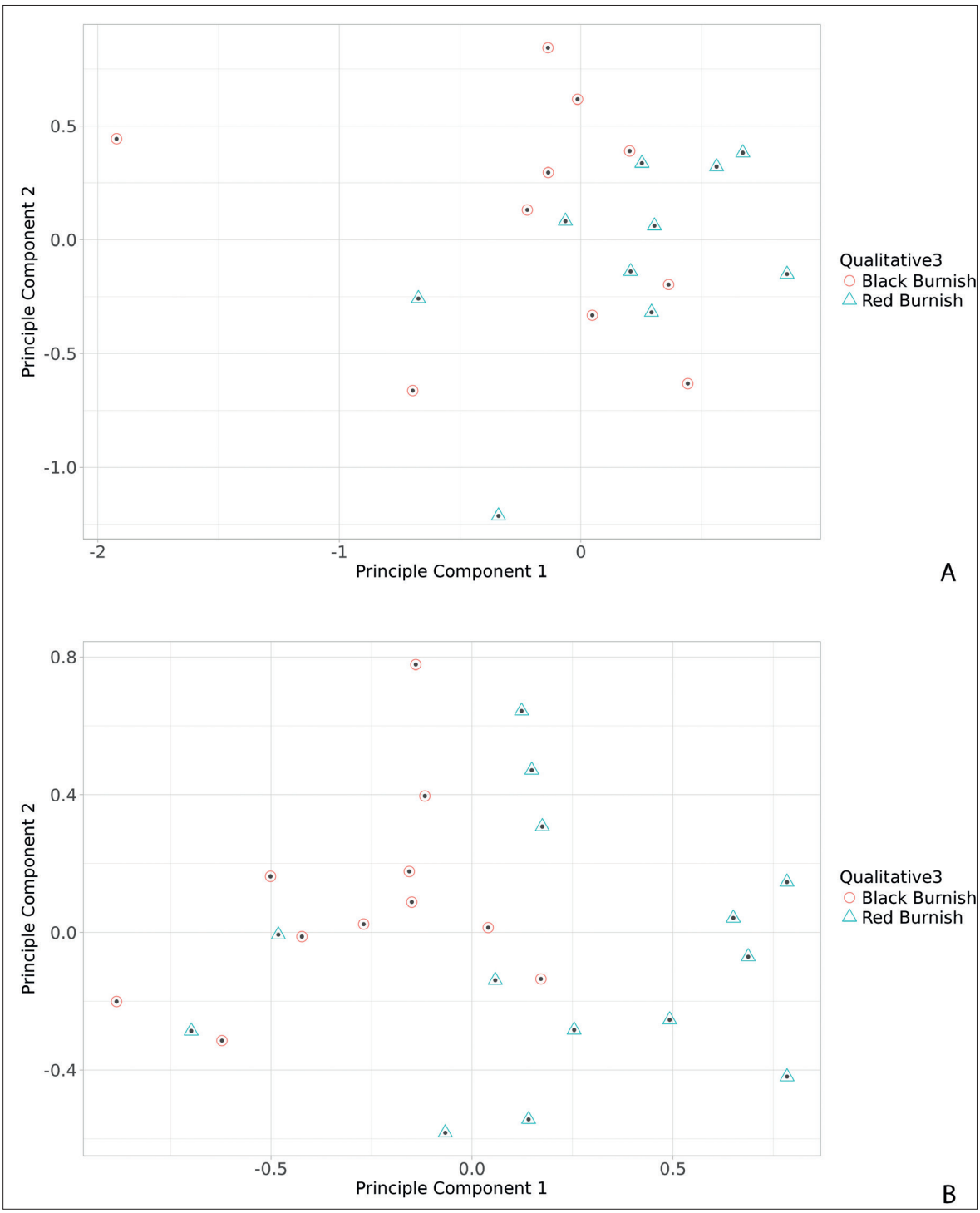


Figure 4: Principal component analysis (PCA) of the decorated ceramic surfaces of red and black burnish ware conducted with the trace element protocol (40 kV and 11.5 μA; 120 sec assaults; in air; Ti (25 μm) and Al (1 μm) filter), **A**: Tell Kurdu, **B**: Ein el-Jarba

in Mesopotamia and Egypt. A Ti-K biplot from the data generated with the major element protocol (15 keV and 25 µA; 60 second assaults; without a filter) is presented in **Figure 5**. As both Ti and K are common components of clays, a linear relationship between them was expected, but the offset between the Tell Kurdu and Ein el-Jarba indicates that while the clays have similar compositions, they are not identical. However, the clusters identified in the Ti-K test overlap significantly, rendering clear discrimination problematic. It should further be noted that sample A162285 falls well within the range of the Tell Kurdu dataset.

The CNN produced training models with 100% and 97.7% accuracy for light and trace data, respectively. The 20% control sample withheld from training to validate the model had an accuracy rate of 100% for both light and trace data. Accuracy and loss for the training set is provided in **Figure 6**, while confusion matrices and accuracy frames are provided in Table A–3.

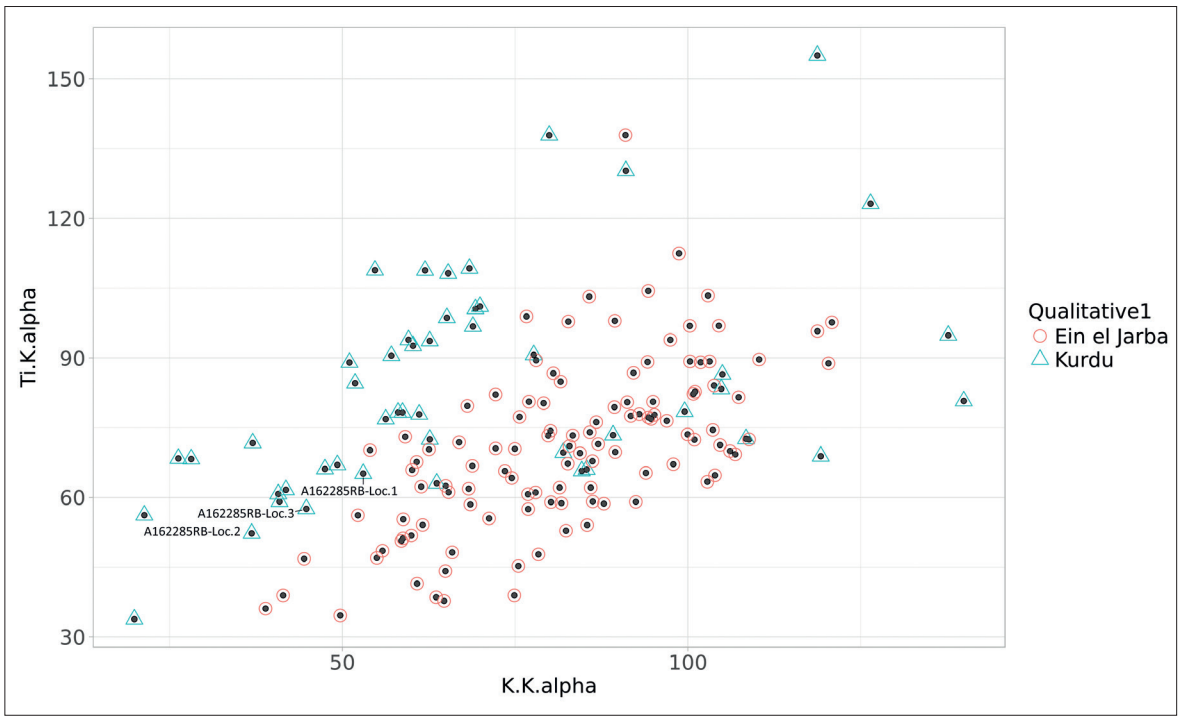


Figure 5: Titanium-potassium (Ti-K) biplot from the data from both assemblages generated with the major element protocol (15 keV and 25 µA; 60 second assaults; without a filter)

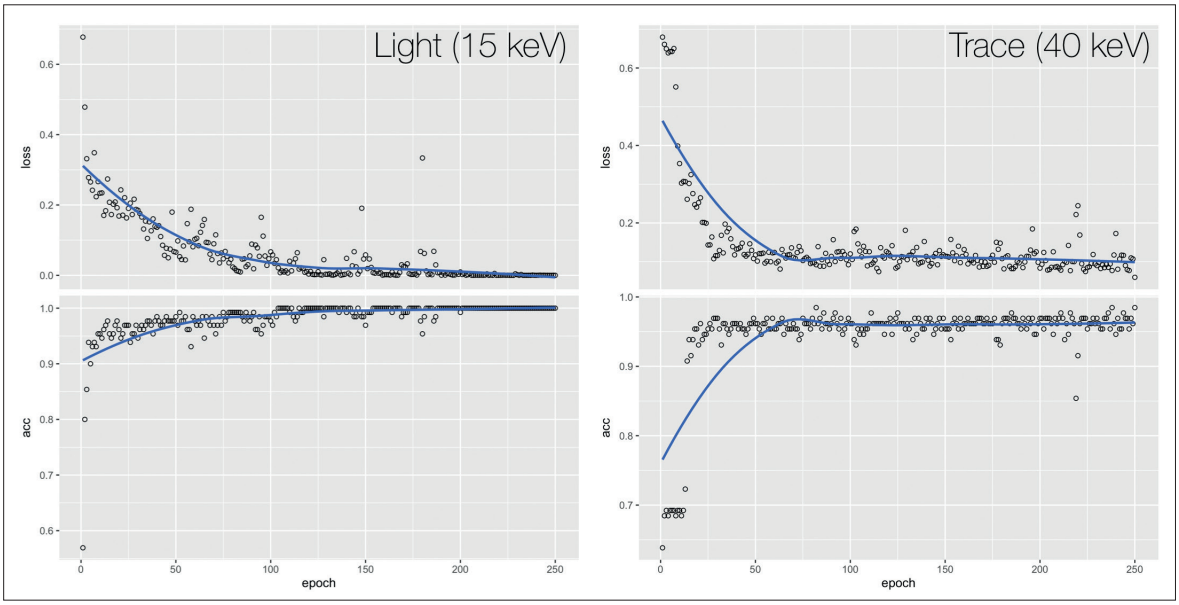


Figure 6: Training categorical cross entropy and accuracy for light (15 keV) and trace (40 keV) data. Both networks show a substantial increase in accuracy within 15 epochs

Discussion and conclusion

The typological analysis of the assemblages from Ein el-Jarba and Tell Kurdu available for this study has shown a strong proximity between these two ceramic traditions. This corresponds well with proposed influence of the northern on the southern Levant in this period, as seen both in the ceramic tradition[53], as well as the general notion of transregional interaction as seen with the import of raw material and artistic concepts in this period[54].

PCA of the fabric measurements conducted with the trace element protocol successfully discriminated between the two assemblages based on their geochemical characteristics, confirming the suitability of this method for source studies of ceramics. The clay of sample A162285, from the Tell Kurdu assemblage, showed a geochemical fingerprint (in both the PCA and the Rb-Fe-Sr scattergram) more closely related to the southern Levantine assemblage. This was not confirmed further by the Ti-K biplot of the same dataset.

pXRF sampling of the characteristic black and red slip present in both assemblages in order to reconstruct raw material preference "recipes" showed no raw material discrimination. This indicates that both in the northern Levantine DFBW and the Wadi Rabah black and red slip no specific raw material recipes have been followed, and the characteristic visual effects were achieved solely with different firing protocols, contrary to later periods when specialised firing recipes have been observed[55].

53. Garfinkel 1999, p. 104–153; Kirkbride 1971; Kaplan 1960.
54. Streit 2020; Schechter *et al.* 2013; Delerue *et al.* 2012; Garfinkel 2011; Getzov 2011; Rosenberg, Getzov, Assaf 2010.
55. Klesner *et al.* 2017.

The pXRF characterisation of 20 sherds from Tell Kurdu and 40 from Ein el-Jarba has provided valuable information regarding the raw materials employed in the production of ceramics and their decoration in the 6th millennium BC. Traditionally, ceramics have been difficult to source due to the limited range of elements upon which pXRF can be used, and the limited detection rates for most elements[56]. While the Tell Kurdu and Ein el-Jarba ceramics were for the most part identified as distinct groups (fig. 3A-B), there is some ambiguity for individual samples, such as A162285. This is typical in ceramic sourcing.

However, CNN analysis of the entire spectrum was capable of predicting the source of Tell Kurdu and Ein el-Jarba ceramic clays with an accuracy of 100% on the control samples. Despite the limited sample size, the method captured the complex variation between ceramics from the two sites and generated a generalisable model for future classification. As studies of limited scope can often be implemented in a very timely fashion, they can provide a valuable first assessment of the potential of ceramic datasets for further investigation. Many of the concerns regarding pXRF use on ceramics remain valid, but CNN models and other machine learning techniques have the potential to resolve some of these difficulties by capturing the multi-faceted nature of ceramic variation in a way that simpler PCA analysis does not.

CNN data has provided clarity on the use of pXRF data, but the reverse is also true. CNN models typically require large amounts of data to work, a problem known in the data science community as "the curse of small data sets." Here, with a sample size of 60 sherds and around three clay measurements each, a strong model was built with 100% test accuracy on cross validation with 20% of the samples. This result shows that 1D CNNs can generalise with high accuracy from very small sample sets.

CNN successfully replicated simple geochemical differentiation of Ein el-Jarba and Tell Kurdu ceramics (fig. 3B) as an independent test running across the XRF spectra. In particular, the randomised cross validation success at 100% illustrates that the approach is not just descriptive, but generalisable. While the differentiation of Ein el-Jarba and Tell Kurdu may not be the most challenging problem for a CNN classifier to address, it establishes this method as a generalisable solution for ceramic classification problems that can be used on more difficult data sets. Importantly, the neural weights of a model can be adapted to new situations; the present findings aren't just applicable in theory to future research, but the model weights included as supplemental material X can be used for other researchers to build on the neural network trained here.

This suggests that spectral data such as that generated by pXRF may not have the steep data requirements that are required for traditional deep learning applications, such as facial or object recognition in images. This could open the door to a wide range of applications in archaeology where large data sets are frequently unavailable.

56. Speakman *et al.* 2011.

Acknowledgments

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Author contribution

Katharina Streit: excavated the material, conducted typological analysis, conducted pXRF analysis; **Brandon Lee Drake**: CNN and PCA analysis.

Data availability statement

All data used to generate these analyses, as well as code and model weights, are available at https://www.github.com/leedrake5/ceramicCNN. Note that deep learning capabilities vary from computer to computer, and some additional local setup work may be needed to run the model on a GPU, however in the event of difficulty all models will fall back to the CPU.

Online-Materials

Figures

Figure A–1: Comparative ceramic typology of the Amuq C and the Wadi Rabah culture[57]
Figure A–2: Representative selection of sherds from the ceramic assemblage of Tell Kurdu (Amuq C/D phase)
Figure A–3: Representative selection of sherds from the ceramic assemblage of Ein el-Jarba (Wadi Rabah Phase, A5 and A6)
Figure A–4: Schematic depiction of pXRF sampling locations for each sherd
Figure A–5: Deep-learning 1D convolutional neural network with fourteen layers, including three 1D-CNN and four dense layers

57. Based on De Contenson 1992; Garfinkel 1999.

Tables

Table A–1: Ceramic assemblage from Tell Kurdu (fig. A–2); Contexts have been reconstructed from the marking on the sherd. Please note discrepancies to the general stratigraphic ascription of the sherd in several instances
Table A–2: Ceramic assemblage from Ein el-Jarba (fig. A–3)
Table A–3: Supplementary Material A
Table A–4: Supplementary Material B

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Anno Hein

Machine learning approaches in provenance studies of transport amphorae using pXRF

Abstract

In provenance studies of archaeological ceramics compositional differences between ceramics manufactured at different production sites are investigated. In order to determine the elemental composition of archaeological ceramics, samples are commonly taken from selected ceramic objects and analysed with laboratory methods, such as NAA or WDXRF, which provide high analytical performance in terms of precision and accuracy. As an alternative the use of hand-held portable energy dispersive XRF (pXRF) systems has become quite popular over the last 20 years, allowing for non-invasive analyses of elemental compositions, which can be condacted in large numbers and comparatively quickly. On the other hand, pXRF has several drawbacks, as it is extremely surface sensitive, the number of determined element concentrations is limited, and the analytical performance is comparably low. Thus, the statistical evaluation of pXRF data following established approaches of multivariate statistics, which are commonly applied to data collected in laboratory analyses, is not always feasible. The data collected with pXRF present a higher variation introduced through the analytical uncertainties of the method. They are thus comparably fuzzier requiring a more flexible approach taking into account the actual data structure rather than assumptions or models based on geochemistry or *chaîne opératoire*. Various machine learning approaches, such as unsupervised and supervised artificial neural networks (ANN), support vector machines (SVM) or random forest (RF), are tested for the automated categorisation of pXRF data of ceramics and more specifically Archaic, Hellenistic and Roman transport amphorae from the Eastern Aegean region.

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Introduction

The first provenance studies of archaeological ceramics based on their elemental composition determined with instrumental methods can be dated back to the mid-20th century[1]. Since then, similarities and dissimilarities among elemental compositions of pottery have continued to be investigated. These are basically affected by the use of geochemically different raw materials selected for pottery manufacture at different production places and it has been demonstrated that pottery of unknown provenance can be assigned in this way to its origin of manufacture. The elemental compositions and their variation allow for the investigation of the organisation of pottery production and for the distinguishing of different production sites. By comparing ceramics of unknown origin with compositional reference patterns, representing ceramics manufactured at specific sites, their potential provenance can be determined. This provides information concerning distribution of specific ceramic wares allowing for the investigation of trading networks and economic or social relations among societies.

Variation of the elemental composition of archaeological ceramics depends primarily on the variation of the actual elemental compositions of the ceramic body of the finished object, taking into account the selected raw materials, sequence of clay paste processing, vessel manufacture and potential post-depositional alterations. This compositional variation, however, is further enlarged during the analytical investigation through sampling strategy and through analytical uncertainties[2]. The increased variation of compositional patterns can potentially obscure similarities or dissimilarities among the particular pottery productions under examination. In order to reduce the effect of analytical uncertainties, laboratory methods with high precision and accuracy are preferred for ceramic provenance studies, usually methods that are used in geochemistry for silicate analysis, such as neutron activation analysis (NAA), wavelength-dispersive X-ray fluorescence spectrometry (WDXRF), inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS)[3]. However, a fundamental disadvantage of these laboratory methods, particularly when dealing with cultural heritage objects or materials, is the necessity of sampling.

During the last 20 years, however, portable energy dispersive XRF (pXRF) has been introduced into the study of archaeological materials and is attracting increased interest[4]. Hand-held pXRF systems provide several advantages over laboratory methods. They can be used on-site for fast, inexpensive and particularly for non-invasive measurements of elemental compositions of a variety of materials, including ceramics. In the case of pottery analyses, however, several issues arise in terms of analytical performance[5]. The method is extremely surface sensitive, exciting X-ray radiation as well as fluorescence radiation is considerably absorbed already in layers of several µm of solid matter and this depending above all on the energy of the radiation. This has to be considered for measurements of slipped, painted or weathered surfaces, which are inapplicable for determining the bulk composition of the ceramic body. Furthermore, the determined element concentrations are commonly considerably less precise than compositional data collected with laboratory measurements. This is essentially

1. Sayre, Dodson 1957; Richards, Hartley 1960.
2. Bieber *et al.* 1976; Hein, Kilikoglou 2017.
3. Hein *et al.* 2002.
4. Morgenstein, Redmount 2005; Shugar, Mass 2012.
5. Chubarov *et al.* 2024.

due to the compact setup and limited power supply of the systems, which restricts the intensity of the exciting X-ray source and the energy resolution of the X-ray detector. The comparably low precision also limits the number of elements that can potentially be measured. In the case of trace elements, the concentrations are, in fact, frequently close to or below the lower limit of determination or quantification, depending, though, also on the measurement time. Ultimately, the sample geometry affects the determined element concentrations as the systems are commonly calibrated for measurements of plane surfaces in direct contact with the detector window.

All these issues impede the statistical evaluation of pXRF data following common exploratory approaches applied to data from laboratory analyses, such as hierarchical cluster analysis or principal component analysis. The comparison with reference data, on the other hand, is limited by the rather moderate analytical accuracy, which depends essentially on the calibration of the specific pXRF system. Nevertheless, it can be demonstrated that pXRF allows for basic categorisation of pottery samples based on their elemental compositions, indicating similarities and dissimilarities among compositional patterns[6]. The discrimination capability of the method, however, still appears to remain behind the performance of laboratory methods, such as NAA. In the present study two pXRF datasets are discussed, one compiled during a case study of Hellenistic amphorae from Cyprus[7], and one compiled in various case studies of transport amphorae from the Eastern Aegean region[8]. In the first study, the pXRF data have initially been evaluated using conventional multivariate statistical approaches[9]. Based on this initial categorisation, a part of the amphora fragments had been selected for additional NAA. The pXRF categorisation and assignment to compositional clusters was compared with grouping of NAA data. In the evaluation of the pXRF data, however, a considerable part of the element concentrations was not considered due to missing values. Another drawback was the lower precision compared to NAA, which was observed for the major part of the element concentrations. The larger analytical uncertainties of the pXRF measurements interfere with the compositional variation expected for ceramics belonging to the same category. The scope of the present study was to explore whether alternative approaches for data evaluation using, for example, non-linear distances can provide additional information. For this, machine learning (ML) approaches were tested, both unsupervised, such as self-organizing maps (SOM)[10], as well as supervised, such as support vector machines (SVM) and random forest (RF)[11]. In the present paper, unsupervised learning as well as supervised learning based on categorisation using NAA will be demonstrated.

6. Hein 2021.
7. Hein *et al.* 2021a.
8. Hein 2021.
9. See Baxter 2001.
10. Kohonen 2001.
11. Baxter 2006.

Compositional data

The element concentrations determined in the analysis of a ceramic sample can be considered as a vector, in which each field corresponds to the concentration of a specific element. Accordingly, an entire dataset of element concentrations determined in a series of samples can be considered as data matrix **X**, in which the value x_{ij} corresponds to the concentration of Element *j* in Sample *i*. In order to investigate compositional similarity or dissimilarity among samples or groups of samples using multivariate statistics it is necessary to define a measurable distance among the sample vectors. A common distance used is the Euclidian distance $d_{x,y}$ between two vectors **x** and **y**[12]. In the case of elemental concentrations, However, it has to be considered that the absolute content of an individual element can range from several ppm (µg/g) for trace elements up to tens or hundreds of thousands ppm for major elements. Differences in major element concentrations, thus, will have more weight than differences in minor or trace element concentrations when determining directly the Euclidian distance. For this, prior data transformation of element concentrations is advisable, for example, scaling, taking into account average values and standard deviations[13]. Alternatively, the element concentrations can be logarithmised or log-ratio transformed[14]. By log-ratio transformation additionally absolute deviations of correlated element concentrations can be taken into account, which can be, for example, due to varying amounts of temper materials or chemical alterations of specific mineral groups[15].

Analytical uncertainties

When evaluating compositional data of archaeological ceramics, uncertainties of the specific analytical method applied, which overlap the natural variation of the sample compositions, have to be taken into account. Analytical uncertainties are mainly due to statistical variation of measured signals and their processing. In the case of pXRF, deviations in sample geometry play an additional role. The analytical precision or repeatability of a particular method, which is the variation of the measured value, can be estimated based on the standard deviation of repeated measurements of a homogenised sample[16]. It depends essentially on the statistical errors of the measured signals attributed to the element content and of the potential background signals, i.e. noise, which have to be subtracted from the overall signal. The statistical error, on the other hand, depends on the signals' intensities or number of counts. The lower limit of detection (LLD) describes the element content, for which the signal attributed to the element can be clearly distinguished from the background noise. The minimum net signal can be roughly estimated with $3.\sigma_{BG}$, where σ_{BG} is the estimated standard deviation of the background signal. The minimum net signal, for which the element content can be quantified with confidence, the so-called lower limit of quantification (LLQ), on the other hand, can be estimated with $6.\sigma_{BG}$[17]. As mentioned above, due to the design constraints of a pXRF system, the intensity of the exciting X-ray source and the energy resolution of the X-ray

12. Hein, Kilikoglou 2017.
13. Baxter 2001.
14. Baxter 1995; Buxeda i Garrigos 1999; Baxter, Freestone 2006.
15. Hein, Kilikoglou 2017.
16. Hein *et al.* 2002, Frahm 2024.
17. Potts 1992, p. 16.

detector are restricted. Compared to laboratory methods, the intensities of the recorded signals are diminished, which eventually impede precision and increase LLDs and LLQs, respectively. The accuracy of an analytical method describes the closeness of the measured value to the expected or true value. Accuracy depends essentially on the calibration of the method including processing of the raw signals commonly on the basis of measurements of standard reference materials (SRM)[18]. In the present case study a preset method has been used, which will be described in the next section. For this, element concentrations determined with the present pXRF setup cannot be straightforwardly compared with measurements using other analytical setups but intercalibration measurements have to be taken into account.

Analytical method

The pXRF measurements discussed in the present paper were carried out using a NITON XL3t GOLDD+ hand-held system (Thermo Fisher Scientific). In all case studies, the preset method "soil" was used providing a large suite of 33 concentrations mainly of minor and trace elements. A large part of these concentrations can be compared with data determined with other analytical methods, such as WDXRF or NAA[19]. Out of these elements 18 provided concentrations above the limit of detection for a considerable number of samples: K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Zr, Ba, Pb, Th and U. The selected duration of the measurements, which were carried out in air, was 120 seconds for each sample, measuring in three energy ranges (main: 60 s; low: 30 s; high: 30 s). Depending on the size of the analysed fragments, the system was either fixed in a stand so that the sample could be placed from above, or it was hand-held. As no collimator was used, the measurement area had an estimated diameter of *circa* 6 millimeters, which was sufficient for measuring broken or cut sections of commonly quite thick amphora fragments. XRF is furthermore a surface sensitive method with an effective analytical depth from several tens of µm up to several hundreds of µm depending on the fluorescence energies of the particular elements. Thus, measuring spots without apparent surface treatment or post-depositional incrustation were selected.

In **Table 1**, median, minimum and maximum values and the lower and upper deciles are listed for the 18 elements under consideration based on the *PAPHOS_AMPH*, dataset, which will be presented in the next section. For the determinations of the quantiles, measurements below the limit of detection (LOD) were not considered. The average error as specified by the system as well as the number of measurements providing a value are indicated in the last two columns of Table 1. For most of the elements the minimum concentration determined exceeds or at least is aligned with the average specified error, which thus appears to be a suitable estimation for the lower limit of detection[20]. The lower limit of detection corresponds to the minimum content of the specific element sufficient for confirming its presence in the sample with confidence. The lower limit of quantification, on the other hand, which exceeds the limit of detection, corresponds to the minimum content

18. Hein *et al.* 2002.
19. Hein 2021.
20. *Ibid.*

for quantifying the element's concentration in the sample with confidence[21]. Thus, element concentrations determined at a level close to the limit of detection commonly lack analytical precision, impeding their distinctiveness and the feasibility of categorizing samples based on their determined concentration values. Nevertheless, even though an element concentration determined at the limit of detection may not provide precise information about the absolute value, the analysis still provides an indication that the content of this specific element in the sample is clearly lower than in other samples analysed.

	Average	Standard deviation	Minimum	Lower decile	Median	Upper decile	Maximum	Average error	Values
K	14637	5218	3562	8343	14018	21686	36026	296	368
Ca	64536	37114	2327	23196	58354	110858	316151	443	368
Ti	3492	998	917	2349	3384	4834	6971	97	368
V	96	28	29	66	92	135	218	23	368
Cr	238	338	29	84	181	394	5416	23	365
Mn	776	354	62	411	726	1182	2712	53	368
Fe	44980	10929	20613	31052	44536	58208	89510	243	368
Ni	133	96	25	50	114	226	905	18	357
Cu	67.4	40.0	17.4	31.4	58.7	111.4	505.8	11.8	356
Zn	104.2	50.2	44.9	67.3	95.6	132.0	546.8	7.9	368
As	21.1	24.0	4.0	7.5	15.7	35.4	278.1	4.0	355
Rb	89.9	45.7	7.9	33.6	82.2	151.5	217.4	3.1	368
Sr	376	156	89	186	355	578	945	4.8	368
Zr	175	60	57	102	172	249	507	3.8	368
Ba	447	251	68	117	452	787	1009	52.6	238
Pb	41.4	44.3	4.6	14.5	29.2	70.3	531.5	4.4	368
Th	11.4	7.0	3.1	5.0	9.9	19.2	56.8	2.8	287
U	10.7	3.8	5.2	6.6	10.1	15.3	34.4	4.6	307

Table 1: Concentration ranges of 18 elements based on 366 cases in the *PAPHOS_AMPH* dataset: indicated are average values, standard deviations, median, minimum and maximum values, lower and upper deciles as well as the average analytical errors and the number of cases, for which concentration values were determined

21. HEIN *et al.* 2002.

Datasets

PAPHOS_AMPH: Hellenistic transport amphorae from Paphos, Cyprus

The pXRF data, used for the present data evaluation tests, were acquired within the framework of a case study of Hellenistic transport amphorae from three excavations at Paphos on the southwest coast of Cyprus[22]. Paphos was primarily a trading and marketplace, so amphorae of various origins were included in the study; local and regional Cypriot amphorae, as well as amphorae imported from the Aegean and even as far away as Sicily. The compositional variation of the examined amphora fragments was expectedly rather high as demonstrated by pXRF as well as NAA. In the first of two pXRF campaigns, 288 individual amphora fragments were analysed by pXRF in 366 individual measurements[23]. For the pXRF measurements preferably breaks or sections of the fragments were selected and, if necessary, additionally cleaned with a small scrubbing brush before the analysis. This practice has proven to provide sufficient estimation of the bulk composition of ceramic fragments, which was feasibly comparable to polished samples of the ceramic body.

Hellenistic and Roman transport amphorae from the Eastern Aegean

For an initial testing of supervised machine learning algorithms for categorizing pXRF data a second dataset was used with more reliably predefined categories. The dataset *KOS_AMPH* comprises 536 pXRF measurements of 202 Hellenistic and 133 Roman fragments of transport amphorae from the island of Kos and, in addition, 34 pXRF measurements of fired clayey raw materials collected on the island. Based on an NAA study of 75 Hellenistic amphora fragments included in this assemblage, seven compositional categories have been defined representing different origins of production on the island as well as probably on the opposite coast of Asia Minor[24]. This allowed for the creation of a training dataset with 180 cases of categorised pXRF measurements. In a second phase, the training dataset was expanded to 296 cases predefining ten additional categories with additional cases of pXRF measurements of amphorae presumedly manufactured on the island of Rhodes, the Knidian Peninsula, in Ephesos, as well as on the islands of Chios, Samos and Thasos[25].

Data evaluation

Multivariate Statistics

During the original data processing the data were evaluated with a series of exploratory statistical methods following conventional approaches applied to elemental compositions of archaeological ceramics measured with laboratory methods[26]. For the initial data evaluation with hierarchical clustering and principal component analysis, 14 element concentrations were considered. From the

22. Hein *et al.* 2021.
23. Hein, Dobosz, Kilikoglou 2021.
24. Hein *et al.* 2008.
25. Hein 2026.
26. Baxter 2001.

above listed element suite Ba, Th and U were disregarded due to eventually too many missing values and As due to geochemical instability. The data were standardised by additive log-ratio transformation (alr) using the Fe concentrations as a common divisor selected based on the determined variation matrix[27]. The scope of the statistical evaluation was to assess the variability of the dataset and to define clusters of data records representing samples of the same compositional category. The hierarchical clustering indicated seven categories of local or regional Cypriot amphorae and ten categories of presumedly imported amphorae[28]. The evaluation of the NAA data collected from a part of the assemblage, however, provided not only an increased number of nine plus 14 distinct compositional categories, but even indicated for some of these categories a specific origin of production based on comparison with the reference database[29]. This raised the question, whether it is possible to improve the detailedness of categorisation as well as the potential for provenancing of the pXRF data using alternative data evaluation approaches based on machine learning.

Unsupervised machine learning with self-organizing maps (SOM)

In an initial case study the dataset *Paphos_AMPH* has been tested with a SOM model, which is basically an artificial neural network (ANN) without hidden layers and a two-dimensional output layer[30]. In order to conform to the evaluation of the same dataset with conventional statistics, which had been published before[31], the number of attributes was reduced to the 14 elements indicated above. For normalisation of the dataset accordingly additive log-ratio transformation (alr) was applied on the element concentrations with the Fe concentrations as common divisor. For the generation of the SOM model the kohonen package (version 3.0.10) was used, which is available for R[32], providing apart from the training of the SOM various visualisation methods. A toroidal 10×10 base map with hexagonal topology was defined. The 100 codebook vectors were first initialised with random values and then stepwise trained with a predefined number of 2000 training steps using the squared Euclidian distance as distance criterion. The resulting codebook vectors were evaluated with hierarchical clustering in order to define 20 clusters, which could be combined in the map (**fig. 1**). Basically, the SOM clusters confirmed the clustering of the same dataset using conventional exploratory statistics[33]. Beyond that, the SOM model indicated a potential subdivision of the original defined clusters, based on conventional statistics. The higher detailedness in defining categories appeared to be indeed at a similar level as can be achieved by the evaluation of NAA data of the same samples. A drawback of the initial case study, however, appeared to be the not always satisfactory reproducibility of the SOM model. This was obviously related to the random initialisation of the codebook vectors, which resulted in ambiguous categorisation of particular cases. Because of this, the significance and uncertainty of categorisation was tested with a series of ten SOM models with different random initialisation. The resulting categories were examined and only cases which appeared to cluster together in at least seven of the ten SOM models were combined in categories,

27. Aitchinson 1986; Buxeda i Garrigos, Kilikoglou 2003.
28. Hein *et al.* 2021.
29. Hein, Kilikoglou 2012.
30. Cortés, Palma 2008; Hein, Kilikoglou 2024.
31. Hein *et al.* 2021.
32. Wehrens, Buydens 2007; Wehrens, Kruisselbrink 2018.
33. Hein *et al.* 2021.

while 35 out of the 366 cases were considered as questionable or loner (**fig. 2**). The comparison of the resulting SOM categories with the categories of confirmed NAA groups, in fact, allows for reinforcement learning by confirming or disregarding individual categories based on the level of conformance with NAA categories.

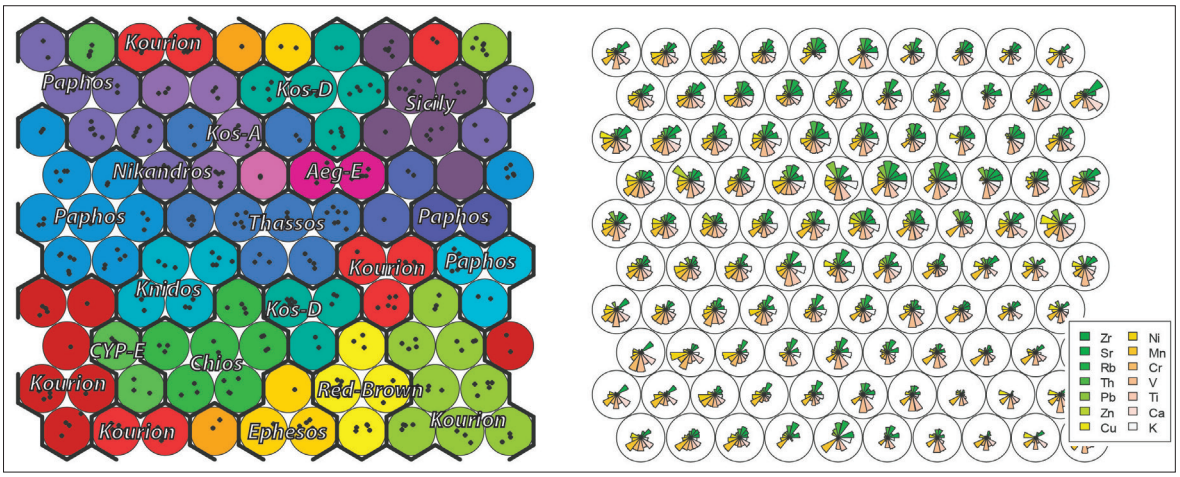


Figure 1: Example SOM model of the *PAPHOS_AMPH* dataset[34]: the fields of 10×10 map have been subdivided in 20 clusters indicated by different colours, which can be linked to specific categories (left). Each field corresponds to a codebook vector, which has been adapted during the training phase (right)

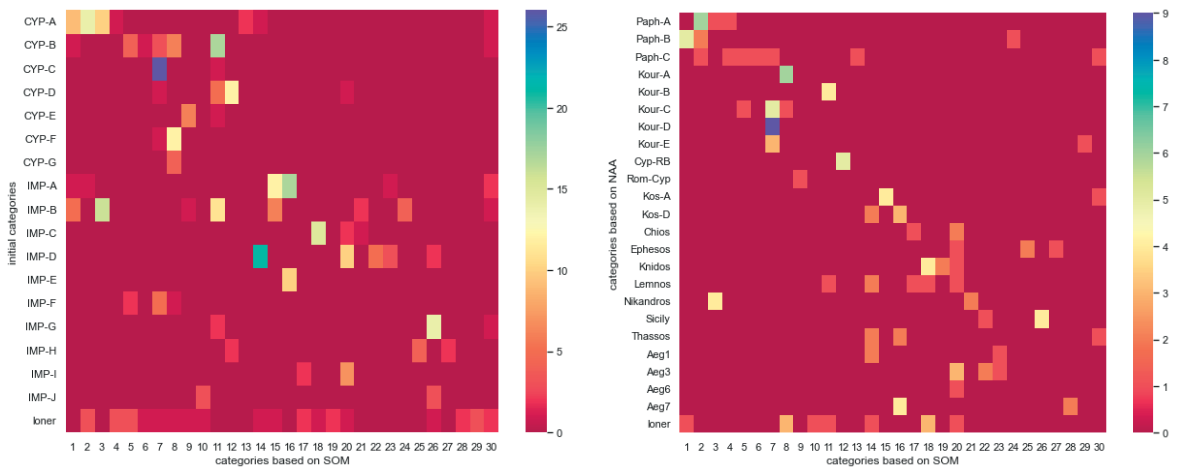


Figure 2: Heatmaps comparing 30 categories based on ten random SOM models of the *PAPHOS_AMPH* dataset with the initial categories of the pXRF data based on conventional statistics (left) and the categories based on NAA of selected samples (right)[35]

34. Hein, Kilikoglou 2024.
35. Hein *et al*. 2021.

Supervised machine learning with support vector machines (SVM) and random forest (RF)

Supervised machine learning for categorizing pXRF data has been tested with support vector machines (SVM) and random forest (RF). During the training of the SVM models, hyperplanes in the multi-dimensional space of the input data are determined, which separate the multivariate data based on the predefined classes by maximizing their margins at the same time. For the generation of hyperplanes, different types of kernels, such as linear, polynomial or Gaussian can be considered. On the other hand, the RF models are ensembles of decision tree classifiers, which are trained with random subsets of the predefined training data. For the implementation of both ML model algorithms the *scikit learn* Python library (Version 1.5) was used (*https://scikit-learn.org/stable/*). The number of attributes in the *KOS_AMPH* dataset was reduced to 17 disregarding only As due to its geochemical instability while missing values of other element concentrations were substituted with minimum values. The data were normalised with additive log-ratio transformation (alr) using the Fe concentrations as common divisor. For training and testing the SVM and RF models the training datasets were divided in a ratio of 70 to 30. In the case of the first training dataset comprising seven categories, the models were trained with 126 cases and tested with 54 cases. While the SVM model (polynomial kernel, degree = 5) provides a factual accuracy of 100.0% the RF model (max_depth = 6, criterion = 'log_loss') presents one false prediction out of 54 still corresponding to an accuracy of above 98.1%. The comparison of both models concerning their predictions for the *KOS_AMPH* dataset shows a general agreement (**fig. 3**). The main disagreement concerns the categories Kos-D and Kos-D2. Both categories are presumed to have been manufactured in the northeast part of the island and the SVM model classifies cases not included in the training data rather to Kos-D2, while the RF model classified them to Kos-D. Apart from this, a considerable number of false positive classifications has to be taken into account as cases can only be classified according to the predefined seven categories. In the case of the extended training dataset, the models were trained with 207 cases presenting 17 categories and tested with 89 cases. The SVM model indicates four false predictions out of 89 and the RF model indicates three false predictions out of 89, which correspond to accuracies of 95.5% and 96.6%, respectively. The comparison of both models concerning their predictions of cases in the *KOS_AMPH* dataset expectedly indicates primarily Koan categories. The main exceptions concern predictions indicating origin of manufacture on the Knidian Peninsula or categorisation according to the two Rhodian categories Rho-B and Rho-E, both of which, however, have presumedly been manufactured in the Rhodian Peraia in Knidos as well. Concerning individual disagreements of categorisation by the two ML models, again potential false positive classification have to be taken into account.

Another issue that has to be considered concerns the small numbers of cases in the training data representing some of the predefined categories and the related imbalance of labeled case numbers. Therefore, the generation of synthetic data based on cases comprised in the predefined categories is also being tested, and will be reported in a future publication[36]. In three different approaches the synthetic data are generated either according to average concentrations and standard deviations, according to random mixtures of cases or according to the covariance matrix determined. Apart from

36. Hein 2026.

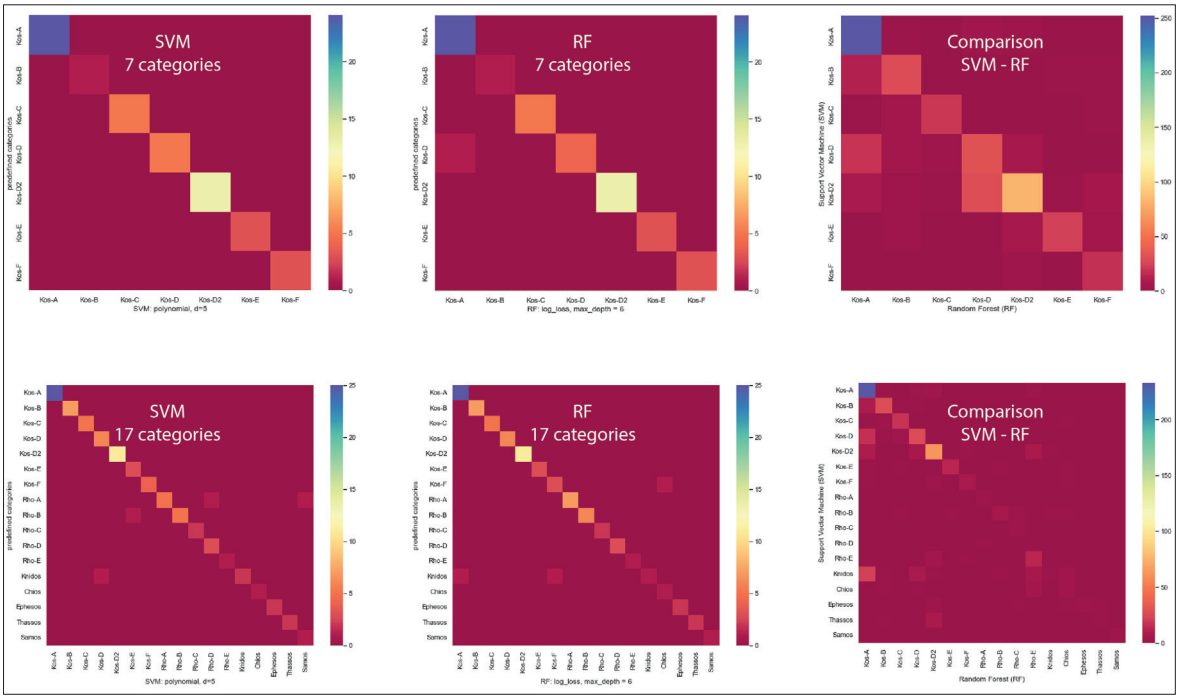


Figure 3: Heatmaps demonstrating the accuracy of the tested SVM and RF model and indicating their agreement in predicting categories for unknown cases: the upper row presents seven categories of Koan amphorae while the lower row includes also Rhodian amphora categories as well as categories from Knidos, Chios, Ephesos, Thasos and Samos

more balanced training data, this allows also for generating sufficient case numbers for testing deep learning approaches, such as artificial neural networks (ANN) including hidden perceptron layers.

Concluding remarks

Machine learning can be applied to automated pattern recognition and categorisation of pXRF data, which eventually provides higher detailedness than can be achieved with conventional multivariate statistical approaches. Taking into consideration additional information, such as compositional categorisation of individual samples based on laboratory analysis, the categorisation can be enhanced towards reinforcement or supervised machine learning. An essential precondition for this is the use of sufficiently large training datasets, which are not always available in the field, such as compositional analysis of archaeological artefacts. The generation of synthetic data based on cases with predefined categories, however, allows for developing and training more reliable machine learning models. The future scope of the present study will be the development of an expert system for automated provenancing of transport amphorae based on their elemental composition determined with pXRF.

Data availability statement

The supplementary data are available at Hein, Dobosz, Kilikoglou 2021 and Hein 2026.

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Part 2

Applying pXRF in practice: case studies in challenging conditions

Holger Becker, Federica Pendolino

A broad field: XRF analytics in daily routine as well as in research projects

Abstract

This study presents a case-based examination of the integration of portable X-ray fluorescence (pXRF) analysis into archaeological provenance research and conservation practice at the LVR-Landesmuseum Bonn. Since 2013, pXRF has been routinely employed within the museum's conservation laboratories to investigate the elemental composition of artefacts from both the permanent collection and ongoing regional excavations, thereby addressing a range of research questions concerning provenance, technological practices and historical metalworking. A standardised analytical protocol has been developed to ensure methodological reproducibility, operator safety, and adherence to the ethical standards of conservation science.

The effectiveness of this approach is demonstrated through the compositional analysis of a series of case studies, including metal fittings, goldsmithing, and medieval pottery held in the Landesmuseum Bonn, as well as 105 ceramic fragments recovered from a Roman sewer system in *Colonia Claudia Ara Agrippinensium* (modern Cologne). The study underscores the potential of conservation laboratories to contribute actively to archaeological research through the application of accessible, non-invasive analytical techniques.

Keywords

Portable X-ray fluorescence (pXRF), LVR-Landesmuseum Bonn, Roman ceramics, provenance studies, Rhineland archaeology

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Introduction

The LVR-Landesmuseum Bonn, one of Germany's oldest archaeological institutions, houses a substantial and diverse collection representing over two centuries of research and curatorial practice. Located in the modern German state of North Rhine-Westphalia, the museum's conservation department operates in close partnership with the communal authority of preservation and care of field monuments (LVR-Amt für Bodendenkmalpflege). Together they function as a central authority in the study and preservation of archaeological materials across western Rhineland. The region itself is archaeologically rich, encompassing remains from prehistoric settlements to complex Roman frontier infrastructure, including major urban centres such as *Colonia Claudia Ara Agrippinensium* (modern Cologne) and *Colonia Ulpia Traiana* (modern Xanten) along the *Limes ad Germaniam inferiorem* (Lower Germanic Limes).

Over the past four decades, archaeological activity in the Rhineland has intensified considerably, in part due to large-scale rescue excavations prompted by the expansion of open-cast lignite mining operations west of Cologne. These excavations have yielded an extensive quantity of material, thereby raising ever more questions that are often difficult to answer. The finds may at times lead to misinterpretations: for instance, a buckle that appears to be silver-coated and is catalogued as such, or terra sigillata ceramics that seem to have been produced in Italy. Such interpretations have, in turn, influenced the reconstruction of archaeological contexts. Moreover, the sheer volume of incoming material and the necessity of processing it rapidly has increased the risk of further errors. This situation has necessitated the development of rapid, reliable, and minimally invasive methods for analysis and documentation. In response, the LVR-Landesmuseum Bonn has increasingly incorporated advanced analytical and imaging technologies into its routine workflows. Among these, X-ray radiography has long been established, while since 2013 portable X-ray fluorescence spectroscopy (pXRF) has become a key component of material characterisation. This article presents four case studies in which such analyses were employed to address research questions in a swift and effective manner.

Both the technical standardisation and methodological integration of pXRF within the conservation practice at the LVR-Landesmuseum Bonn will be presented. The principal objective is twofold: first, to document the development of a standardised pXRF workflow that aligns with the specific requirements of museum-based conservation and research; and second, to illustrate the analytical capabilities of this approach through a series of case studies.

Methods: development and standardisation of X-ray and pXRF techniques at the LVR-Landesmuseum Bonn

Since 1974, X-ray imaging has been standard practice in the conservation laboratories of the LVR-Landesmuseum Bonn, employing an Eresco X-ray tube manufactured by the Seifert Company, located north of Hamburg. From these early days onwards, X-ray investigations have helped to get deeper understanding of the materiality of objects in the museum collections. Until 2006, all images were detected on film, using Agfa Structurix D2, D4, or D7 films. In 2006, acquisition on a new X-ray unit DP 435 Vario of GE Inspection Technologies was made. The introduction of this

imaging technique also marked the museum's entry into the realm of digital imaging, through the use of a VISTALUX® image intensifier television system. Finally, in 2019 the detecting unit was replaced with a DXR 250 Flatpanel and Vistaplus V software.

In 2013, the purchase of a portable XRF device extended the possibilities of X-ray based examination techniques to the field of chemical analysis. The Niton XL3t GOLDD+ XRF Analyser (**fig. 1**) is equipped with an Au-anode with 50 kV electric tube (maximum tension). In parallel with the established practice of X-ray imaging, the application of pXRF analysis has been employed to investigate a wide range of objects, from archaeological artefacts to works of art. This technology has significantly expanded the laboratory's analytical capabilities, enabling the non-destructive examination of material composition and broadening the portfolio of available diagnostic techniques. For smaller objects, with dimensions under 20 cm x 20 cm square and 15 cm high, the use of a special sample chamber in the form of a benchtop test stand has become very practical. The XRF analyser is fixed beneath the sample chamber and controled via a connected laptop, allowing standardised examination runs. Supplied with a lead covered lid, the sample chamber follows all requirements of radiation protection. X-ray imaging as well as XRF analysis are carried out by authorised specialists and are part of the services provided by the museum's conservation department.

pXRF application in practice

With the growing number of material analyses, it became necessary to establish standardised workflows. With a view to the research objectives and the intended use of the acquired data, the processing procedures had to be aligned with the requirements of the end use. In practice, the analytical workflow is context-dependent, aiming to deliver the required information while avoiding unnecessary or excessive data. Internal requests for XRF analyses on objects from the collections of the LVR-Landesmuseum Bonn typically come from archaeologists, art historians and conservators.

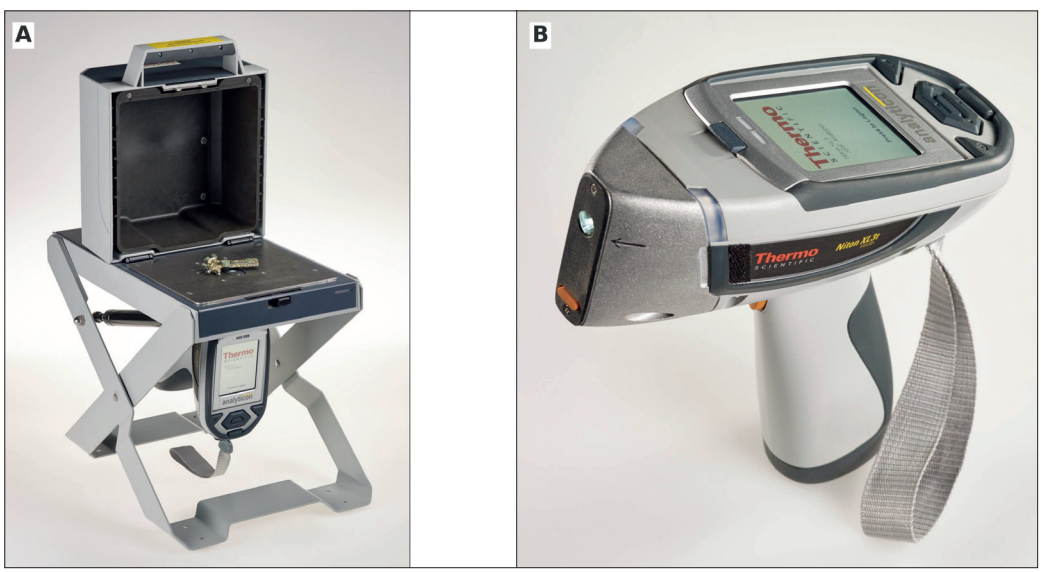


Figure 1: The Niton XL3t GOLDD+ XRF analyser (Jürgen Vogel, LVR-Landesmuseum Bonn)

These requests are mostly focused on giving evidence on certain material. For example, in the examination of copper alloys, pXRF helps to distinguish between bronze and brass. In the case of gilded surfaces, confirming the presence of gold is a primary objective; the detection of mercury, moreover, can provide insight into the specific gilding techniques employed. Given the heterogeneous collection of the Rhineland Museum, all kind of objects of different materials are the subject of investigation, such as metals, ceramics, glass, paintings and sculptures.

In practice, the workflow was established as follows. Initially, the problematic has to be discussed with the requester, in order to determine whether X-ray fluorescence is the relevant method to reveal information. First, the object will be documented photographically with general images and detailed photos of the areas selected for analysis. These images will be needed later to locate the analysed spots in the final documentation. In over 70% of cases, analyses are conducted in the special sample chamber. If the samples are too big or analyses have to be conducted on full objects such as bigger vessels, sculptures or paintings, a free hand-held examination is requested. In such cases, analyses must be conducted under strict safety protocols, with the help of an easy to assemble backscattering shield, making sure that neither the researcher nor persons in the surrounding area could be exposed to radiations. From the six different pre-set modes provided by the Niton XL3t GOLDD+ XRF analyser software, it turned out that in the majority of our specific analytical problems, two modes are relevant: *alloy* to examine metals and *mining with copper and zinc* for ceramics and in some cases for glass.

The standardised software adjustment for analysing in *alloy* mode takes 120 seconds each measurement, performing analyses to cover three energy ranges: standard (60 s), low (30 s) and light (30 s). Accordingly, the tension for each range varies between 50 kV in the standard range, 15 to 20 kV in the low range and 8 kV in the light range. The standard range cover the following elements: Zr, Nb, Ti, Hf, V, Ta, Cr, Mo, W, Re, Mn, Fe, Co, Pd, Ni, Cu, Au, Ag, Cd, Zn, Pb, Sn, As, Sb, Bi and Se. The low range covers Mg, Al, Si, P, S and the light range Ti, V and Cr. In the *alloy* mode, the chemical elements Rb, Ca, Sr, Y and K are not detectable.

The standardised software adjustment of the *mining with copper and zinc*-mode, established for analysing pottery, provides the full range of methodical possible chemical elements. It takes 270 s each measurement for four energy ranges: standard (160 s), low (60 s), light (30 s) and high (20 s). The tension for these ranges varies between 50 kV in the standard range, 15 to 20 kV in the low range, 8 kV in the light range and 50 kV in the high range. The standard range detects already a wide series of elements: Rb, Sr, Zr, Nb, Y, Hf, Ta, Mo, W, Re, Mn, Fe, Co, Ni, Cu, Zn, As and Se. Measuring in the low range will deliver information about the elements K, Ca, Ti, V and Cr, the light range about Mg, Al, Si, P, S, Cl and, finally, the high range covers the elements Ce, Ba, Sb, Sn, Cd and Ag. Each single range works with specific excitation filters and tube tensions adapted to the sought-after groups of elements. Accordingly, the standard range is performed at 50 kV, the low range at 15-20 kV, the high range again at 50 kV and the light range at 8 kV.

Basically, three measurements will be taken on each spot. If the revealed data shows homogenous results, this will be the basis for a first conclusion. If an examination shows no distinctly interpretable results, further measurements have to be taken. Sometimes there are methodological causes for mismeasurement. In this case the workflow has to be scrutinised, looking for reasons for the critical data. Finally, in communication with the requester it has to be stressed that in some cases, data could only reflect information about close surface regions. The higher the grade of absorption

of X-ray energy, the lower is the depth of penetration. Especially regarding metal alloys, these data could deviate from the composition of elements in deeper regions. If more accurate information is necessary, drill core samples will be helpful. From the position of an ethical imperative using only non-destructive testing in conservation science, this could lead to substantive discussion.

pXRF analysis at the LVR-Landesmuseum Bonn: case studies in artefact characterisation and archaeological provenance research

The routine application of portable X-ray fluorescence (pXRF) analysis at the LVR-Landesmuseum Bonn has enabled the comprehensive investigation of diverse artefact materials across internal and collaborative research contexts. This section presents a selection of case studies from museum practice that demonstrate the utility of pXRF for rapid material identification and compositional analysis in addressing specific research questions. These are followed by a collaborative project that serves as a more extensive demonstration of the method's applicability in archaeological provenance research.

Examples from internal conservation and research practice

Roman belt buckles

Two disc-shaped belt buckles (*baltea*) from a Roman military *cingulum*, dated to the 2nd–3rd century AD and recovered in Aldenhoven (Düren district), exhibited a silvery surface over a greenish substrate (**fig. 2, A**). Preliminary visual assessment suggested a copper-based alloy, possibly tinned or silvered. pXRF analysis confirmed the base material to be bronze, composed of approximately 35% copper, 25% tin, and 18% lead. No silver was detected, supporting the hypothesis that these items were deliberately tinned to imitate silver. This result highlights the role of surface treatments in Roman metalwork and the potential of pXRF to non-invasively identify such technologies.

Gold fibula from Nideggen

A rare gold fibula from Nideggen (Eifel region, Düren district), dated to the 1st century AD, exemplifies high-status personal adornment. The fibula displays intricate craftsmanship, including granulation and inlaid gemstones (fig. 2, B)[1]. pXRF analysis of the metal body revealed a composition of 92% gold and 3.7% silver, equivalent to over 22 carats. Analysis of the green inlay identified it as glass, with silica (SiO_2) at 28%, calcium at 4%, aluminium at 1.4%, and potassium at 1.2%. These results confirm both the high purity of the gold and the use of coloured soda-lime glass in the decorative scheme.

1. Deschler-Erb *et al.* 2022.

Pingsdorf ware

Pingsdorf (or Bardorf) ware represents a medieval high-fired earthenware produced in the Rhineland from the 9th to 13th centuries, particularly in areas now part of Brühl (fig. 2, C). Compositional analysis of six sherds excavated from the same context was conducted on freshly fractured surfaces to minimise the influence of surface contamination. While the samples exhibited broadly similar elemental profiles, elements such as magnesium, vanadium, chlorine, and sulphur were detected only in some samples and in low concentrations. These results point to subtle variability in raw materials or firing conditions. Although the laboratory possesses a vibrating ball mill for producing homogenised powder samples, its use remains restricted due to conservation ethics prioritising non-destructive techniques.

These examples collectively demonstrate the capacity of pXRF to support museum-based research objectives, including material authentication, technological characterisation, and contextual interpretation.

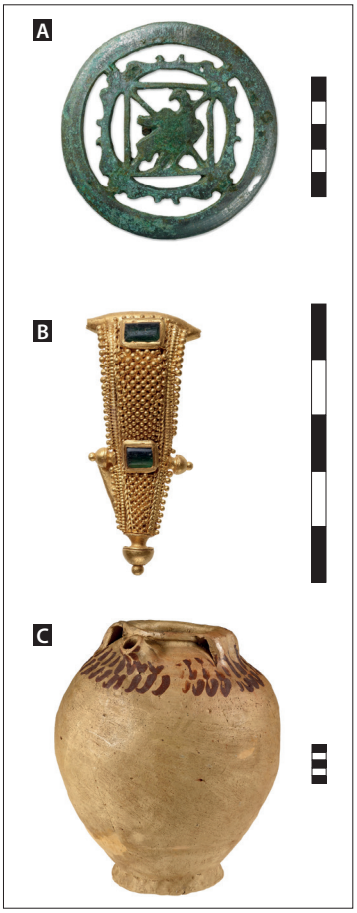


Figure 2: A. Roman belt buckle; **B.** gold fibula from Nideggen; **C.** Pingsdorf ware (Jürgen Vogel, LVR Landesmuseum Bonn)

A collaborative project in partnership with MiQua. LVR-Jewish Museum in the Archaeological Quarter Cologne

As part of a collaborative research initiative with MiQua LVR-Jewish Museum in the Archaeological Quarter of Cologne, the Conservation Department of the LVR-Landesmuseum Bonn contributed to the analytical study of a Roman ceramic assemblage recovered from a sewer system in *Colonia Claudia Ara Agrippinensium* (modern Cologne). The principal research question at the time of discovery concerned the precise place of production of these ceramics, with the aim of reconstructing aspects of the economy of Roman Cologne. Traditionally, such information has been derived from the external examination of ceramics (for example, colour, inclusions, and surface characteristics). This approach, however, is notoriously unreliable, as it has been shown that identical clay sources and kilns may produce vessels of differing colours, depending on a range of factors. To address this limitation, the Conservation Department of the Landesmuseum Bonn conducted

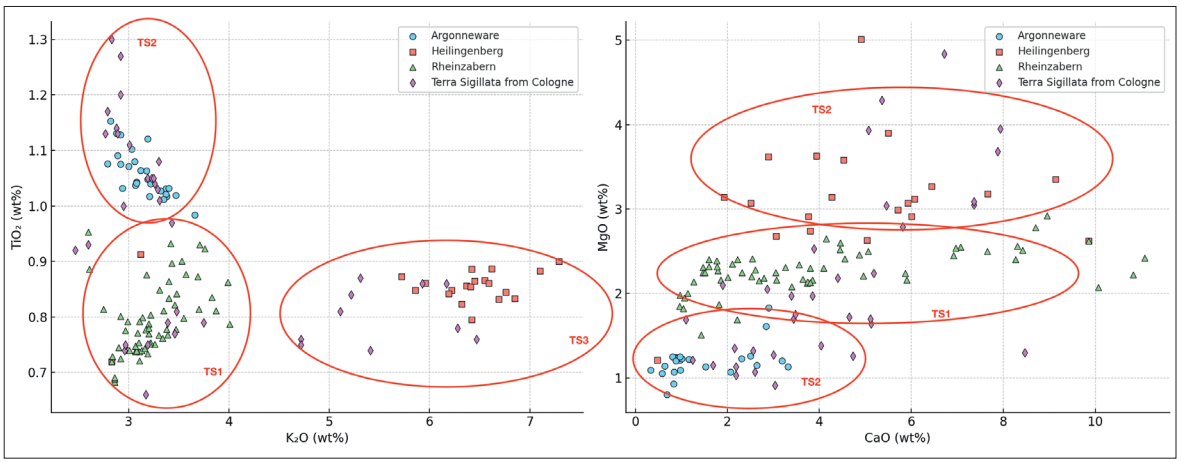


Figure 3: Scatter plots illustrating the distribution of key chemical components in terra Sigillata samples from Cologne, benchmarked against reference datasets drawn from LÖSCHEN 2005; BIEGERT 2003; REUTER 2013; SCHNEIDER 2005

chemical analyses on a selected sample of ceramics, with the objective of establishing their provenance on a strictly scientific basis.

The assemblage, which spans a chronological range from the 1st century AD to late antiquity, encompasses several ceramic types, including terra sigillata, slip-coated pottery, smooth-walled ware, and terra nigra. A total of 105 samples were analysed using the museum's standardised portable X-ray fluorescence (pXRF) workflow. To corroborate and refine the elemental groupings, a subset of 20 samples was additionally examined through inductively coupled plasma multi-acid/elemental spectrometry (ICP-MA/ES). The primary aim of this joint analytical programme was to establish the provenance of the ceramics, differentiate between locally produced and imported wares, and explore compositional variability within local production traditions.

The analysis initially focused on fragments of terra sigillata (**fig. 3**). The chemical data were first compared with material from the Cologne kilns and subsequently with terra sigillata from other production centres. As demonstrated in Figure 3, the results indicate a complete absence of local manufacture and confirm that the fragments represent imported material. This interpretation accords with archaeological evidence from the Cologne kiln sites, where only a single kiln (Kiln 18) shows traces of terra sigillata imitation. Three principal compositional groups could be distinguished among the analysed samples. **TS1** corresponds closely to products from Rheinzabern production centre, a major supplier of terra sigillata to the provinces during the 2nd and 3rd centuries AD. The samples in this group are characterised by variable levels of calcium oxide (CaO) and phosphorus pentoxide (P_2O_5), reflecting known clay mixing practices at Rheinzabern[2]. **TS2** aligns with Argonne ware, based on strong chemical similarity with published reference datasets[3], while **TS3** exhibits elevated concentrations of potassium oxide (K_2O), aluminium oxide (Al_2O_3), and magnesium oxide (MgO)[4], indicative of ceramics produced at Heiligenberg. Additional fragments

2. SCHNEIDER 2005, p. 74–78; SCHNEIDER 1978.
3. BOCQUET 1995; BRULET, BOCQUET, LADURON 1994; ASAL-HIRT 2005; REUTER 2013.
4. BIEGERT 2003.

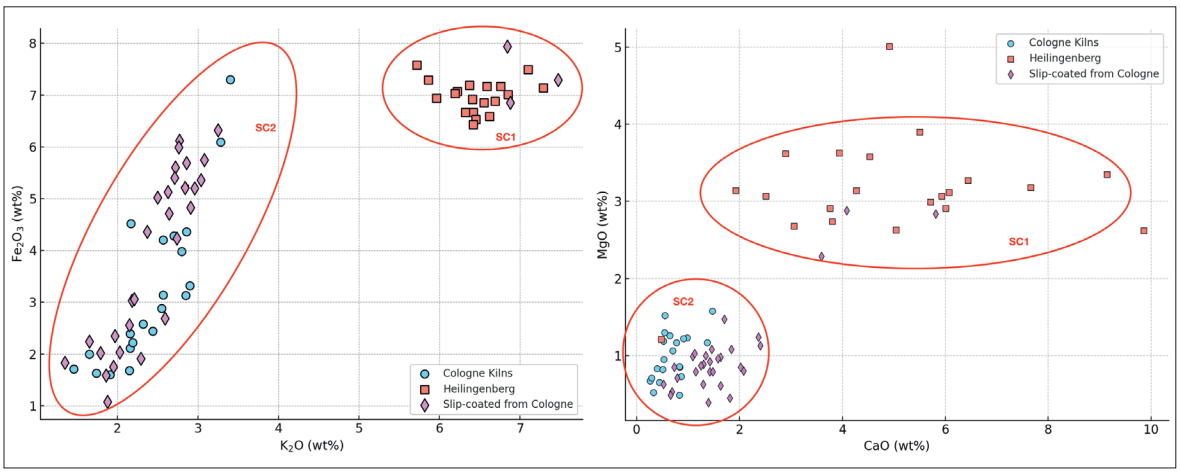


Figure 4: Scatter plots illustrating the distribution of key chemical components in slip-coated ceramic samples from Cologne, benchmarked against reference datasets drawn from SCHNEIDER, HÖPKEN, DASZKIEWICZ 2004; BIEGERT 2003

show affinities with material from La Graufesenque (**TS4**) and Lezoux (**TS5**)[5], confirming the presence of imports from both southern and eastern Gaul within the assemblage. These findings support a pattern of long-distance ceramic exchange in the Roman period and reinforce Cologne's role as a major urban and commercial centre with broad access to external production networks.

The slip-coated pottery category (**fig. 4**), in contrast to terra sigillata, is largely of local origin, though chemical variability within the group reveals significant diversity in raw material sourcing and workshop practice. **SC2a** stands out for its elevated levels of iron oxide (Fe_2O_3), as well as higher concentrations of K_2O, MgO, and MnO. These characteristics set it apart from the low iron concentration profiles observed in **SC2b**, and likely point to the use of a distinct clay bed or a separate workshop tradition, possibly associated with Kiln 18 or the production area at Lungengasse[6]. One additional cluster, designated as **SC1** within the slip-coated category, shows a markedly different profile, with high concentrations of potassium, iron, and calcium. These values are more consistent with imports from Heiligenberg and suggest that slip-coated vessels from beyond the local region were also present in the assemblage, albeit in lower numbers.

Smooth-walled wares (**fig. 5**) display similar compositional patterns, reflecting both local production and external influence. **SW1** is chemically homogeneous, with only minor internal variation, particularly in Fe_2O_3 content. Its consistency supports attribution to Cologne-based workshops, likely including those using clay with elevated levels of iron. **SW2**, by contrast, shows a distinct chemical profile, marked by elevated CaO (ranging from 6 to 13%), higher Fe_2O_3 (3–6%), and lower Al_2O_3 (10–16%) values. These characteristics diverge from typical Cologne clays and instead align with known profiles for Rheinzabern production. The presence of this group within the assemblage suggests that imports of smooth-walled wares occurred alongside local terra sigillata manufacturing, although to date, only a single fragment of smooth-walled ware from Rheinzabern workshops has

5. SCHNEIDER 1978.
6. *Ibid.*, p. 490–493.

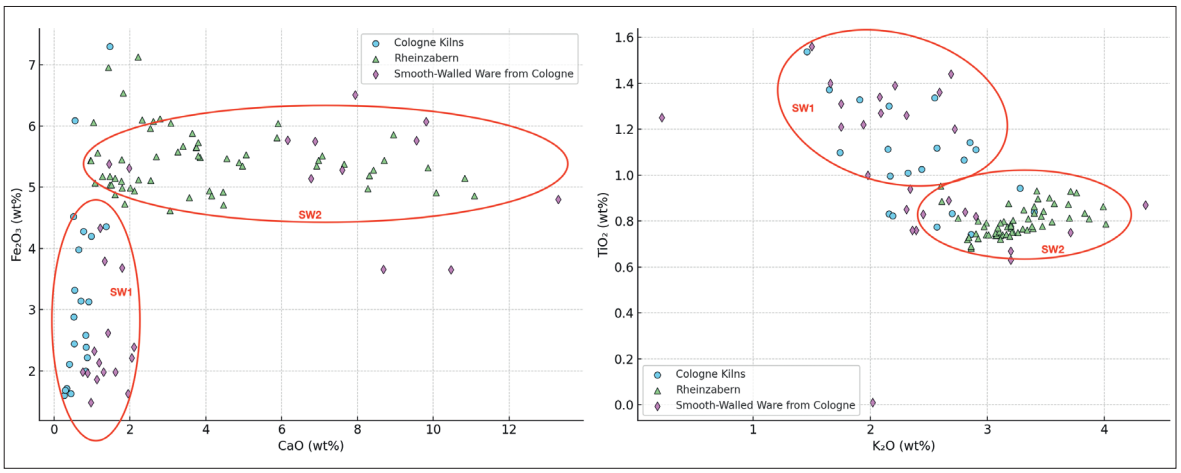


Figure 5: Scatter plots illustrating the distribution of key chemical components in smooth-walled ware samples from Cologne, benchmarked against reference datasets drawn from SCHNEIDER 2005; BIEGERT 2003; SCHNEIDER, HÖPKEN, DASZKIEWICZ 2004

been analised with pXRF and published, supporting its attribution to local production[7]. A third group, designated as **SW3**, could not be matched with any existing reference dataset but was compositionally homogeneous. The internal consistency of this group suggests production by a single, yet unidentified workshop, possibly within the regional network surrounding Cologne.

Terra nigra (**fig. 6**) was represented by four fragments, three of which show chemical profiles consistent with local Cologne production (**TN1**). The remaining fragment corresponds closely with Rheinzabern ware (**TN2**), corroborating previous findings that terra nigra was produced at that site, a fact already established in earlier studies[8].

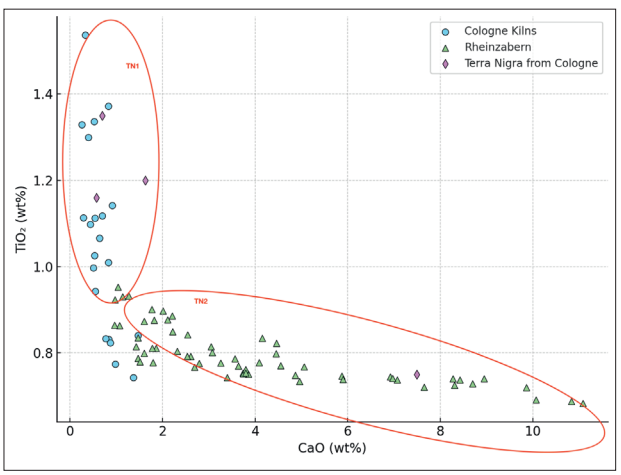


Figure 6: Scatter plot illustrating the distribution of key chemical components in terra nigra samples from Cologne, benchmarked against reference datasets drawn from SCHNEIDER 2005; BIEGERT 2003; SCHNEIDER, HÖPKEN, DASZKIEWICZ 2004

To validate the pXRF findings, a subset of 20 samples was analysed using ICP-MA/ES (**fig. 7**) by Dr. Torbjörn Brorsson (Ceramic Studies, Sweden). The results confirmed the main groupings established through pXRF analysis. **ICP1** was initially attributed by Dr. Brorsson to a possible provenance in southern France, based on compositional similarities with reference samples from that region. Notably, pXRF analysis identified a specific match with the Heiligenberg production centre, located along the lower Rhine in France, thereby corroborating the results obtained through ICP-MA/ES. In contrast, **ICP2** was confirmed as locally produced, originating from the Cologne–Bonn region. **ICP3**,

7. *Ibid.*, p. 79.
8. *Ibid.*, p. 101–112.

which appeared homogeneous in the ICP-MA/ES dataset, was further subdivided via pXRF into two related subgroups, interpreted as originating from Argonne and Rheinzabern respectively. **ICP4** was identified as a distinct cluster of an unknown origin based on ICP-MA/ES analysis. In contrast, the pXRF data indicate a correspondence with local production; however, three fragments within this group exhibit slight deviations in trace element concentrations. These anomalies, which were not detected in the ICP-MA/ES dataset, suggest a non-local origin for these specific pieces.

Overall, the consistency between the pXRF and ICP-MA/ES results reinforces the reliability of the provenance classifications. Both methods produced comparable groupings and supported similar interpretations regarding the origins of the analysed ceramic materials. The findings confirm the coexistence of imported and locally produced ceramics in *Colonia Claudia Ara Agrippinensium*. While all terra sigillata fragments were identified as imports, originating from Rheinzabern, Argonne, Heiligenberg, and other Gallic production centres, the slip-coated and smooth-walled wares were predominantly local, albeit with notable variation in raw material sources. The combined application of pXRF and ICP-MA/ES provided a robust framework for provenance analysis, underscoring the complexity of Roman trade networks and the diversity of local manufacturing practices.

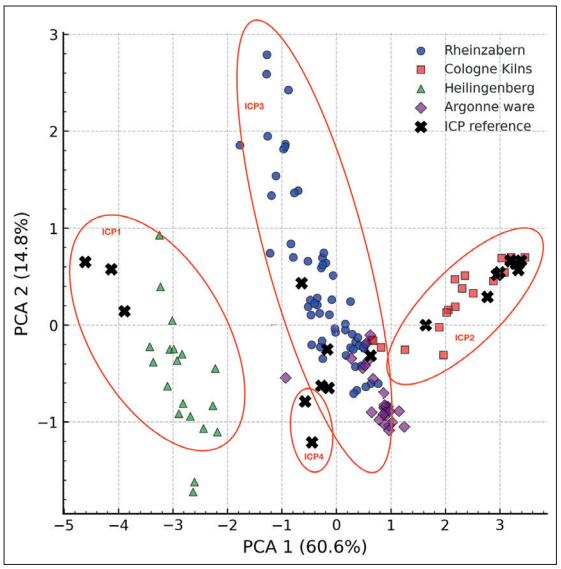


Figure 7: Scatter plot of the first two principal components (PCA 1 and PCA 2) derived from the chemical composition of ceramic samples from Rheinzabern, Cologne Kilns, Heilingenberg, and Argonne ware (reference datasets drawn from SCHNEIDER 2005; BIEGERT 2003; SCHNEIDER, HÖPKEN, DASZKIEWICZ 2004), compared with the ICP reference

Conclusion

Since its adoption in 2013, portable X-ray fluorescence (pXRF) has become a core component of the analytical and conservation strategy at the LVR-Landesmuseum Bonn. Through the development and implementation of a standardised workflow, pXRF has proven to be a highly effective non-destructive technique for the elemental characterisation of a wide range of archaeological and artistic materials. Its integration into the museum's routine laboratory practice has enabled not only the support of internal conservation diagnostics but also the advancement of research-led archaeological enquiries.

The case studies presented here demonstrate the versatility of pXRF in both isolated and collaborative research contexts. Internally, the technique has facilitated material identification and surface analysis in diverse artefact types, ranging from Roman metalwork to medieval ceramics. Externally, the collaborative study of ceramic material from *Colonia Claudia Ara Agrippinensium* has exemplified the method's value for provenance research. The ability of pXRF to distinguish between local

and imported wares, to identify discrete production traditions, and to detect compositional variability within regional workshops underscores its analytical potential.

Furthermore, the combination of pXRF with complementary laboratory methods such as inductively coupled plasma multi-acid/elemental spectrometry (ICP-MA/ES) enhances both resolution and interpretative reliability. The congruence between the two datasets in the ceramic case study validates the use of pXRF as a robust tool for preliminary provenance determination, particularly when used within a multi-methodological framework.

This research highlights the important and often under-acknowledged role of museum conservation laboratories in contributing to archaeological science. By deploying accessible and non-invasive technologies such as pXRF, these institutions are well-positioned to generate meaningful analytical data that inform both conservation and broader scholarly debates. The model developed at the Landesmuseum Bonn offers a valuable precedent for integrating analytical rigour with conservation ethics in museum-based research.

Data availability statement

The data are not publicly available due to strict data management of the institution / employer LVR.

Author contribution

Holger Becker: conceptualisation, investigation, data curation, original draft, review and editing;
Federica Pendolino: validation, formal analysis, investigation, data curation, review and editing, visualisation.

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Thomas Faucher, Alexandre Bodet

Two case studies for a proper use of pXRF on archaeological copper alloy coins

Abstract

This study examines the judicious application of portable X-ray fluorescence (pXRF) as a complementary tool for the non-destructive analysis of ancient copper alloy coins. We present two case studies to demonstrate pXRF's potential while also quantifying its inherent biases. First, we compare surface and core elemental compositions of 135 sectioned coins to highlight the unreliability of surface-only analyses, particularly for lead and tin. Second, a large-scale pXRF survey of 400 Ptolemaic coins, conducted under strict archaeological regulations, reveals its utility for identifying outliers and confirming historical numismatic compositions, despite the limitations of semi-quantitative analysis. The work underscores the importance of a well-defined methodological approach to ensure pXRF use leads to meaningful scientific results.

Keywords

pXRF, ancient coins, copper alloys, metallurgy

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Introduction

This study examines the application of portable X-ray fluorescence (pXRF) for the non-destructive analysis of metal alloys, with a specific focus on ancient coinage. While numismatists face unique analytical challenges, these challenges broadly reflect the issues encountered by archaeologists in the study of ancient copper alloy artefacts. Although numerous analytical methods provide reliable results, this work aims to demonstrate the potential of pXRF, when employed rigorously and judiciously, as a complementary tool in the investigation of ancient monetary alloys.

A long-lasting interest in bronze coin composition

As outlined by François de Callataÿ, the study of the composition of ancient bronze coins has advanced progressively since the 17th century[1]. Early researchers like Savot, Caylus, and Dizé explored medal materials and initiated chemical analyses, identifying key elements such as copper, tin, and zinc. By the late 19th century, wet chemistry had advanced knowledge, though research saw a pause until the 1930s. The analysis of Greek and Roman coins took a significant turn with the pioneering work of Earle R. Caley in the mid-20th century[2]. Using rigorous scientific methods like emission spectroscopy on hundreds of coins, Caley's analyses revealed significant variations in elemental proportions, providing valuable insights into metallurgical practices, metal sources, and monetary policies. For example, his studies on Parthian coins showed that composition could vary considerably depending on the place of manufacture[3]. Although not without critics[4], Caley's work established that coin composition varies based on factors like the place of minting, the period, and the denomination[5]. Since the 1970s, the development of non-destructive analysis methods has opened new perspectives, allowing researchers to refine their knowledge and focus on more specific, localised questions[6].

1. Callataÿ 2021, p. 51: "There has always been an interest for coin metal composition, and for ancient bronze as illustrated by the 27 entries for 'aes', 'aerei' or 'aeres' documented in the index of the 1561 edition of the 'De re metallica' by Georgius Agricola (1494-1555)".
2. Blet-Lemarquand 2013, 2019.
3. Cammann 1958; Caley 1955.
4. Smith 1965, p. 650 stresses that Caley's book is too narrow in its focus on analytical methods and does not provide sufficient guidance on the proper interpretation and reporting of analytical results.
5. Callataÿ 2021, p. 54: "The conclusive pages of his monograph about ancient Greek bronzes remain today as the best starting point to quickly grasp the general frame of the topic with its main issues and historical hypotheses." For Roman coins, Adelson 1954 traces some of the earlier literature; see also King, Metcalf, Northover 1992; Griesser *et al.* 2016.
6. Cope *et al.* (ed.) 1997.

Cheap, fast and reproducible?

Recent studies have focused on specific monetary phenomena, such as variations in composition between mints or changes in monetary policy at the regional level. They also frequently highlight the limitations of the pXRF method. This article does not aim to judge the analyses carried out by pXRF over the past three decades. However, it seems crucial to warn non-expert users against misuse of this technique. The pXRF, although affordable and seemingly easy to use, requires a thorough understanding to ensure reliable results. It is also crucial to emphasise the importance, in scientific publications, of a clear statement of the method used. This allows researchers not only to evaluate the methodology, but also to compare and correlate the different results obtained. Too often, the method is not presented, leaving no room for further research or comparison. In particular, articles should systematically mention the type and brand of equipment used, the standards employed for calibration, and the sample preparation method (prepared, sectioned, polished surface, etc.). This information is essential to ensure the reproducibility of analyses and to allow a rigorous evaluation of the quality of the data obtained. Without these details, it is difficult to determine whether the results are reliable and comparable, which significantly limits the scientific value of the studies.

While it is now clear that surface analyses cannot guarantee reliable results (both for major and trace elements)[7], the use of pXRF (and XRF in general) should not be systematically excluded from the study of elemental compositions. Several scenarios lend themselves to a relevant use of this technique. pXRF is excellent for rapid, non-destructive screening and sorting of large numbers of objects based on their elemental composition. This can help identify potential outliers or groups of objects for further, more detailed analysis using other techniques. Several scenarios warrant its appropriate use.

Within the framework of the Frapper Monnaie project, funded by the Nouvelle Aquitaine region and the Université Bordeaux-Montaigne, we have undertaken to identify all publications presenting compositional analyses of Greek and Roman coins, and to compile this data into a database. In conjunction with a broader study conducted by Alexandre Bodet on the compositional analyses of copper alloy coins of the Graeco-Roman period[8], it is clear that the number of analyses carried out on coins far exceeds that performed on other copper alloy objects. This substantial database (it gathers already 161 references with thousands of analyses) will offer the scientific community a valuable tool for understanding the alloys used, the production methods, and the impact of these techniques on the supply of copper and tin.

However, it is important to note that among the thousands of analyses performed; only a small part provides reliable information on trace elements. Indeed, the analysis of trace elements is crucial in determining the origin of the metals used, and the majority of these analyses, regardless of the method employed, do not yet allow for such determinations. The aim of this paper is not to present a complete overview of these results, nor to advocate for any particular analytical method.

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7. Giumlia-Mair 2005, p. 42: "surface analyses in general do not seem, at least up to now, to be suitable for quantitative analyses of ancient oxidized or corroded metals or of alloys prone to segregation phenomena". Nicholas, Manti 2014, p. 1: "Although bench-top XRF is readily employed and the physicochemical matrix effects are understood, little research focuses on challenges presented by HHpXRF employed on the surface of archaeological copper alloys".
8. This project provided funding for a thesis defended by Alexandre Bodet in March 2024, available at this link: https://theses.fr/s245170. https://una-editions.fr/les-monnaies-grecques-et-romaines-en-alliages-cuivreux/.

Two study cases

We have chosen two specific cases, conducted with a methodological approach, that can teach us about the inherent biases in compositional analyses of copper alloy coins, while trying to quantify them. In the second case, it is also about showing that a study with a pXRF device, even if only qualitative or semi-quantitative, can, in some cases, answer certain questions. The goal here is to use the three most advantageous aspects of the pXRF method: the very low cost of analysis; the very limited measurement time; and, thanks to its portability, the analyses of objects that cannot be moved.

Surface vs core elemental composition

The Frapper Monnaie project allowed for the acquisition and sectioning of 135 ancient copper alloy coins, minted between the 5th century BC and the 4th century AD[9]. Each coin was analysed using various methods (pXRF, XRF, EDX[10], and for some, Cyclotron Rapid Neutron Activation[11]) on a polished section, avoiding biases related to surface corrosion or enrichment, and allowing for precise study of the microstructure, hardness[12], and elemental composition of each coin[13]. Through this project, we were able to compare elemental composition measurements carried out using pXRF on the surface of coins with measurements carried out on the sections, i.e. on sound metal core.

Each coin was sectioned approximately in the middle (on x axis, vertical cut), thus offering the opportunity to carry out both metallographic observations (taking into consideration the sound core of the coin and the faces of the coin, both of which bore witness to the striking marks) and also to measure the elemental compositions on a sound metal core, representative of the coin alloy used. Having the remaining half of each coin available, a systematic study comparing surface and core compositions was implemented. One measurement was taken on each face, while the section was analysed at three points and averaged (with a collimator: 1.2 x 1.2 mm). Although this approach is not entirely new, the size of the corpus studied within the framework of this project seems unparalleled.

In their article, Di Fazio *et al.* use electron microprobe analysis to reveal compositional differences between corroded surfaces and uncorroded cores of ancient Roman brass coins[14]. Corroded areas show significant dezincification and decuprification, while uncorroded cores exhibit homogenous distribution of major elements (Cu, Zn) and minor/trace elements (Sn, As, Fe). This highlights again the importance of analyzing uncorroded areas to determine the original alloy composition and understand ancient metallurgical practices. Nicholas and Manti say the same for copper-alloy objects. Their study reveals that pXRF analysis of corroded surfaces can lead to misleading results

9. The samples studied within the framework of the project (photographs, elemental composition and hardness analyses) are available on the Nakala platform at this address: https://nakala.fr/collection/10.34847/nkl.bcaagc33. https://una-editions.fr/les-monnaies-grecques-et-romaines-en-alliages-cuivreux/. See also the documentary on the project: https://vimeo.com/701678193.
10. These analyses were conducted at the Archéosciences Bordeaux laboratory.
11. These analyses were conducted at the Institut de Recherche sur les ArchéoMATériaux – Centre Ernest Babelon, Orléans.
12. Hardness measurements were carried out at the IUT Sciences et Génie des Matériaux, Bordeaux.
13. For a review of these aspects for Greek coinages, see BLET-LEMARQUAND 2019. For those specifically done at the IRAMAT, BLET-LEMARQUAND 2013.
14. DI FAZIO *et al.* 2022.

due to dezincification, decuprification, and tin enrichment[15]. They also advocate that analyzing the uncorroded core of the coin provides a more accurate representation of the original alloy composition. This comes as no surprise.

In our sample, some coins clearly exhibit surface enrichment or surface copper depletion, the thickness of which can vary significantly, ranging from a few microns to several hundred microns[16]. The mechanisms behind these phenomena are diverse and complex and it would be too lengthy to detail them here. Di Fazio's article bibliography is a good starting point for a comprehensive overview of this issue[17]. Surface enrichment or depletion is observed regardless of the coin's alloy, whether it is pure copper or various alloys of bronze and brass, however, it is often more pronounced on coins containing a high lead content. It is important to note that the intensity and depth of surface enrichment or depletion is undetectable by surface observation alone. Only a cross-section allows this phenomenon to be understood.

While corrosion may not always be visible to the naked eye on polished sections, it is almost systematically detectable on a macroscopic scale. A coin minted by the Ptolemies in Cyprus in the 1st century BC[18] shows clearly a homogeneous layer where lead has largely disappeared from the surface[19]. This is a rather particular case. Generally, this layer is neither regular in depth nor evenly distributed over the coin's surface. The analysis results presented here are derived from the average of three analyses performed on the section. While the device used for these analyses features a 3 x 3 mm collimator, this figure should be considered approximate. Tests conducted on embedded samples revealed that the resin surrounding the coin was also detected, even when outside the theoretical surface area analysed. Consequently, all pXRF analyses in this study were carried out on cross-sections without resin embedding.

For our analyses, we used an Olympus VANTA C SERIES VCR portable XRF spectrometer[20], equipped with an aluminum filter and the AlloyPlus reference library. This device allows for fast and accurate measurement of elements, including light elements, thanks to its secure analysis chamber and an integrated camera for positioning samples. The aim of the analyses was not to study the corrosion process, but rather to conduct a qualitative investigation to estimate the content of major elements. The acquisition time was limited to 30 seconds per analysis[21]. Tests conducted with longer durations did not show any significant improvement, especially since the analysis focuses on heavy chemical elements. The calibration was performed using the instrument's proprietary software, which offers limited customisation options. Calibration is performed on the main elements

15. NICHOLAS, MANTI 2014, p. 2: "Corrosion of low-tin bronzes results in tin enrichment that could reach compositions similar to tinning remains"; and p. 8: "Results showed that HHpXRF is not capable of producing highly accurate quantitative data on corroded surfaces, due to object geometry, source-to-sample distance and Sn-enrichment due to corrosion".
16. https://www.nakala.fr/10.34847/nkl.cbffp14u#c2980928799ff15329dcc4dfec7c9451366307a1; https://www.nakala.fr/10.34847/nkl.75f2o048#cec249292bb20c59bea9bd88a24153dacff5e3bc; or https://www.nakala.fr/10.34847/nkl.dacar4e2#cea9092bd8c61f7e9fbab6aa3b03fe3949e3c9a2.
17. DI FAZIO *et al.* 2022.
18. https://www.nakala.fr/10.34847/nkl.4dba46if.
19. https://www.nakala.fr/10.34847/nkl.4dba46if#fca8f84a7fddf3e73bf32a30d7b500b9f7199724.
20. Tube: 40 kv, 0.2 Ma.
21. The beam without light elements was used, 40kv allowing the following elements to be measured: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Nb, Mo, Pd, Ag, Cd, Sn, Sb, HF, Ta, W, Re, Pb, Bi.

found in archaeological copper alloys: Fe, Co, Ni, Cu, Zn, Ag, Sn, Sb, Au, Pb, Bi[22]. A set of five standards, chosen for their composition similar to archaeological alloys, was analysed by pXRF to validate measurement accuracy[23], are available in the appendix. This approach, using five standards, aligns with recommendations from previous studies, ensuring adequate precision.

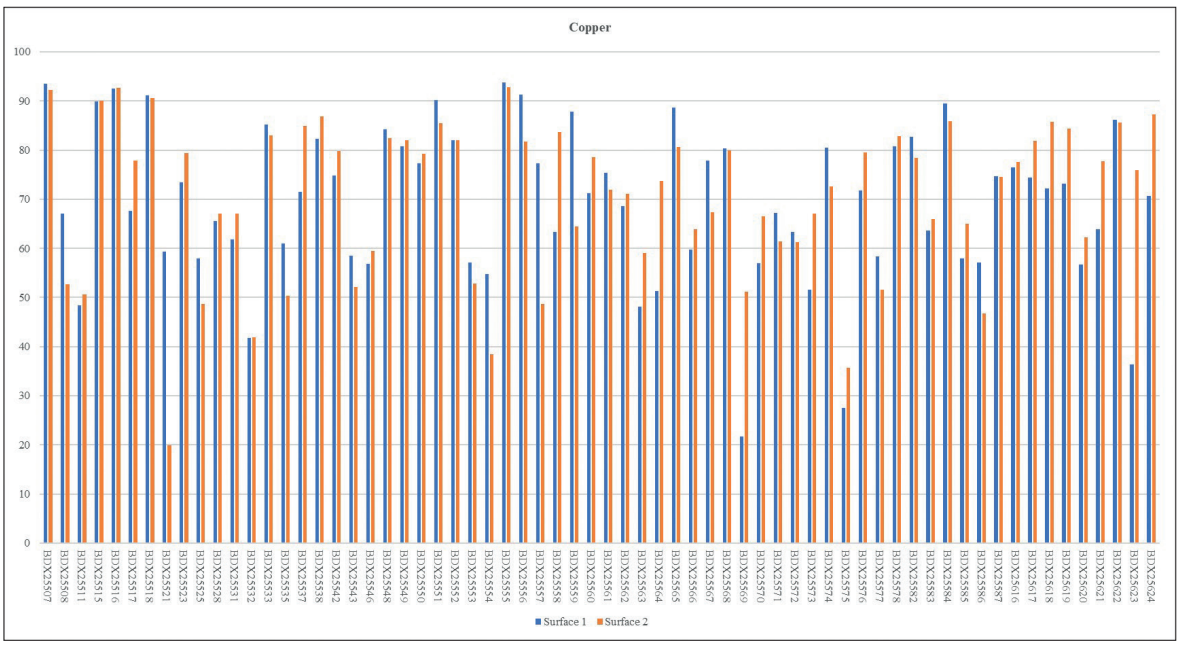


Figure 1: Copper content of surface 1 and surface 2

It is important to note that measurements between the two faces of the same coin can already show significant differences. Some detected elements, such as calcium, sulfur, and iron, come from corrosion products, which explains the discrepancy between the values measured on the surface and those measured at the core of the sample. The surface condition, including the patina, cannot be used to correlate the differences in results observed between the sides of a coin. The patina, that superficial layer resulting from oxidation or other chemical reactions, can mask or accentuate defects without necessarily influencing the results. Thus, coins in seemingly perfect condition or with a uniform patina can exhibit notable differences, while coins with visible defects may have similar results.

Furthermore, the discrepancies between an analysis of a corroded surface and the healthy core of the material are also considerable. Although for some samples the surface values are relatively close to those of the core, for others, the discrepancies are too large for the surface results to be usable.

These discrepancies are particularly pronounced for lead and tin, as the electrochemical corrosion phenomena tend to enrich the surface with these elements, at the expense of copper.

22. Bourgarit, Mille 2014.
23. The certified compositions of the standards were purchased from MBH Analytical Ltd (33X GM21, 32X 93700, 32X SN6, 33X GM7, 32X LB14).

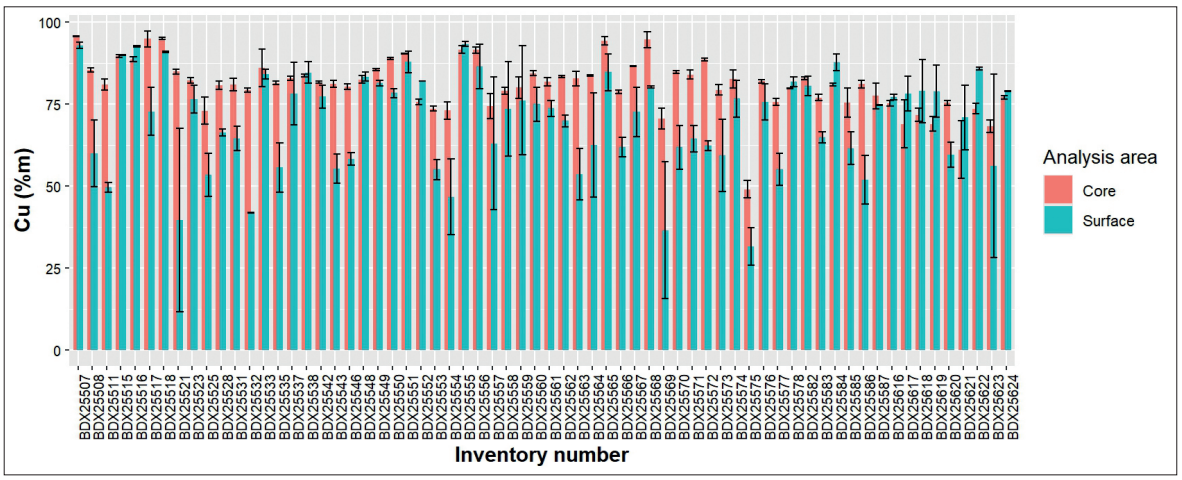


Figure 2: Comparison of the copper content in the core of the coin (in orange) and on the surface (in blue)

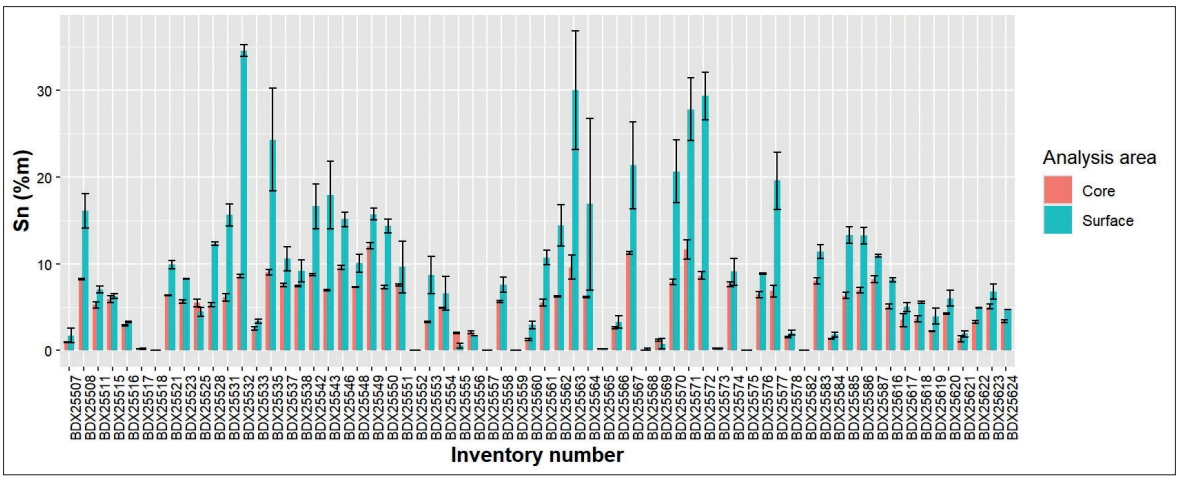


Figure 3: Comparison of the tin content in the core of the coin (in orange) and on the surface (in blue)

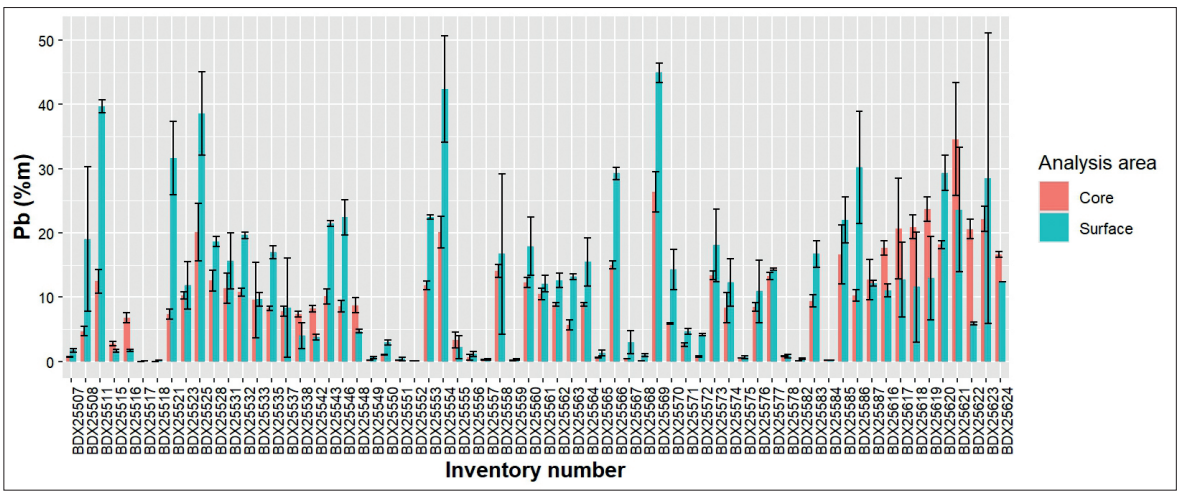


Figure 4: Comparison of the lead content in the core of the coin (in orange) and on the surface (in blue)

The analysis of lead within archaeological coins presents a uniquely intricate challenge, primarily due to the significant influence of surface corrosion. This corrosion layer, often characterised by the presence of lead compounds, can lead to substantial variations in measured lead concentrations, resulting in either over- or under-reporting of the element's true abundance. Even with meticulous efforts to mitigate these discrepancies, such as attempting to redistribute corrosion-related elements like calcium and sulfur, the observed differences between surface and core lead measurements remain persistently significant. While the existence of these analytical biases is well-documented, the opportunity to systematically examine this phenomenon across a large sample of sectioned coins offers invaluable insights. Specifically, the mechanisms of corrosion, which are profoundly influenced by the burial environment as detailed in studies such as Turo[24], contribute to the surface enrichment of certain elements, notably tin. This surface enrichment, in turn, plays a crucial role in explaining the observed discrepancies between surface and core elemental compositions. Furthermore, variations in the burial environment, including soil composition, pH levels, and moisture content, can lead to diverse corrosion products and rates, further complicating the accurate determination of original alloy compositions. It is important to note that restoration processes can often lead to changes in the surface composition of treated objects. This aspect is frequently overlooked. However, old, and sometimes even recent, restorations carried out with aggressive chemicals, particularly on coins, can alter the surface. In some cases, these products can penetrate up to several tens of microns inside the metal, especially if it has not been stabilised after treatment. In addition, lead is poorly miscible with copper (solubility of 0.007%[25]), and in the microstructure it is distributed in the form of heterogeneously dispersed nodules. Despite these biases, can qualitative analysis help to distinguish different series within the same coinage and thus facilitate the identification of coins?

Semi-quantitative outlier element determination

The Ptolemaic kingdom of Egypt, from the death of Alexander the Great to Cleopatra (4th–1st century BC), was one of the Hellenistic kingdoms that produced the largest number of copper alloy coins. European coin collections are well-stocked with these coins, enabling precise analyses of their elemental composition.

Elemental composition analysis was conducted as part of previous research[26], taking advantage of the extensive collection of the Department of Coins, Medals, and Antiquities at the Bibliothèque nationale de France, facilitated by the collaborative agreement between this institution and the CNRS IRAMAT-Centre Ernest Babelon laboratory. This laboratory historically maintained regular access to a cyclotron, enabling non-invasive analysis through Fast Neutron Activation Analysis (FNAA)[27]. This method yielded comprehensive bulk composition data, effectively mitigating the influence of surface corrosion. In that research, approximately 120 Ptolemaic copper alloy coins were analysed, establishing a compositional timeline for bronze coinage within the region from the early 3rd to the late 1st century BC. However, the operational complexities associated with the cyclotron, including cost and analysis duration, constrained the sample size. Furthermore, while

24. For example, see Di Turo, Coletti, De Vito 2020.
25. Davis (ed.) 2001, p. 34.
26. Faucher 2013.
27. https://iramat.cnrs.fr/spectrometrie-de-rayonnement-gamma/.

the Bibliothèque nationale de France possesses a preeminent collection of Ptolemaic coins, certain specimens were unavailable for analysis.

The coin collection from the Centre d'Études Alexandrines' archaeological excavations in Egypt[28], combined with the availability of a portable X-ray fluorescence (pXRF) device, offered a valuable opportunity to complement our analyses. However, due to the strict regulations enforced by the Egyptian Ministry of Tourism and Antiquities, destructive analysis, such as sectioning, was explicitly prohibited. Therefore, surface analysis using pXRF became the necessary and sole methodological approach. The provenance of these coins, meticulously documented through their excavation context, provided a critical advantage. Unlike surface analyses conducted on unprovenanced coins, these samples possessed a well-defined burial history, offering a crucial framework for interpreting the analytical results. This contextual information, which includes detailed stratigraphic data and environmental records, allowed for a more nuanced understanding of the surface alterations and corrosion phenomena that might otherwise obscure the original alloy composition. Furthermore, the stringent regulations prohibiting the export of archaeological materials from Egypt underscored the importance of on-site analysis. Utilizing pXRF directly at the excavation site or within Egyptian institutions allowed for the non-destructive study of these invaluable coins, ensuring their preservation while simultaneously contributing to a deeper understanding of their composition and historical significance. This approach not only adhered to the legal and ethical considerations surrounding cultural heritage but also maximised the scientific potential of the available resources, providing a robust dataset within the constraints imposed by the preservation imperatives.

We employed a Niton XL3t GOLDD+ portable X-ray fluorescence (pXRF) device for the analyses[29]. The instrument was calibrated using the same reference standards previously described, and the standards demonstrated satisfactory performance. As explained previously, the calibration is performed on the main elements found in archaeological copper alloys: Fe, Co, Ni, Cu, Zn, Ag, Sn, Sb, Au, Pb, Bi[30]. The team conducted the analyses during the winter of 2022, selecting a sample of 400 coins. For each coin, two measurements were performed (one on each side of the coin). These measurements are few in number, of course, but as this is an exploratory study, the choice was made to gather as large a sample as possible. These two measurements are then averaged. Differences of ± 3 to 4% can be observed but are in line with other studies[31], with corrosion being one explanation.

The selection primarily focused on coins from the first half of the Ptolemaic reign, particularly due to the known lower lead content during this period. Initially, we intended these analyses to be exploratory and methodological, with limited expectations regarding the substantive results. However, the results proved valuable in several key aspects.

28. www.cealex.org.
29. Spot size: 8 x 8 mm; 3 filters (10 s per filter): 30 s per analysis; 6-50 kV, 0-200 µA for General Metal mode: 50 kV, 40 µA with main filter which analyses the following elements: Al, Sb, Sn, Pd, Ag, Mo, Nb, Zr, Bi, Pb, Se, W, Zn, Cu, Re, Ta, Hf, Ni, Co, Fe, Mn, Cr, V, Ti.
30. Bourgarit, Mille 2014.
31. Calligaro *et al.* 2019, p. 36.

These coins, studied over a period of nearly 30 years, are either worn or very worn[32]. Reading them is therefore often difficult, sometimes impossible, and it was obvious that a certain number of errors of identification could have crept into our databases.

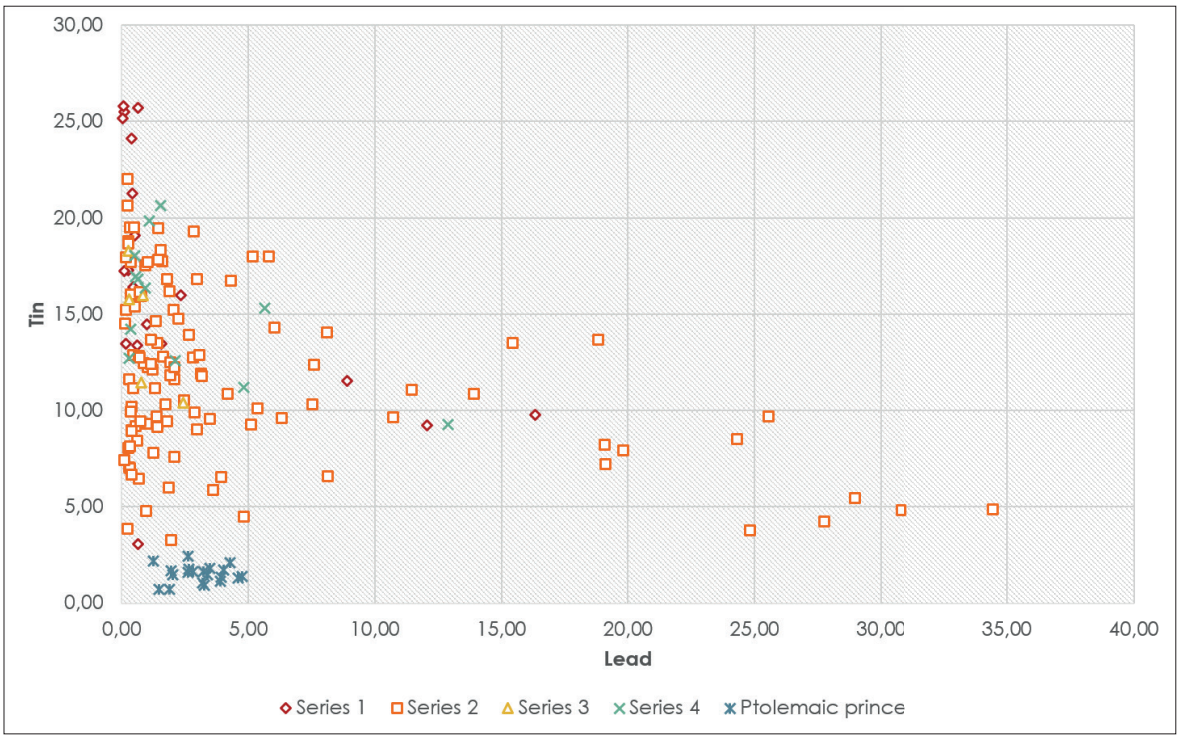


Figure 5: Tin and lead content of coin series 1 to 4 + Prince series

Early Ptolemaic coins, minted until the beginning of the 2nd century BC, typically exhibit a high tin content (up to 15%) and a very low lead content (often below 3%)[33]. The analyses generally confirmed these established compositions. Coins with abnormally high lead content, exceeding 10%, primarily fell into two categories. First, several coins presented identification errors. Re-examination of these specimens revealed misidentification or raised significant doubts about their original classification[34]. Second, contemporary imitations constituted another group. While the team had previously identified cast imitations, these analyses demonstrated that the phenomenon was far more prevalent than initially recognised. This underscores the paramount importance of analyzing archaeological collections. European collectors or curators of non-archaeological collections may have historically favoured aesthetically pleasing coins with standard alloy compositions, potentially overlooking or discarding these less visually appealing imitations. Consequently, the actual number of genuine anomalies—well-preserved, correctly identified coins with abnormal lead content—proved to be minimal.

32. Some coins are already online: www.coins.cealex.org. It would take too long here to present a full catalogue of the coins analysed.
33. FAUCHER 2013.
34. For classification of Ptolemaic bronze coins, see PICARD, FAUCHER 2012.

The second notable result stems from the analysis of a unique coin assemblage. This group of 56 coins, discovered during the excavations of the Centre d'Études Alexandrines on the Cricket Ground in Alexandria between 1994 and 1997, lacks any known parallel[35]. Specifically, these coins have not been documented in any other find. They feature a bare head, possibly depicting Apollo, on the obverse, and a falcon on the reverse. This representation deviates significantly from established Ptolemaic coinage, which consistently employs the royal eagle. Furthermore, these coins are anepigraphic, an anomaly within Ptolemaic numismatic traditions. Consequently, researchers dated the coins based on their archaeological context and associated ceramic material, placing them within the late 3rd or early 2nd century BC.



Figure 6: Coin of the Cricket Ground hoard, CEAlex excavations

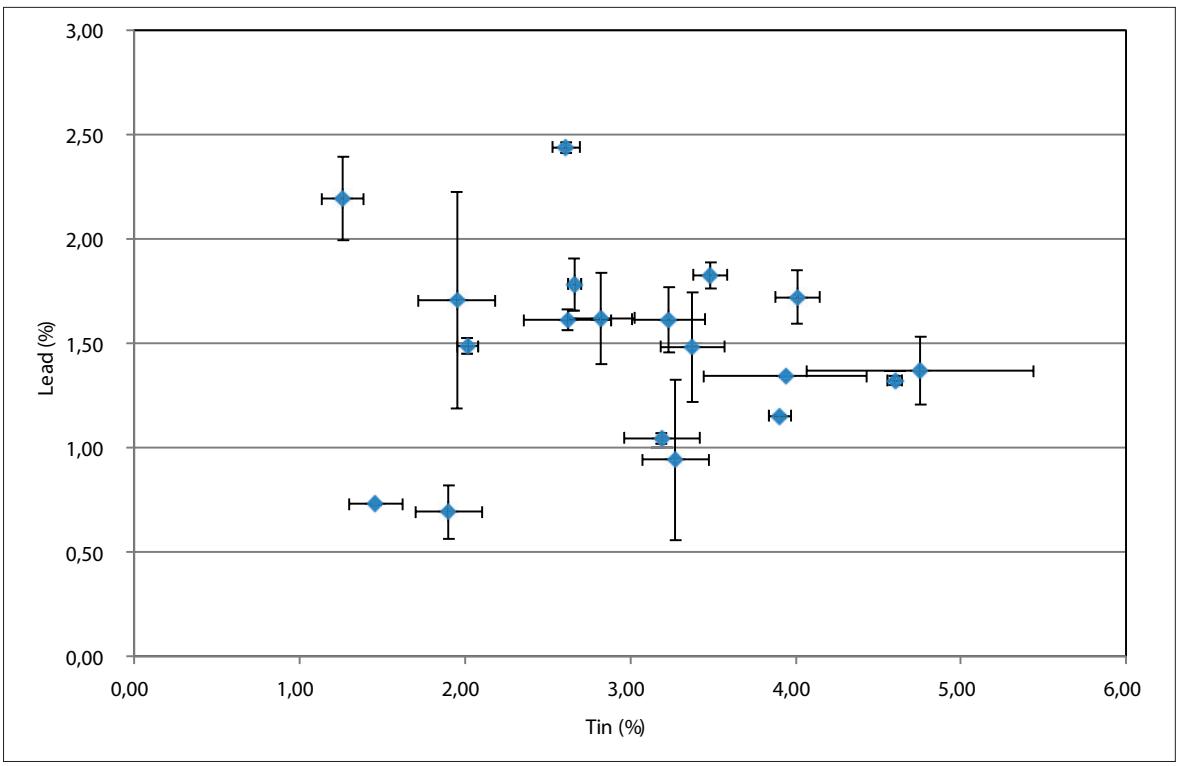


Figure 7: Tin and lead composition of the Prince series

35. PICARD 1999.

The elemental composition of this coin assemblage revealed notable deviations from typical Ptolemaic standards, further emphasizing their exceptional nature. While the lead content, although consistently below 2.5%, aligned with the general trend of low lead concentrations observed in early Ptolemaic coinage, it is important to acknowledge the inherent limitations of portable X-ray fluorescence (pXRF) in precisely quantifying lead levels. However, the most striking characteristic lay in the remarkably diminished tin content. This paucity of tin represents a significant anomaly for coins attributed to this chronological period, which traditionally exhibit higher tin concentrations. The rarity of such a composition within the Ptolemaic context strongly suggests a unique metallurgical practice or a distinct minting origin. Consequently, the atypical elemental profile of these coins reinforces their status as an exceptional and enigmatic numismatic discovery. The combination of their unique iconography, anepigraphic nature, and unusual alloy composition underscores their significance and warrants further investigation into their production and historical context.

Conclusion

In conclusion, this presentation has sought to demonstrate that pXRF analysis, despite its inherent limitations in accurately quantifying certain elements and fully accounting for surface effects, offers a powerful tool for investigating ancient coinage when researchers apply it with a clear understanding of its capabilities and potential biases. The case studies presented herein highlight the critical importance of a well-defined methodological approach, the synergistic combination of pXRF with complementary analytical techniques, and the essential role of contextual information. Through meticulous analysis and thoughtful interpretation, pXRF can significantly aid in identifying misattributions, uncovering previously undocumented coin series, and contributing to a more nuanced and comprehensive understanding of ancient minting practices and economic history. While acknowledging the need for continued research and methodological refinement, this study underscores the substantial potential of pXRF as a valuable tool. Its application extends beyond numismatics, offering broader implications for the exploration of copper alloy object production and the reconstruction of past technological and economic systems.

Author contribution

Thomas Faucher: funding acquisition, project administration and supervision, data curation, conceptualisation, methodology, investigation, validation, review and editing, visualisation and writing original draft;
Alexandre Bodet: data curation, conceptualisation, methodology, investigation, review and editing.

Data availability statement

The supplementary data are available at 10.34847/nkl.e49ak2f3.

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Ilian Finkeldey

Distortion through conservation: variation in pXRF data on bronze objects due to chemical alterations as a result of old and new conservation methods

Abstract

As part of the authors master's thesis from 2023/2024 *Traces of craftsmanship in metal – X-ray fluorescence-based analysis of the two Bronze Age hoard inventories from Schellhorn and Fahrdorf (Schleswig-Holstein)*, bronze objects from two hoards[1], were examined using non-destructive portable X-ray fluorescence analysis (pXRF), digital microscopy and later partly re-examined using laser induced breakthrough spectroscopy (LIBS). The following article discusses the interpretation of the generated data with a focus on the identification of distortions in pXRF readings caused by some conservation measures and their possible corrections. As museums and collections often require non-destructive analyses, pXRF readings are the method of choice albeit influenced in their results by any chemical changes on the object's surface including by conservation methods. Both hoard inventories processed in this case study showed high amounts of elements that do not match the expected compositions of prehistoric artefacts and their natural corrosion layers. To identify the cause of these anomalies, several possibilities had to be considered, in particular modern and prehistoric surface treatments. Ultimately, all anomalies found can be classified as the traces of different restoration measures and thus compensated for in the processed data. The trace elements present in the adjusted data correspond largely with the composition typical for this period and region.

Keywords

Bronze Age hoards, tin bronze, Fahrdorf, Schellhorn, corrosion, archaeometallurgy, pXRF, LIBS

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1. Discovered in Schleswig-Holstein, Schellhorn 1902; Fahrdorf 2021.

Introduction

Apart from grave goods, hoard finds from the Nordic Bronze Age (NBA) make up the majority of Bronze Age metal artefacts in Schleswig-Holstein[2]. Unlike the furnishings in graves, hoard finds from the Early Nordic Bronze Age often contain collections of everyday bronze objects, especially tools, such as axes and sickles. The use of material analysis to understand the relations between objects in an individual hoard, as well as their comparison to other hoards, can help to characterise material distribution and craftsmanship within a region. However, only a few hoards from northern Germany have been analysed to date[3]. This is partly due to the destructive nature of most scientific analytical methods. As one of the few methods that can be used completely non-destructively, (portable) X-ray fluorescence (pXRF) analysis can be used directly in collections or in the field. However, using pXRF analysis needs an understanding not only of the method itself but also of its limitations regarding the condition of each individual object. The analysed hoards of Fahrdorf, Kr. Schleswig-Flensburg, LA 105 and Schellhorn (Scharsdorf), Kr. Plön, LA 37 are both dated to Period II (1500-1250 BC) of the NBA and contain a typical combination of bronze objects including palstaves, sickles, and spearheads. All objects in this study can be assumed to be functional tools or weapons made from an original alloy of workable tin bronze, which was rapidly introduced to the region through trade in the late stages of the local Neolithic[4]. For the NBA Period II a ratio of ideally about 9 parts copper to 1 part tin (between 8 and 12 wt% tin) would be expected[5]. Bronze with lower amounts of tin has a higher melting point and is overall softer. Low-tin bronze is generally only found in earlier artefacts. Higher amounts of tin is usually considered too brittle for tools or weapons and might be used more in decorative objects. Both hoards were chosen for this study based on the seemingly well-preserved surfaces on most objects and their similar context and typology. The goal was to produce a set of comparable data without further invasive testing. To validate the results of the initial analysis some objects' surfaces from Schellhorn were re-examined in late 2024 using minimally invasive Laser Induced Breakdown Spectroscopy (LIBS).

Methods

All objects from the two hoard inventories were initially scanned using a KEYENCE™ VR-600 3D-Profiler. This allowed for later comparison of the objects' sizes and shapes. Any signs of use-wear Jantzen 2008, p. 7 and production marks or areas of interest as well as types of corrosion and patina were observed under a digital KEYENCE™ VHX microscope (**fig. 1**). For the pXRF analysis a Niton Xl3t Goldd++ portable XRF analyser was employed, and each object was assayed on up to four different spots in the general "metals mode" for 120 seconds. This included surfaces with heavy corrosion as well as the best-preserved surfaces on each object. Several measurements are

2. Endrigkeit 2010, p. 1; Franke 2012.
3. Freudenberg, Glaser 2015, p. 24.
4. Nørgaard *et al.* 2025, p. 223.
5. Jantzen 2008, p. 7.

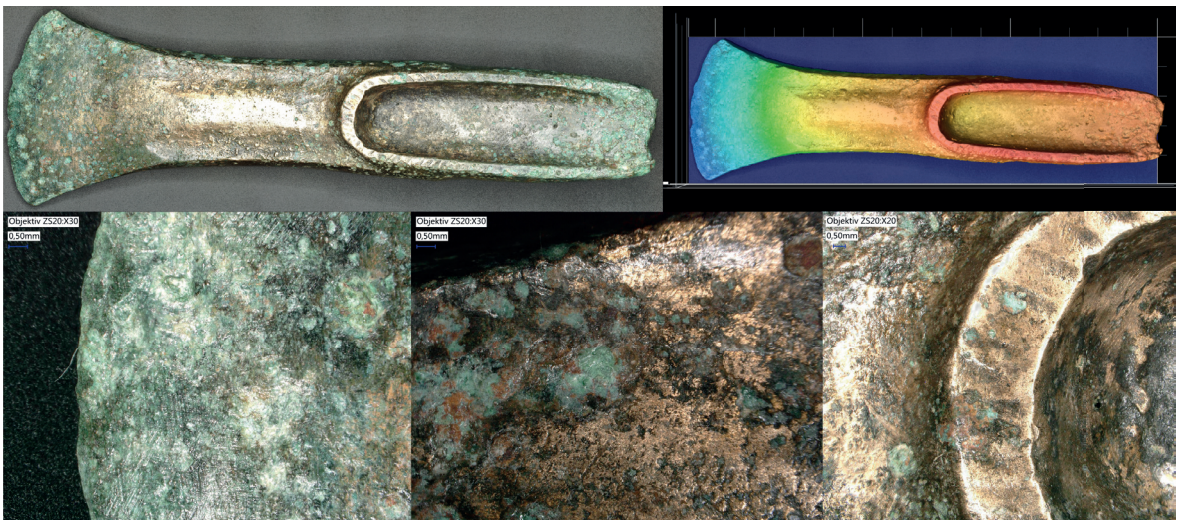


Figure 1: Palstave Fahrdorf SH2021-130.23 with excellently preserved surfaces, signs of metalworking and traces of crystalline pitting on the edge (3D profile and digital microscope, author's images supported by B. Meller, N. Joachimsthaler, J. Harms)

necessary because the condition of bronze artefacts is usually not homogeneous[6]. Thus it was possible to identify specific but largely consistent elemental patterns within each hoard inventory. These trends reflect the state of corrosion and possibly some modern contamination. By comparing these two groups of closed finds an attempt was made to identify these kinds of modern disturbances and determine the original alloys and trace elements. To further analyse the composition of the surface layers (patina) and possible remains of modern surface contamination, a KEYENCE EA-300 microscope with an inbuilt LIBS-spectrometer was employed for re-examination of a selection of artefacts from Schellhorn. LIBS is generally less precise than pXRF with a limit of detection (LOD) generally at 1 wt% with micro-scale heterogeneity of the alloys also making several readings necessary to achieve representative results[7].

Corrosion

Reactive materials, such as copper alloys, are prone to selective chemical reactions with their surroundings which heavily affect the results of non-destructive surface analysis and must therefore be understood to generate meaningful conclusions. When corrosion sets in, a layer of copper oxides usually forms on the surface. During millennia buried in soil, this layer starts to mineralise and forms different layers of corrosion products, which – depending on the conditions in the soil – slowly change the composition of the surface and the bulk metal. These complex corrosion processes can be classified after Luc Robbiola[8] into two types (**fig. 2**). Type I usually forms a

6. Emmitt, McAlister, Armstrong 2021, p. 11–13.
7. Arafat *et al.* 2013, p. 268.
8. Robbiola 2015.

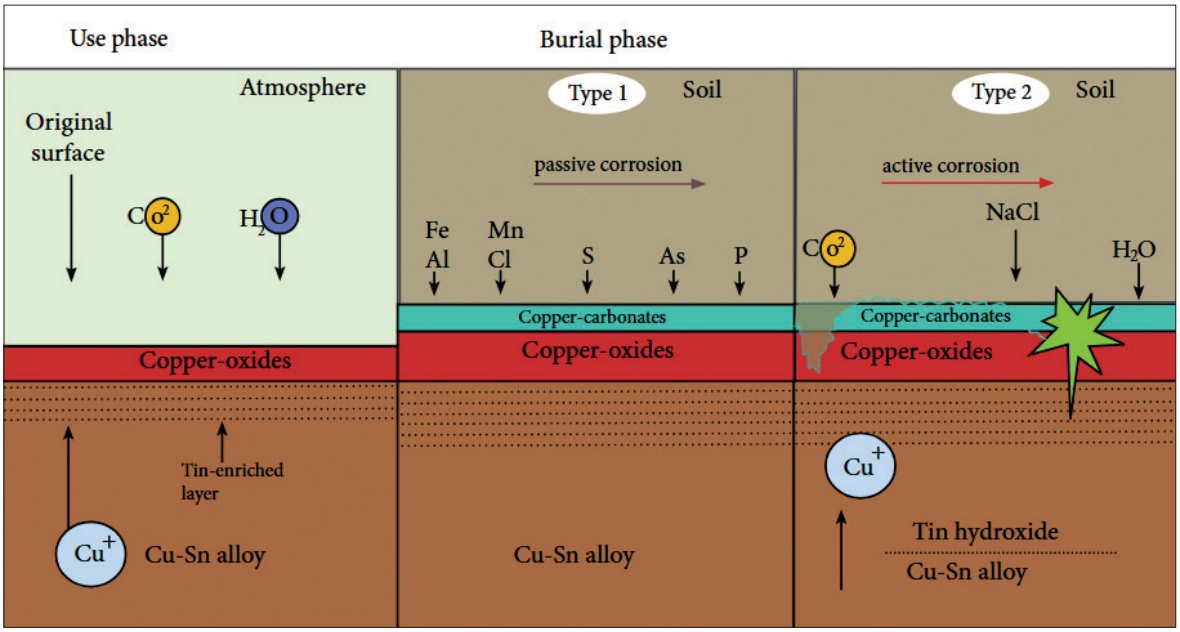


Figure 2: Simplified model of the forming of corrosion layers according to BERGER 2012 and ROBBIOLA 2015 (by S. Weihmann)

shell of mineralised copper carbonites on top of the first oxidation phase and is therefore always two-layered. Type I corrosion layers are often called noble patina because of their ability to protect surfaces from further corrosion if left undisturbed. Noble patina is therefore desirable for conservation purposes. The carbonite layers also accumulate elements from the surrounding soils[9]. More common than a flawless noble patina are several corrosion layers and proliferations of different, possibly unstable corrosion products in various stages. On contact with moist air or certain elements, for example, in cleaning agents or chemically treated storage boxes, these products can reactivate the corrosion process. An incomplete protective layer is described by Robbiola[10] as Type II with at least three layers. Type II corrosion forms a rough surface and includes all forms of active corrosions like pitting or selective corrosion and bronze disease. Different types of corrosion are often present on the same object. This means that surface readings from prehistoric bronze can be highly distorted due to an overrepresentation of the composition of superimposed layers of corrosion products and elemental changes in patina layers[11]. While this data can still be worked with for most research questions regarding objects from the same context, the quantitative comparability of data sets with other finds, however, is strongly limited[12]. The problem is amplified by the uneven surface and variable thickness of corrosion layers that influence the detection depth of the fluorescence and alter the ratio of corrosion layers to the measured bulk metal. There are currently no means to accurately correct the distortion in pXRF readings from these complex, often unpredictable and varied forms

9. GEILMANN 1956, p. 207–211.
10. ROBBIOLA 2015.
11. NØRGAARD 2017, p. 104, 120.
12. BERGER 2012, p. 18.

of corrosion without deploying invasive methods[13]. Some progress has been made using Monte Carlo Simulations[14]. However, these still rely on parameters such as layer thickness, which are only measurable by destructive means[15]. For this reason, invasive analysis is often preferred in large-scale comparisons, as it allows to compare bulk (i.e. original) compositions that are often better preserved in the core of artefacts[16]. This means that non-destructive pXRF analysis can only ever provide approximate values for the original composition. This approximation can then be used to characterise the objects and categorise them with comparable finds[17]. Elements that do not fit into the typical chemical reaction patterns of corrosion or are unusually high, however, must be given individual research and explanation, so that a reasonable interpretation can be considered.

Conservation

The conservation methods applied to copper alloys during and after storage in collections or exhibitions can also result in lasting changes to the chemical composition on the surface of objects that further distort pXRF readings. Today, the conservation of artefacts aims to preserve the object in stable conditions without significantly changing its appearance or composition. To prevent further deterioration during storage in the museum or archive, only light varnishes or coatings are applied once the artefacts have been dried and cleaned. Historically, this was not always possible or wanted. Previously applied preservation methods originated from techniques developed for iron artefacts. These can be more drastic to combat the rapid decay of iron effectively. These chemical solutions could also significantly affect the colour and appearance of bronze objects. Until the mid-20th century it was popular to restore bronze to an authentic classical look by artificially staining, coating or even repatinating bronze objects after conservation[18]. Many of these older restoration measures are poorly documented or not at all[19]. As a result, the chemical change caused by restoration measures is difficult to predict, especially in the case of older artefacts. In his 1905 curator's guide, Friedrich Rathgen described the removal of the different types of patina as a restorative procedure using various acids to restore the bronze colour and lustre. In addition to these chemical methods, mechanical cleaning and colourants were also used to achieve the desired antique aesthetic[20]. The treatment of early finds, such as the ones in this case study from Schellhorn found in 1902, may have been carried out using a wide variety of methods and perhaps even involved agents invented by the restorers themselves. Only since the mid-20th century, more gentle and standardised conservation measures have been developed. In recent years aspects such as the sustainability and toxicity of the agents used have also been criticised[21]. Today corrosion layers are rarely removed entirely as it would destroy the remains of the original surface.

13. Gianoncelli, Kourousias 2007, p. 862.
14. Bottaini *et al*. 2018.
15. Emmit, McAlister, Armstrong 2021 p. 4.
16. Pearce 2018, p. 84.
17. Radivojević *et al.* 2019, p. 10–17; Orfanou, Rehren 2015, p. 395–396; Franke 2014.
18. Manti, Watkinson 2022, p. 158.
19. Scott 2002, p. 352–353.
20. Risser, Saunders 2013, p. 45–46.
21. Kosek, Ropret 2021, p. 65.

Chemical, mechanical or electronic processes are only used to remove corrosive salts from the surface, which otherwise may continue to decompose under the protective coating, and crack protective layers or coatings[22]. The modern protective varnishes made of BTA (benzotriazole) or acrylic resin, such as Paraloid B-72, and adhesives, such as nitrocellulose glue used by modern restorers, consist of organic compounds[23]. The elements in such varnishes are usually too light to be measured with pXRF and a thin layer should therefore not noticeably affect such measurements. This applies to the recent finds from the hoard of Fahrdorf, which have only been discovered (and restored for that matter) in 2021. Varnishes can however hinder the detection depth of the fluorescence of deeper layers reducing the overall precision. Some substances known to be used as alternative protective coatings (resins, oils, rust inhibitors or paraffin wax) may contain elements that can be problematic for pXRF analysis. For example, transparent nitrocellulose-based varnishes (e.g. nail polish), which also exist since the middle of the 20th century, may contain metallic or mineral additives for improved gloss, colour or durability, which then appear in the (measured) XRF readings.

Trends

When examining pXRF data possibly containing distortion from both corrosion and conservation, it is important to understand which elements are changed by either process. Comparing data from multiple measurements and multiple objects from the same closed find can help to identify changes caused by corrosion as trend within the data. Even though corrosion often does not behave in a linear manner, all objects from the same find should have been subjected to the same conditions overall, showing their varying progress of decay as a gradual trend within the data. Elements enriched by corrosion are generally corresponding to the state of decay of the original copper alloy and are unevenly distributed within the corrosion layer while those elements added by modern treatment are generally more stable across all surfaces. The elements making up the bulk composition of the alloy, in this case copper and tin, are reduced by corrosion in variable amounts showing the overall state of decay. As corrosion processes are complex chemical reactions, this trend will likely have several outliers and therefore needs the multiple measurements from the same object and ideally multiple objects from the same context to express an overall trend[24]. Minor and trace elements that are drastically increased in measurements from high corrosion areas must therefore either be overrepresented on the surface due to slower decay than the major components of the original alloy or are additionally migrated and enriched from elements present in the surrounding soil[25]. Elements that increase on better preserved areas and decrease on high corrosion areas are usually part of the original composition. Elements that do not correspond to these behaviours can be assumed to be either modern contamination or elements that are resistant to reactions with the surrounding elements. These patterns in the combined data can then be used to better distinguish between distortion from corrosion and chemical changes caused by conservation.

22. Oudbashi 2015, p. 30.
23. Finšgar, Milošev 2010, p. 2737.
24. Emmitt, McAlister, Armstrong 2021, p. 11–13.
25. Nørgaard 2017, p. 106.

Results from Schellhorn

The results of the pXRF measurement of the 11 complete artefacts from Schellhorn are immediately notable for the high uniformity of qualitative alloy components and trace elements present, although not in their quantitative proportions. Cu values vary between 83.48 wt% measured on the back of palstave SH1902-4.1 and 20.7 wt% measured on the socket of spearhead SH1902-4.4. This variation is a typical distortion attributed to corrosion processes. Depending on the type of soil in which the object was buried, the copper on the surface is often reduced as it oxidises and distributes to the surrounding soil leaving a higher concentration of Sn and other less reactive elements on the surface or underneath the initial crusting and patina[26]. On objects showing a lower Cu wt%, like the above mentioned spearhead, the patina is generally visibly thicker, suggesting a worse state of decay. Corrosion processes are expected to enrich some minor elements on the surface or incorporate elements like silicon from sand present in the surrounding soil. This can be seen with the objects from Schellhorn, in which particular elements, such as silicon, are especially high while copper levels are strongly reduced. Similar behaviour is somewhat visible on the most prevalent minor elements, As and Fe, which are overall strongly overrepresented. In particular, the iron content is in some measurements extremely high (average 4.8 wt% up to 16 wt%), which would hint at an unusually strong contamination. The iron levels follow a typical pattern, in which higher concentrations correspond with low levels of copper. However, the measured iron levels exhibit greater fluctuation than measured As, Ni and Sb levels, whose measured values vary less and whose variations appear more random (**fig. 3**). The latter elements would be considered to originate from the original ore and were part of the original composition but dissolved and enriched during corrosion and are therefore overrepresented even on cleaned surfaces. Similarly to these, iron was not fully separated

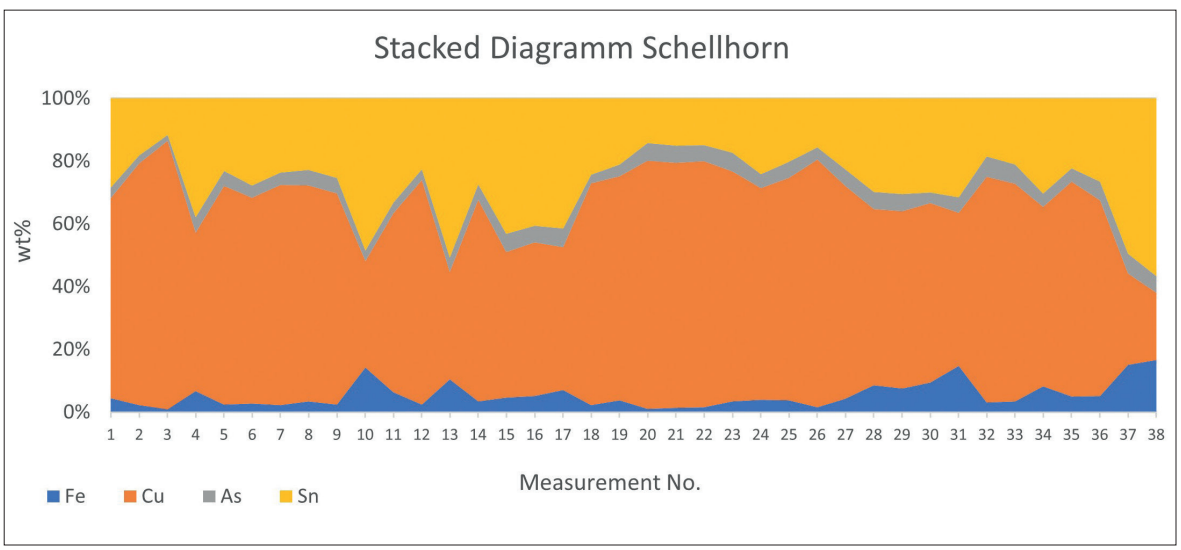


Figure 3: Cu in relation to Sn, As and Fe (normalised to 100%) overall measurements on the objects from Schellhorn. As is relatively consistent, while Fe corresponds to low Cu with extreme peaks. (Full Datasets in REPOSITORY)

26. WADSAK *et al.* 2000, p. 161–163; GEILMANN 1956, p. 205–206.

during prehistoric smelting of common copper ores, such as arsenic fahlore ((Cu, Fe)12As4S13) or chalcopyrite (CuFeS2), yet the average amount of iron is not expected to significantly exceed levels of *circa* 1 – 2 wt% (which are still soluble in copper), as amounts much higher then that would render the copper-based alloy unworkable. On the other hand, iron is not reactive with bronze alloys per se, but as one of the most common elements in the Earth's crust, it is almost always present in soil and often penetrates the patina of prehistoric bronze objects in small amounts[27]. This is also seen in comparable objects like the ones from Fahrdorf[28]. The extreme measurements of iron are unlikely to stem from corrosion or production. Therefore, different influences like conservation efforts must be considered.

Inv. No.	DIAG. 1 No.	Measuring point	Cu	Sn	Fe	Al	As	Ni	Si	Ag	Pb	Sb	S
SH1902-4.1	1	Blade	63	28	4	n.d.	3	0,1	n.d.	n.d.	0,3	0,2	n.d.
SH1902-4.1	2	Blade back	75	18	2	n.d.	3	0,2	0,7	n.d.	0,2	0,2	1,0
SH1902-4.1	3	Centre ridge	83	11	1	n.d.	2	0,3	1,1	n.d.	0,1	0,1	0,6
SH1902-4.1	4	Neck gruve	49	37	6	n.d.	5	n.d.	1,0	n.d.	0,3	0,3	0,5
SH1902-4.10	28	Blade	54	29	8	n.d.	5	0,6	1,5	n.d.	0,1	n.d.	1,7
SH1902-4.10	29	Blade back	54	29	7	n.d.	5	0,5	1,7	n.d.	n.d.	n.d.	1,5
SH1902-4.10	30	Centre ridge	54	28	9	n.d.	3	0,6	3,3	n.d.	n.d.	n.d.	1,3
SH1902-4.10	31	Socket	47	30	14	n.d.	5	0,6	1,4	n.d.	n.d.	n.d.	1,0

Table 1: Schellhorn Measurements (in wt%) from well-preserved palstave 4.1 and thickly patinated spearhead 4.10 with noticeably overrepresented minor elements (Full Datasets in FINKELDEY 2024)

Results from Fahrdorf

The measurements from the 18 objects and fragments from Fahrdorf appear very similar to those from Schellhorn with a similar uniformity and composition of elements. The variability is less pronounced, but the highest amount of Cu measured is only at 76.9 wt%, while Sn can measure over 50 wt% on some extremely corroded surfaces. Since these objects can be assumed to have had a Cu amount above 80% before corrosion began, these measurements imply that the state of decay is worse than that of the objects from Schellhorn. The effect and overrepresentation of invasive (e.g. Si) and reactive elements (e.g. As) also seem to be much higher than in Schellhorn (As up to 13 wt%, Si up to 4 wt%). As and the much less reactive Ni (up to 0.6) can still be considered to be the main trace elements in these objects but the analyses also showed an additional unusually high yet consistent amount of up to 11.45 wt% Al (**fig. 4**). The results for iron (average <0.9 wt%) in the Fahrdorf artefacts appear more plausible than the values measured with the Schellhorn artefacts. The contamination with aluminium is difficult to assess, as the measurement of aluminium

27. ORFANOU, REHREN 2015, p. 393.
28. BUNNEFELD 2016, p. 94 Tab. 6; PERNICKA 1999, p. 165–170; HAUPTMANN 2020, p. 311–318.

is inconsistent with pXRF analysers. However, the device used deploys an "AI" calculation that attempts to avoid this inconsistency. A software error within the device appears unlikely since the measurements of aluminium were consistent and also not found in other readings. Small amounts of Al might also be integrated in patina from soil, however, since the widespread use of metallic aluminium is a very recent development these unusually high levels indicate a modern contamination.

Inv. No.	DIAG. 2 No.	Measuring point	Cu	Sn	Fe	Al	As	Ni	Si	Ag	Pb	Sb	S
SH2021-130.2	17	Blade	69	20	0,2	7	1	0,2	2	n.d.	0,1	n.d	0,4
SH2021-130.2	18	Blade back	61	25	0,2	9	2	0,2	3	n.d.	n.d.	n.d.	0,2
SH2021-130.2	19	Centre ridge	71	20	0,2	4	1	0,2	2	n.d.	n.d.	n.d.	0,2
SH2021-130.2	20	Neck gruve	67	23	0,2	5	1	0,2	2	n.d.	n.d.	n.d.	0,1
SH2021-130.29	21	Blade	27	49	1,4	8	8	0,6	5	n.d.	0,3	0,2	n.d.
SH2021-130.29	22	Blade back	57	30	0,3	2	8	0,4	1	n.d.	0,3	0,1	0,3
SH2021-130.29	23	Centre ridge	31	48	0,8	6	9	0,6	2	n.d.	0,3	0,2	n.d.
SH2021-130.29	24	Socket	33	45	0,8	8	9	0,5	2	n.d.	0,3	0,2	n.d.

Table 2: Fahrdorf Measurements (in wt%) from well-preserved palstave 130.2 and strongly corroded spearhead 130.20 with noticeably overrepresented minor elements (Full Datasets in FINKELDEY 2024)

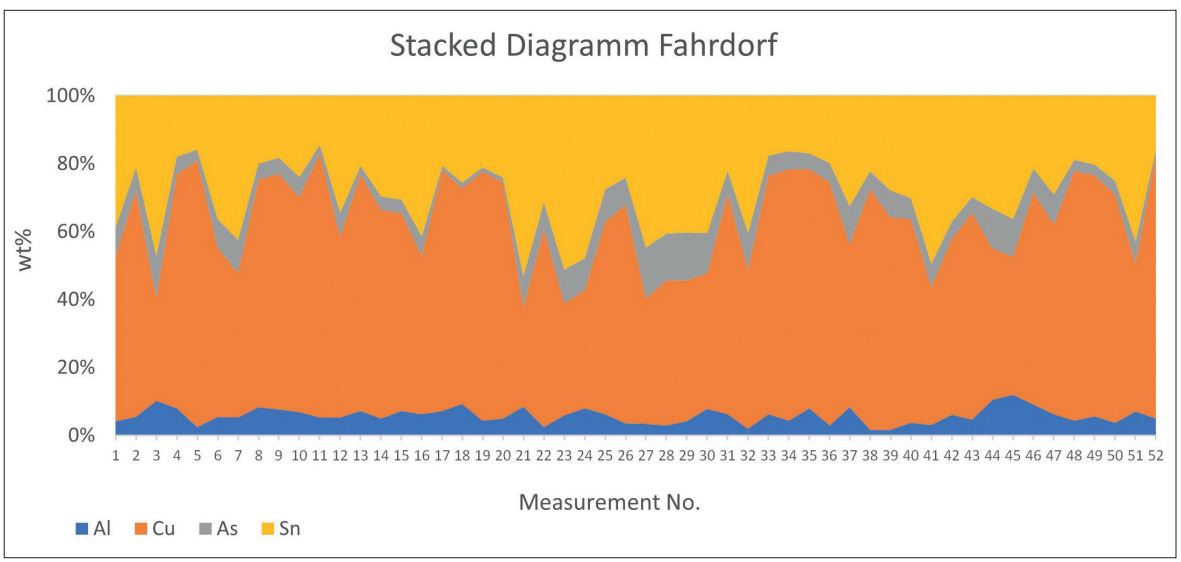


Figure 4: Cu in relation to Sn, As and Al (normalised to 100%) over all measurements on the objects from Fahrdorf. As and Sn are very variable, both appear with high values at low copper content. Al is very consistent across most measurements. (Full Datasets in REPOSITORY)

Discussion

Despite their relatively clean surfaces being presumed optimal for pXRF, both hoards showed unique anomalies as well as typical distortion from corrosion processes in their respective readings which needed to be identified individually. Resolving these issues is crucial to further interpretation of pXRF data. Surfaces with thicker patina, sometimes rough or pitted, are less homogenous and show reduced copper amounts while tin and minor elements are strongly overrepresented. On the better-preserved surfaces measurements are much more reliable but rarely meet the assumed ratios. As mentioned above this is to be expected on all prehistoric objects when working with non-invasive pXRF, even on seemingly clean and shining surfaces. Results like these can still be used for a general characterisation[29]. Besides the mentioned anomalies, both hoards have similar characteristics that fit very well within the so-called AsNi-Group. Following Liversage[30], bronze artefacts can be categorised in groups after their primary minor elements which arise from the original ore. Alloys with As and Ni as their major secondary elements with only small amounts of Sb and Ag, as seen in all objects from Fahrdorf and Schellhorn, except one[31], are part of a group that is considered typical for the older NBA and is present in several studies from this region[32]. Therefore, it is mainly the unusual contents of iron and aluminium that are anomalies which need to be discussed further for each hoard. Since one hoard was discovered in 2021 and the other over a century earlier in 1902, differences in conservation methods seem a likely cause of the irregularities, however, alternative explanations must also be considered.

After completion of this project the author discovered some irregularities in the factory calibration of the pXRF device for arsenic, which might further explain the unusually high overrepresentation of arsenic in some measurements. This issue apparently led to an exponential overestimation of all arsenic peak values, which was later confirmed by Niton, meaning that the original values might not be that unusual and will be excluded from further interpretation. For further information, see Notes in repository.

Schellhorn

Identifying the origin of iron content within the finds from Schellhorn is challenging. Original information on the finding and context of the hoard from 1902 is very sparse[33]. The condition of the artefacts was described as remarkable, and a very uniform brown bog patina was observed. When the objects were analysed for this case study it became immediately clear that this description no longer applied. Three objects are covered by an almost black patina, while three other objects are almost completely devoid of any patina, with the remaining artefacts being in between, with one seemingly having developed some greenish corrosion over the remaining dark patina. In his

29. Franke 2012.
30. Liversage 2000, p. 20–22.
31. Finkeldey 2025.
32. Melheim *et al.* 2018, p. 96–99; Bunnefeld 2016, p. 93–94; Nørgaard *et al.* 2025, p. 227.
33. Willroth 2017, p. 81.

work on the regional hoard inventories, Karl-Heinz Willroth[34] described the different conditions on the objects from Schellhorn as the remains of a removed bog patina. This coincides with the observations made with the digital microscope. The clean metal surfaces themselves look pitted in places but show very little corrosion products, such as mineralised copper. The surfaces also show some open casting deficits, which are usually closed or reworked on original surfaces. The edges of the typical engravings on spearhead SH1902-4.4, one of the still thickly patinated objects, seem unusually worn and rounded. The remains of the patina itself, however, looks rather thick and oily, and do not fit the original description. Especially under the microscope the surface structure looks more like organic material than the expected mineralised corrosion products. In combination with the initial results these observations indicated that the surface had either been tempered with or that these objects could be fakes or replicas. Some 19th century fakes/replicas had been identified recently within another hoard inventory from the museum's collection[35]. The latter, in combination with the observations and results from Schellhorn, lead to some suspicion concerning the authenticity of this hoard as well. However, since the qualitative bronze composition without the iron is typical for the period, this seemed unlikely. The head conservationist applied some acetone to clean a small spot on sickle SH1902-4.2 of any suspected coating. The spot turned its colour to a rusty red (**fig. 5**),



Figure 5: Button sickel Schellhorn SH1902-4.2 with remains of dark "bog patina" and rust-red stain (digital microscope, own images supported by B. Meller, N. Joachimsthaler, J. Harms)

34. Willroth 2017.
35. Freudenberg, Glaser 2015.

which aroused further suspicions that the surface might have been treated with an iron bearing chemical, as bronze should not react to the low acidity of acetone. In autumn 2024, the surface layers of some objects from Schellhorn were reanalysed using laser-breakthrough-spectroscopy (LIBS). Measurements from the spot treated with acetone showed that the acetone had washed off all other elements and left behind pure copper, meaning that whatever had composed the surface besides copper, was soluble to the acetone and separated completely from the copper.

To identify the actual cause of these phenomena several possibilities needed to be considered. One often overlooked, but in this case unlikely, possibility is the prehistoric treatment of metal surfaces. Besides practical metallurgical techniques, such as annealing, aesthetic or protective techniques, such as colouring, conservation and artificial patinating are present on prehistoric bronzes[36]. In ancient Egypt, black bronze was achieved through tempering, chemical treatments or organic colouring[37]. Some written accounts mention the use of ammonia, oil or pitch to preserve or stain bronze in classic antiquity[38]. This was apparently also done in the NBA, for example, on a belt box from the Tollense valley using pitch[39]. While it cannot be fully ruled out that some of the objects were initially coloured in some nonchemical way, they do not show any signs of colouration in their cleaned state.

In the case of the objects from Schellhorn, an attempted artificial patination might be the most likely explanation for their current condition. Willroth[40] states that the surfaces of all objects seem to have been cleaned; this could have been achieved using chemical means, as no concrete evidence of modern mechanical polishing were found. As the bronze surface might not have had the right colour after cleaning[41], the objects could have been given a more antique look by staining them with an iron-rich agent. Staining agents based on iron or iron nitrates are still used in bronze working and sculpting today. These are usually applied with heat to ensure a bind to the surface which could explain the observed reaction to acetone. Recipes for similar agents and artificial patina can be found in restoration and metalworking manuals of the time[42]. The brown-blackish "patina" substance found on some objects might be remains of this staining agent as objects with a thicker coating also appear to have a higher iron content. Further probing of the patina on 1902-4.2, as well as spearheads SH1902-4.4 and SH1902-4.10 using LIBS, confirmed that the surface layers were not composed of corrosion products (and therefore not an actual patina) but mostly an organic substance (C, H, K); probably a thick varnish, which on closer inspection also contained Sn, Fe, O, Cu and sometimes K and Na (**fig. 6**). This layer seems to prove the use of iron oxides with an organic binder which are bound to some of the corrosion products on the surface. Eventually, the actual bronze alloy was measured underneath this layer. Remains of the same coating was also seen on the socketed chisel SH1902-4.9 which has a much cleaner appearance with bronze shining through. Therefore, the unusually high contamination of the Schellhorn artefacts must indeed be anthropogenic.

36. Berger 2012b.
37. Aucouturier *et al.* 2010, p. 314.
38. Manti, Watkinson 2022, p. 159; Berger 2012a, p. 84–85.
39. Malchow 2019.
40. Willroth 2017.
41. Scott 2002, p. 353–355.
42. Rathgen 1905, p. 35; Buchner 1920, p. 166.

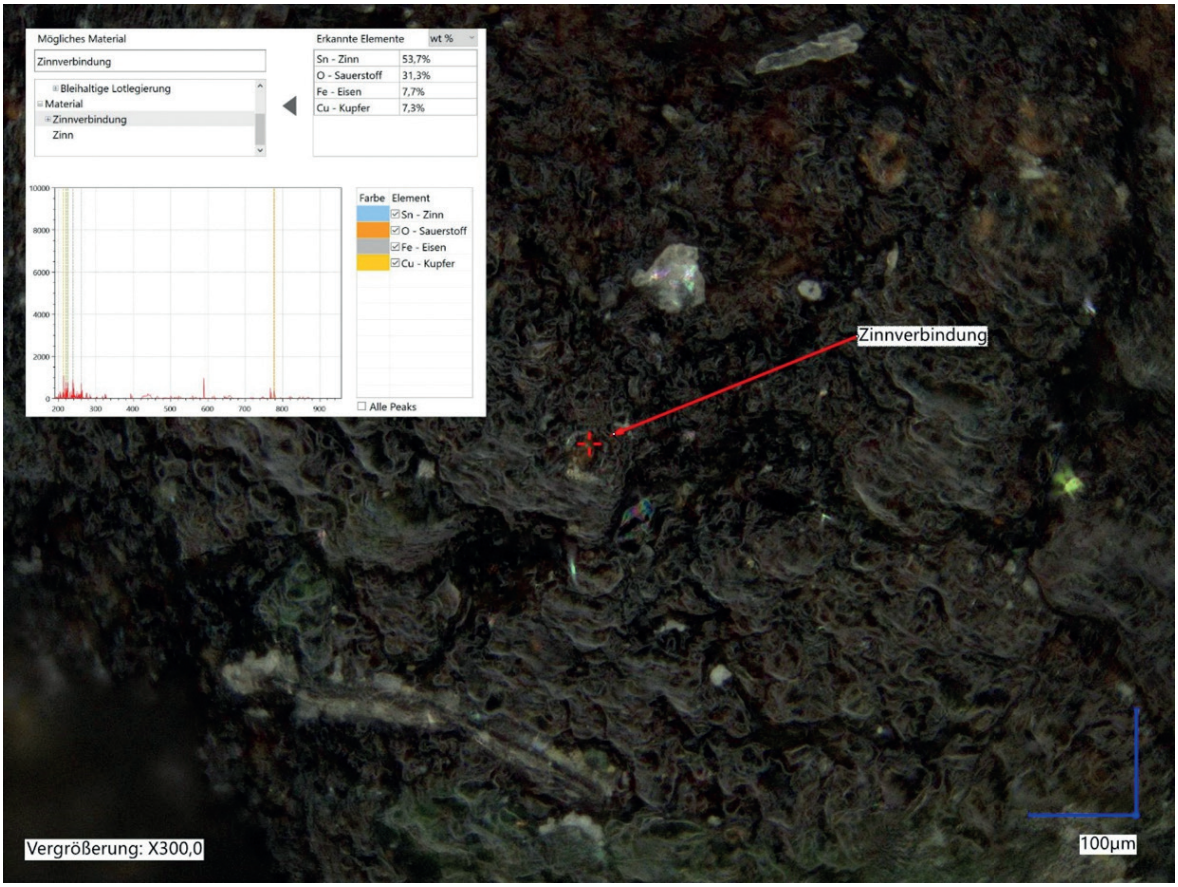


Figure 6: Measurement image of the microscale probing of the patina on SH1902-4.10 using LIBS, revealing a layer enriched with Sn and Fe oxides (Full Datasets in REPOSITORY)

Since it is partly organic with less iron near the surface, this artificial patina could also have been the result of several coatings. In sum, it must be presumed the treatment was meant to preserve the object while trying to emulate the original bog patina.

For the interpretation of the pXRF data this means that high iron content can largely be ignored. To slightly correct the data the Fe values were strongly reduced with the other elements adjusted accordingly. As the actual process and effect on the pXRF of the applied coating was not fully determined, the full extent of change from this method is unknown and cannot be modelled accurately. Since the relative wt% of copper is apparently reduced the most, the removed values of iron were added to the copper and not spread evenly. The latter would only exacerbate the overrepresentation of some elements from the persisting corrosion issue. The resulting compensated data is of limited use but is more comparable to the hoard of Fahrdorf than in its original state (**fig. 7**).

Fahrdorf

In the case of the high aluminium content within the artefacts from Fahrdorf the measured amounts did not correspond with higher concentrations on the corroded surfaces (low cu values) and was assumed to be likely of modern origin. A contamination with aluminium from prehistoric ores in these amounts would be very unlikely. A permeation of aluminium from the surrounding soils could be considered possible, however, the amounts measured would still be unlikely to be that high. The most probable explanation came from consulting head conservationist Corinna Mayer on the previous treatment of the objects. When she received the objects from Fahrdorf in 2021[43], they showed signs of bronze disease. To avoid this deteriorating effect, she used a chemical treatment to remove the corrosive copper chloride from the surface. For this, a solution containing agar-agar cells was applied on each object and wrapped with aluminium foil, and then stored in a warm and wet environment. Once the moisture starts the reaction, freed chlorides from the copper salts on the surface migrate through the solution as they are more reactive with the aluminium than with copper. The chlorides therefore bind with the aluminium and disintegrate the foil instead of the object. This reaction can be described in the following formula:

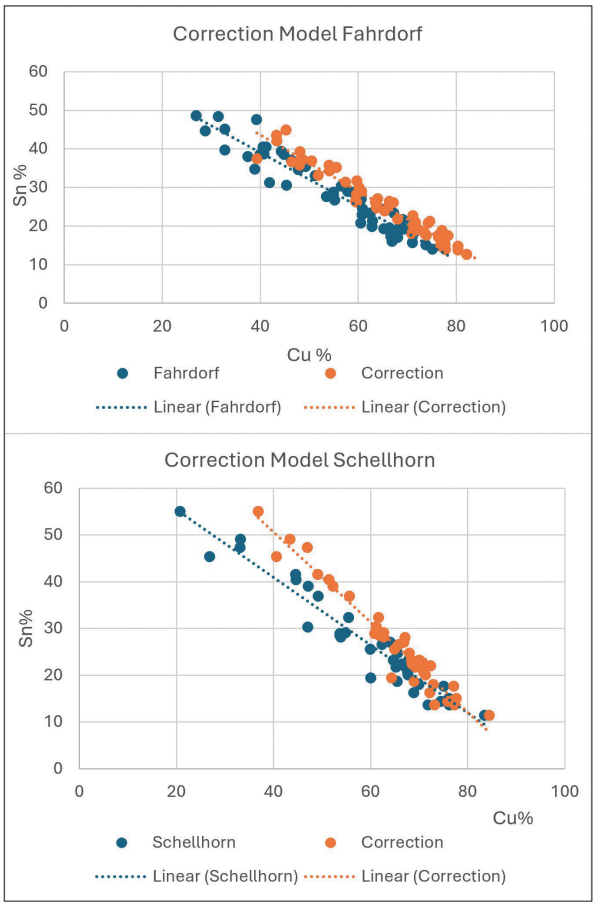


Figure 7: Cu/Sn trend of all measurements before and after correction for contamination from conservation in wt% (Full Datasets in REPOSITORY)

$$3CuCl(aq) + Al(s) \rightarrow 2AlCl3 + 3Cu\downarrow$$

This conservation method was thought not to interfere with the remaining surface since the soapy aluminium chloride is simply rinsed off with the agar solution. However, it seems very likely that some of the aluminium used in this reaction stuck to the bronze surface instead. Possibly some of the remaining elements on the desalted surface were also reactive with the aluminium chlorides. Most of the freed copper parts must also be assumed to have been washed off. This method seems to be a variation of the electrochemical Rosenberg method[44]. It is a standard procedure recommended

43. Klooss, Freudenberg, Fischer 2022.
44. Scott 2002, p. 367–368.

when BTA (benzotriazole) treatment is unlikely to stop active bronze disease, but it should only be applied to light cases of bronze disease as objects with high amounts of copper chlorides are severely damaged or even disintegrated through this active desalination.

When trying to factor out the chemical reaction in the measurement data, theoretically the process can be simplified. The reaction frees up to three parts copper for one part of aluminium used, the original amount of copper replaced by aluminium then can be assumed to be more than three times the amount of aluminium present. The reaction formula can therefore be reversed by increasing Cu values by up to three times the amount of Al subtracted from the data to create a simple calculation that removes the Al from the dataset. The remaining elements then need to be adjusted accordingly by subtracting two times the amount of Cu added. This resulted in a realistic correction set for the originally compiled data which might give a better idea of the original composition and provides us with a better means of comparing data from one hoard with those of other finds from the same region and period. However, when considering the results after such adjustments, the non-ideal conditions of surface analysis and the differences in penetration depth depending on the preservation of the analysed spot should still be taken into account.

Conclusion

Some bronze objects have been the subject of scientific interest since the 19th century although recent changes in their condition and appearance are rarely described or questioned. Friedrich Laux[45] lamented the loss of information on the surfaces of many bronze age objects due to the restoration methods of the past. To prevent this, it is paramount for archaeologists to work in close cooperation with conservators and curators, to document methods and insights more closely, and also to use technological advances like pXRF and supporting methods to reinvestigate and build biographies for older or contextless collection artefacts. The increasing availability of non-destructive devices, such as hand-held XRF analysers, offers the possibility for archaeologists to evaluate the composition of any copper-based artefact. This also allows the re-evaluation of older finds in museums and other collections without damaging them. Combining pXRF readings with previous interpretations can give new context and insights into these objects. Especially reactive materials like copper alloys are difficult to analyse non-invasively, as their surfaces, and in some cases also their core compositions, are changed by corrosion processes making it challenging to interpret data from non-destructive analysis only. For this reason, non-destructive pXRF analysis on copper and bronze objects as a standalone method has severe drawbacks when looking into the quantitative composition of artefacts[46]. Interpretation of pXRF readings can only be done by abiding to these limits and only with a good understanding of the analysed objects' condition and modern history. This includes the formation and effects of corrosion on bronze objects in different environments but also an understanding of possible later chemical changes during restauration. When using pXRF on bronze objects, unknown factors like undocumented treatments of the surface need to be addressed. This case study shows two

45. Laux 2017, p. 11–13.
46. Pearce 2018, p. 84; Nørgaard 2017, p. 120.

cases in which these changes were recognisable in singular elements as distortions within the data and were identifiable with the help of digital microscopy and LIBS. The data was thus slightly corrected to exclude the distortion caused by anthropogenic conservation methods for further comparison. The distortion in readings on suboptimal surfaces caused mainly by corrosion processes however remain. The corrected data on the better-preserved surfaces improved the comparability as it has come closer to the expected composition. For this result, it was crucial not only to work with individual finds, but to look at a collection of artefacts from two closed finds and comparable contexts. Both groups showed patterns in their data that are unique to their respective degradation process. It was possible to identify consistent minor elements that can be attributed to impurities of their original alloy. These elements were similarly present in both hoards and thus prove a close relationship between the artefacts from both sites. The potential of non-invasive pXRF measurements in combination with other analytical methods and historical research for the re-examination of bronze artefacts from museum collections has thus been demonstrated.

Acknowledgements

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Statement on the use of artificial intelligence

During the preparation of this work the author used the free version of DeepL.com AI aided translator to improve readability of certain paragraphs. After using this tool/service, the author reviewed and edited the content as needed and takes full responsibility for the content of the publication.

Data availability statement

The supplementary material for this chapter is available in Finkeldey 2025, "Distortion through conservation" at DOI: 10.25592/uhhfdm.17581 or URL: https://www.fdr.uni-hamburg.de/record/17581.

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Abbreviations

ANN: artificial neural network
CARE: Collective Benefit, Authority to Control, Responsibility, Ethics
CNN: Convolutional Neural Network
CPU: Central Processing Unit
CUN: Ceramic Users Network
FAIR: Findable, Accessible, Interoperable, Reusable
FP: Fundamental Parameters
GPU: Graphics Processing Unit
HH: Hand-Held
ICP-MS: Inductively Coupled Plasma Mass Spectrometry
ICP-OES: Inductively Coupled Plasma Optical Emission Spectroscopy
IRN: International Research Network
LIBS: Laser Induced Breakthrough Spectroscopy
LLQ: Lower Limit of Quantification
LOD: Limit of Detection
LOQ: Limit of Quantification
MAE: Mean Absolute Error
ML: Machine Learning
NAA: Neutron Atomic Activation
NBA: Nordic Bronze Age
PCA: Principal Component Analysis
ppm: parts per million
pXRF: portable X-Ray Fluorescence
RMSE: Root Mean Square Error
SDD: Silicon Drift Detector
SRM: Standard Reference Material
WDXRF: Wave Dispersive X-Ray Fluorescence

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Methodological innovations in pXRF studies brings together 12 contributions exploring the challenges and methodological innovations related to the use of portable X-ray fluorescence (pXRF) as applied to archaeology, geology, and heritage science. This volume focuses first on the protocols, calibration strategies, and data processing essential to the quality of the end results. The authors define guidelines for good practice in the field and the monitoring of instrument performance. They emphasise the importance of the implementation of comparative studies (inter-laboratory and inter-device) and the integration of machine learning for the statistical processing of data. The second part illustrates the application of pXRF in restricted conditions (museology, restoration and numismatics). These studies highlight the standardisation of procedures for heterogeneous materials and the limits of non-destructive analysis. This volume prioritises data quality, transparency, and reproducibility. It thus constitutes a common reference for the harmonisation of practices within the community.

Methodological innovations in pXRF studies rassemble 12 contributions explorant les défis et les innovations méthodologiques liés à l'utilisation de la fluorescence X portable (pXRF) appliquée à l'archéologie, à la géologie et aux sciences du patrimoine. L'ouvrage se concentre d'abord sur les protocoles, les stratégies de calibration et le traitement des données essentiels à la qualité des résultats. Les auteurs y définissent des cadres de bonnes pratiques pour le terrain et le suivi des performances instrumentales. Ils soulignent l'importance d'études comparatives (inter-laboratoires et inter-appareils) et l'intégration du *machine learning* pour le traitement statistique des données. La seconde partie illustre l'application de la pXRF en conditions contraintes (muséologie, restauration, numismatique). Ces travaux mettent en lumière la standardisation des procédures pour les matériaux hétérogènes et les limites de l'analyse non destructive. Cet ouvrage met l'accent sur la qualité des données, la transparence et la reproductibilité. Il s'impose comme une référence pour standardiser les pratiques au sein de la communauté scientifique.

يضم هذا المؤلف ١٢ مساهمة علمية تستكشف التحديات والابتكارات المنهجية المتعلقة باستخدام أجهزة القياس بفلورية الأشعة السينية المحمولة (pXRF) المطبقة في مجالات علم الآثار، والجيولوجيا، وعلوم التراث. يركز الكتاب في المقام الأول على البروتوكولات، واستراتيجيات المعايرة، ومعالجة البيانات الضرورية لضمان جودة النتائج. كما يحدد المؤلفون أطرًا لأفضل الممارسات الميدانية، ومراقبة أداء الأجهزة. ويشدد الباحثون على أهمية الشفافية في التبادلات العلمية لتسهيل إجراء الدراسات المقارنة بين المختبرات والأجهزة المختلفة وإدماج تعلم الآلة فيها، بما يفتح آفاقًا جديدة في المعالجة الإحصائية للبيانات. ويستعرض الجزء الثاني، من خلال دراسات حالة في مجالات المتاحف، والترميم، وعلم المسكوكات، تطبيقات استخدام pXRF في ظل الظروف المُقيدة. تسلط هذه الأعمال الضوء على توحيد الإجراءات الخاصة بالمواد غير المتجانسة، وحدود التحليل غير المُدمِّر. ومن خلال وضع جودة البيانات والشفافية وقابلية التكرار في قلب منهجه، ينخرط هذا المؤلف تمامًا في مبادرة العلوم المتاحة. وبذلك، فإنه يشكل مرجعًا مشتركًا للابتكار المنهجي وتنسيق الممارسات داخل المجتمع العلمي.

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