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# The Technological versus Methodological Revolution of Portable XRF in Archaeology

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## Review

## The technological versus methodological revolution of portable XRF in archaeology

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## ABSTRACT

Portable X-ray fluorescence (pXRF) instruments have gained considerable attention within the archaeological community. Few other recent instrumental developments have generated such debate. Much of this debate, which is dominated by scepticism over analytical performance, has occurred in informal settings. Rather than judge the use of pXRF based on unpublished work and conference banter, we conducted an extensive literature review of peer-reviewed research that used this technology. Our focus is developing an understanding of how, where, and why pXRF is being used in archaeology. What interests us most are research designs into which only pXRF could be integrated and the new research approaches these instruments may facilitate. Trends that emerged from the literature are surprising. For example, only 43% of the archaeological “pXRF” papers actually involve handheld instruments. In addition, more than four-fifths of handheld pXRF in archaeology is apparently conducted in laboratory contexts. Only 3% has been conducted in a fieldhouse or on-site laboratory, and 15% at an excavation, on a survey, or inside a historic structure. Here we argue that, while the technical capability to analyse archaeological materials using portable instruments may exist, it is not necessarily true the methodological and theoretical frameworks are in place to allow such activities to be archaeologically successful and significant. Because handheld pXRF is uniquely suited to *in situ* analysis, we expect the first changes in methodological and theoretical approaches will involve space, context, and related frameworks.

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## 1. Introduction

Portable X-ray fluorescence (pXRF) instruments and their applications have gained considerable attention within the archaeological community in recent years. Few other instrumental developments have generated such fevered debate for decades, it seems. To date, much of the debate has occurred in informal settings, including workshops, conferences, and the gatherings at bars afterwards, such as that cited by accomplished XRF analyst M. Steven Shackley in a high-profile editorial. The editorial starts with an anecdote about one such “bar” discussion during a Society for American Archaeology (SAA) conference that created “animosity[,] heated opinion[,] and an amity-enmity atmosphere” (2010:17). Shackley argues pXRF causes such a reaction because archaeology is

“not necessarily prepared for it intellectually” (17). We hold that, while the technical revolution to analyse archaeological materials in the field has occurred, there is yet to be a revolution in our methodological and theoretical frameworks. It is evident, even now, pXRF is making XRF technology available to more archaeologists than ever. Our community, however, has yet to see the widespread development of new questions or methods. Most archaeological pXRF research, we show here, works within the paradigm of conventional lab-based techniques and thus follows established perspectives on question, method, and ultimately theory.

Scepticism over analytical performance has so far dominated the debate. Shackley (2010) claims that what “marks nearly all [recent pXRF-centric articles] is that the decades of protocol developed for laboratory XRF analysis is completely ignored” (18). The effect, as put by Grave et al. (2012), is that the “wider archaeological applications of pXRF continue to be cautiously treated, principally because of a perceived lack of analytic rigour or understanding” (1674). A view that use of pXRF constitutes invalid observations is at odds with the nature of much archaeological research. Consider geophysical surveys, for example. Ground-

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penetrating radar (GPR) can provide archaeologically useful information in some settings but not others, and its data are not directly comparable to data from magnetic surveys in settings where both work favourably. Technique combines with research context, rather than sits in isolation, to create validity.

We suspect much of the concern is based on a fear of hitherto restricted technology being released to a wider community that has not always acknowledged (or understood) the efforts and experience of the archaeometric community. Crowds at vendors' conference booths and discussion among archaeologists eager to discover new possibilities should not be mistaken for either the broad or unbridled deployment of pXRF in the field. If we consider conference papers as a metric for research, there is less pXRF use than one may expect. At the 2011 SAA conference, there were fewer than two dozen talks and posters on the use of pXRF among 2000 presentations in 270 sessions. In a comparison of timely "hot topics," the Clovis symposium attracted 26 talks, whereas the pXRF session attracted eleven.

We concur with Shackley (2010) that there is "potential misuse" of this technology (18). A particularly discrepant use of pXRF was presented at the aforementioned conference. Rather than bringing a pXRF instrument to analyse soils at two potential sites in New Mexico, Boggess et al. (2011) collected leaves, sent them to a laboratory in another state, dried and reduced them to ashes, and measured Sr, Rb, S, K, and Ca through plastic sample bags. These procedures were also followed at Cahokia in Illinois (Lundin et al., 2011). Even if one accepts that leaves contain identifiable elemental traces of human effects on the soils and that XRF is the best technique to measure such signals, there was no reason given to use pXRF in place of tried and tested lab-based instruments (or to analyse specimens through sample bags, which negatively affects the measurements). It superficially seems a case of using pXRF as direct substitution for laboratory instruments. This is troublesome because authors of these talks have also organised a half dozen pXRF workshops and symposia. If pXRF affects the practice of our discipline, it should be for reasons other than (perceived) ease of use.

However, rather than judge use of pXRF based on unpublished work or conference banter, we conducted an extensive literature review of peer-reviewed research that used this technology. In doing so, we did not focus on instrument performance. Prior reviews do so sufficiently (e.g., Shackley, 2010, 2011; Liritzis and Zacharias, 2011; Goodale et al., 2012). In addition, issues such as the effects of specimen surface morphology and size on XRF data have recently been explored experimentally (Forster et al., 2011; Davis et al., 2011; respectively). Our focus is different. In a chapter on obsidian studies, Tristan Carter notes, in writing such a review, "one has to be wary of merely revelling in the details of the archaeometric techniques at the expense of considering the anthropological significance" (in prep). The same is true regarding pXRF. Our focus here is developing an understanding of how, where, and why pXRF is being used in archaeology and how we might orient future studies. Trends that emerged from the literature are surprising. As with any successful technological development, the contexts of innovation and adoption are as important as technical issues. We see the uptake of pXRF as critically dependent on *method*. The technical capability to analyse archaeological materials using portable instruments may exist; however, it is not necessarily true that methodological and theoretical frameworks are in place to allow such activities to be successful and archaeologically significant. We anticipate – and perhaps see hints of – a revolution roughly analogous to a Kuhnian "paradigm shift," whereby archaeologists are developing new approaches the community previously would not have considered valid.

## 2. Instrumental typology: labXRF, pXRF, and HHpXRF

The ready adoption of pXRF by archaeologists could have been anticipated in light of the successful use of XRF in archaeology for decades. Laboratory-based XRF ("labXRF") has been a staple of archaeological science since the 1960s (e.g., Hall, 1960; Olsen, 1962; Hall et al., 1964; Yao and Stross, 1965; Jack and Heizer, 1968). Portable versions of XRF instruments date to the same time (Bowie et al., 1965; Bowie, 1968), and the initial archaeological applications included prospecting for copper smelting sites in Oman (Hauptmann, 1985) and other archaeometallurgical fieldwork in Jordan and Turkey (Helmig et al., 1989). "New" discussions about, for example, the effects of metal artefacts' corroded surfaces on pXRF results have antecedents in the archaeometric XRF literature that date back more than fifty years (e.g., Roberts, 1960).

There is no more "the" pXRF analyser than "the" visible-light microscope. Just as different microscopes differ in performance characteristics, so do pXRF instruments. In fact, the term "pXRF" has varied definitions, ranging from "being able to be carried by porters" (Jones, 2008) to "handheld" (Phillips and Speakman, 2009). An appreciable number of these instruments have used radioactive isotopes rather than miniaturised X-ray tubes, making them difficult to transport across borders, so the extent of their "portable" status is debatable.

Hence the label "pXRF" has been used to describe to a wide variety of instruments. At one end of the scale, some "pXRF" instruments are small benchtop systems, portable only in the sense they can be loaded into a vehicle and driven to a museum or fieldhouse with compatible electricity. While technically "transportable," we do not include such systems in our discussion.

Next are small, commercial "deconstructed" benchtop systems capable of use in a museum or fieldhouse. These instruments are primarily intended for museum use to assist in identifying materials for conservation, authentication, and art historical studies, as evidenced by trade names such as ArtAX. Here we refer to this as "museum-type" pXRF.

There are also the set-ups of XRF components that may be transported and reassembled in a museum or fieldhouse, but such systems also require electricity and are not conducive to being carried into the field. These instruments are commonly developed by research centres, and they are sometimes referred to as "homemade" (Appoloni et al., 2009; Roldán et al., 2010) or "in-house developed" (Karydas, 2007; Provatas et al., 2011) systems. To build them, X-ray sources, detectors, and other components are purchased from companies, such as the Experimenter's Kit from Amptek. We refer to this as "components-type" pXRF.

Last are the handheld instruments, which are the current focus of archaeological interest. These instruments are truly field portable and are easily brought to excavations or geological resources/outcrops. Commonly "field-portable XRF" and "handheld pXRF" are used in the literature as a way to distinguish these types of analysers. Here we use "HHpXRF" to avoid confusion with other acronyms.

HHpXRF analysers are approximately the size, shape, and weight of a cordless drill and have a similar trigger. This physical similarity highlights a trade-off for portability. HHpXRF instruments have not simply been reduced in size to make them portable. Weight and power consumption are also concerns for field use. The simplest analogy is that of desktop and laptop computers: to gain portability, one sacrifices performance. The main sacrifice of HHpXRF is a less-than-ideal arrangement of miniaturised, low-power components.

## 3. Fundamental parameters: from lab to field

HHpXRF instruments, which can provide potentially useful quantitative data in the field, are commonly described as "point and

shoot” analysers (sometimes with positive connotations, other times negative). The apparent ease with which accurate data may be acquired is what we feel has caused much concern among established archaeological scientists. It seems to suggest method development is no longer an implicit part of materials analysis.

What enables manufacturers (and some archaeologists) to claim “point and shoot” ability is the use of fundamental parameters (FP) calibration. FP calibration is as key a development in HHPXRF as hardware miniaturisation. This approach is not new and has been used routinely in select XRF applications for two decades. The development of powerful processors, though, has broadened the appeal of FP calibration to include HHPXRF manufacturers.

The relationship between the intensity of the characteristic X-ray emission of an element and its concentration within a material is not simple. Various effects, including the excitation of lighter elements by X-rays emitted from heavier elements, occur within a material, changing the measured intensities. To account for them, conventionally analysts have used a series of coefficients to “correct” their X-ray measurements. In practice this means use of calibration standards “matrix matched” to the materials for analysis. This necessitates (1) *a priori* knowledge of the unknown materials’ approximate compositions and (2) judgement regarding the compositional range over which the standards are suitable. Therefore, an analyst’s knowledge and experience are critical, in part, for recognising when data may be compromised by inappropriate calibrations.

In contrast, the FP approach to calibration does not rely on the conventional coefficients to mitigate these matrix effects. Instead this approach relies on the mathematical description of instrumental conditions (e.g., tube emissions, detector efficiency) and instrument-independent parameters for each element (e.g., fluorescence intensities, absorption coefficients, absorption edges). These parameters are brought together in an algorithm that solves a range of nonlinear equations describing the relationship between emission intensities and elemental concentrations. In effect, correction coefficients are being uniquely calculated for each unknown at the time of analysis itself. This is a significant advantage for many applications and eliminates an analyst’s subjectivity regarding appropriate calibration standards.

The attraction of FP calibrations to manufacturers is clear. Instruments calibrated in such ways can be used effectively in a wide variety of tasks where only the general material type must be known. For instance, HHPXRF instruments commonly offer various metals, soil, and plastics modes. The idea is that, once a mode is selected, FP calibration is sufficiently robust to generate accurate data over a range of compositions. While not our subject here, we have been impressed by the performance of commercially available FP calibrations. However, to argue FP calibration facilitates the archaeological applications of HHPXRF is to miss our point.

Non-expert use of HHPXRF in various commercial applications is now well attested. For instance, workers routinely use these instruments in scrap-metal sorting to good effect. Effective use in such a context is very different than how the instruments may be used in archaeology. Scrap metals show variations between known compositional levels, conform to known types (e.g., steel grades), and are derived from known processes. In archaeological science, however, one is characterising materials that are often truly unknown and/or derived through processes yet to be established (with perhaps the exception of applications such as geochemical surveying or obsidian sourcing).

When used sensibly and evaluated carefully, FP calibrations likely do expand the range of individuals who can make compositional determinations. This, however, is not to undermine the role of the expert analyst, and we strongly contend that experts should not show distain for these instruments because they appear to

undermine their own accrued expertise. On the contrary, the proliferation of HHPXRF instruments should, and most likely will, raise the demand for expert knowledge to ensure their effective deployment in archaeology. It might not be the expert who actually pulls the trigger, but it will almost certainly be the expert who decides when the trigger is pulled and, more importantly, at what the instrument is aimed.

#### 4. A second XRF transformation

We view HHPXRF as something of a *second* transformation in the history of XRF. The first was online workstations that gave immediate feedback to an analyst, rather than having to wait for a mainframe session to convert measured peak intensities into elemental concentrations. Nelson (1975) reports that data collection and processing were not simultaneous at the time: “the spectrum of an artefact can be taken in 5 minutes. The raw data are then transferred to a large computer... The total identification time is perhaps 30 minutes” (95). This data transfer involved carrying punch cards from one computer to another.

Online workstations add immediate feedback from specimens to the analytical process, and that feedback allows instantaneous monitoring and alteration of the initial scheme an analyst has in mind. An analyst can consider results in light of what was expected, assess new possibilities, and adjust analytical procedures. Measurement is no longer a passive process in which one has to acquire raw X-ray counts, hope for the best, and find out in the computer centre whether the analyses are good. Still, one remains limited to the previously selected specimens for analysis.

Feedback from HHPXRF, in contrast, enables one to adjust a sampling strategy during a survey, excavation, or other fieldwork. Given the relevance of sampling in archaeology, from the artefact to regional level, there is great potential regarding this aspect of HHPXRF. Sampling strategies could be determined less by the logistics of shipping and more by the intellectual framework within which a study is conceived. For instance, how communities have used the internal space of structures has gained significance in many archaeological communities over the last two decades (e.g., Fitzpatrick, 1991; Richards and Parker Pearson, 1994; Oswald, 1997). Such questions lend themselves to high-resolution soil chemistry surveys across multiple contexts, yet few studies have used this strategy because of the time required for such sampling and the resulting analytical burden. Further, results may take years to produce, requiring an unusual commitment to such studies for a field director to pursue them with laboratory-based techniques. Thus the ability of HHPXRF to generate data *in situ* and instantaneously means that field directors can evaluate results and adapt their excavation and sampling strategies within the normal cycle of an excavation season rather than waiting for laboratory results between seasons. The reduced feedback cycle means directors need commit less to speculative modes of enquiry and therefore should be more likely to pursue approaches to characterise space at high resolution.

Often export restrictions and/or sampling permits introduce bias so that artefacts meant to represent an assemblage are not actually representative. For certain applications, it may no longer be necessary to collect samples from an excavation, send them to a laboratory, and wait for results until months or years after they could have informed the excavation strategy. Another advantage is avoiding collecting more material from a site than one could responsibly handle (and wasting limited resources to do so). We also argue that, in cases where the HHPXRF instrument is used by the same individual who would have done labXRF, there are also great advantages to having that expert in the field to inform the excavation strategy and to aid in the expert’s own interpretations of

the results. In this light, HHPXRF should be seen as a facilitating technology, eliminating the physical barriers that have often segregated archaeological and scientific practice into the field and laboratory.

One may argue, though, random sampling, if done properly, would yield the same results in the lab or field. Why then would it matter if HHPXRF or labXRF is used? Consider an example given by Orton (2000): “formal [sampling] methods are to some extent a rational response to a state of ignorance, and the more we know about a situation, the less necessary they may be... to ignore evidence from aerial photographs or geophysical surveys in designing a purely random sample of (for example) test-pits would be wasteful and unproductive, and a more targeted approach would be likely to give more useful results” (2). This extends to chemical analyses in the field. The more we know about artefacts, sediments, or other materials while they are available and relevant, the better informed our sampling strategy can be. Knowledge about artefacts months later cannot inform their sampling in the field.

We fully concur that HHPXRF is not an answer for all questions; however, we also believe it can be used as a standalone for certain types of questions. There are clearly research designs in which one could substitute “labXRF” for “HHPXRF” or vice versa, and the only difference would involve the instruments’ technical specifications. These are not necessarily invalid uses of HHPXRF, but they do, though, operate within the paradigm of labXRF. What interests us most are those research designs into which only HHPXRF could be integrated [that is, what Kuhn (1970) would consider “subversive” to the established paradigm] and the new research approaches these instruments may facilitate.

## 5. The present: literature survey

To develop an understanding of how, where, and why pXRF is being used in archaeology, we surveyed 200 English-language peer-reviewed papers, principally from archaeology but also related fields such as art history, museum curation, environmental testing, and the earth sciences. This focus on English-language publications introduces only a minor bias. Montgomery (2004) estimates that 80–90% (or more) of papers in scientific journals are written in English, an increase from 60% during the 1980s. Our survey also includes numerous international journals (Table 1), so we are confident the publications adequately represent the geographic distribution of pXRF users. Additionally, our sample includes cases in which research initially published in, for example, Spanish was later published in English (e.g., Ikeoka et al., 2010, 2012). Ultimately, the observed trends, we contend, are sufficiently strong to consider as accurate despite any margin of error due to imperfect sampling.

In each publication, “portable” XRF was identified as a technique in the study. Hence the papers included the full range of instrument variations discussed above. We removed benchtop systems from consideration and divided the remaining studies between HHPXRF and other pXRF types, that is, museum- and components-type systems. When appropriate, we compared the studies to 60 recent English-language archaeological papers from the same journals that used labXRF.

**Question #1 (Fig. 1):** What are the proportions of the various types of “portable XRF” in archaeological research?

Fewer than half (43%) of the archaeology papers actually involved HHPXRF instruments. Contrary to impressions that vast numbers of archaeologists are running around with HHPXRF instruments, nearly 60% of papers relate to the less mobile pXRF systems restricted to museums, laboratories, and fieldhouses. A small portion (4%) actually used small benchtop systems, and several studies (3%) offer no information about the instrument.

**Table 1**

List of journals included in our literature review.

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Annali di Chimica
Antiquity
Applied Clay Science
Applied Geochemistry
Applied Physics A: Materials Science and Processing
Applied Radiation and Isotopes
APT Bulletin: The Journal of Preservation Technology
Archaeological and Anthropological Sciences
Archaeological Prospection
Archaeology in Oceania
Archaeometry
Bulletin of the American Schools of Oriental Research
Bunseki Kagaku
Construction and Building Materials
Environmental Geochemistry and Health
Environmental Monitoring and Assessment
Environmental Science & Technology
Field Analytical Chemistry and Technology
Geoarchaeology
Geoderma: A Global Journal of Soil Science
Geomorphology
Geoscience in Southwest England
Geostandards and Geoanalytical Research
Hesperia
Journal of Agricultural, Biological, and Environmental Statistics
Journal of Analytical Atomic Spectrometry
Journal of Anthropological Archaeology
Journal of Archaeological Science
Journal of Cultural Heritage
Journal of Environmental Monitoring
Journal of Geochemical Exploration
Journal of Hazardous Materials
Journal of Non-Crystalline Solids
Journal of Radioanalytical and Nuclear Chemistry
Journal of Raman Spectroscopy
Journal of South American Earth Sciences
Materials Characterization
Microchemical Journal
Microscopy and Microanalysis
Near Eastern archaeology
North American archaeologist
Northeast Historical Archaeology
Nuclear Instruments and Methods in Physics Research A
Nuclear Instruments and Methods in Physics Research B
Oxford Journal of Archaeology
Pramana: Journal of Physics
Proceedings of the National Academy of Sciences
Quaternary Geochronology
Quaternary International
Science of the Total Environment
Significance
Society For Archaeological Sciences Bulletin
Soil Science
Soil Use and Management
Spectrochimica Acta part B
Studies in Conservation
X-ray Spectrometry

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**Question #2 (Fig. 2):** How does the proportion of HHPXRF versus other pXRF types in archaeology compare to related fields?

About three-quarters of pXRF in environmental testing (79%) and the earth sciences (73%) papers involve HHPXRF. On one level, this is logical. Both fields are highly fieldwork-based and involve large-scale surveys, so museum- and component-type pXRF systems are of limited utility. On the other hand, these are fields with well defined analytical procedures and often strict protocols. Certain environmental analyses even come under legislation. The use of XRF in economic geology operates under similar restrictions. It is telling that these fields appear to have readily embraced HHPXRF, deeming it acceptable for various applications. Archaeology seems comparably more hesitant. Cost and speed are other likely factors in this acceptance of HHPXRF, especially in fields such

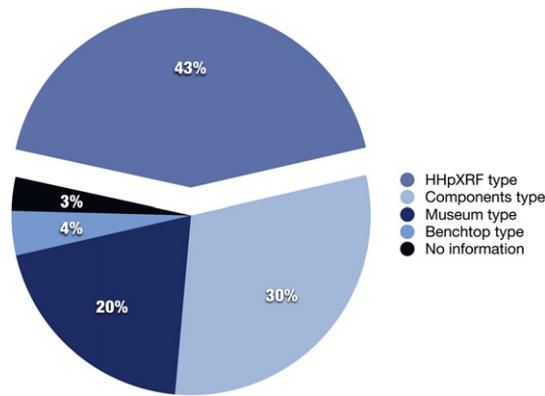


Fig. 1. Proportions of the various types of “portable XRF” in published archaeological studies.

as mining exploration. Widespread adoption of HHpXRF may have to do with keeping cost low and time expenditures short in commercial applications. The clear implication for archaeology is that we should expect to see greater use of HHpXRF in contract archaeology rather than in academia. Consider, for instance, the sponsorship of recent HHpXRF workshops by private resource-management consulting firms.

Only one third of art historians (32%) and one quarter of curators (27%) use HHpXRF instruments. Their studies are largely limited to collections in museums, churches, and similar locations and thus do not require field-portable systems. Often they are analysing *objets d'art* in a museum's conservation laboratory or even while on display.

Question #3 (Fig. 3): What reasons are explicitly given in the publications for using HHpXRF in archaeology?

The most frequently cited reason for using HHpXRF (a mere 21%) was that the analyses needed to be done on-site at museums, churches, cemeteries, memorials, and similar locations. This does not include excavations. For some locations, including museums and churches, there is no apparent incompatibility with museum- and component-type pXRF. For other locations, including cemeteries and memorials, HHpXRF seems most practical.

A close second (20%) is technique development. That is, authors were largely focused on evaluating instrument performance and/or compatibility with other techniques. Sometimes this involved archaeological artefacts, other times experimental materials. Their approaches varied greatly. Often two or more datasets are simply

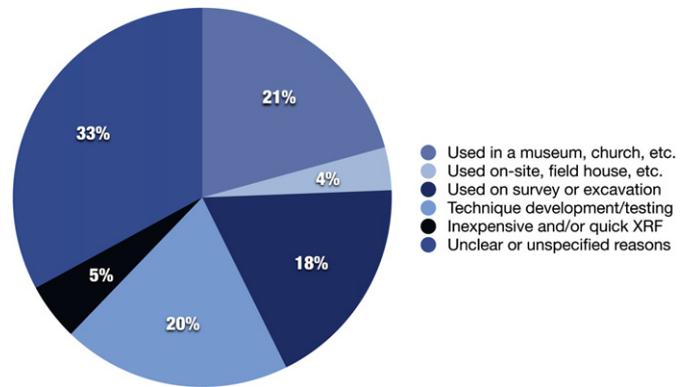


Fig. 3. Reasons explicitly given in publications for using HHpXRF in archaeology.

put side by side to compare accuracy, and a table of replicate measurements is occasionally used to address precision.

The third most cited reason (18%) is that the HHpXRF instrument was used on a survey or excavation. Among the best examples of this application is that of Davis et al. (2012), who used HHpXRF to create a chemostratigraphical framework at an archaeological site in Idaho. Davis and colleagues used the analyses, conducted directly on excavated wall profiles, to link artefact-associated sediments to a lithostratigraphic sequence and to identify disturbances. Their work is an example of how HHpXRF can be uniquely applied to questions involving artefact context and spatial relationships. In this instance, the stratigraphic assignment of a particular artefact is transformed from a potentially subjective observation to a rigorous and powerful quantitative measurement.

Use of HHpXRF in a fieldhouse or on-site laboratory was the least frequently cited reason (4%). We imagined HHpXRF may become widely used as part of artefact processing in a field laboratory as a way to document large numbers of recovered objects. One could query the database for trends that would otherwise be invisible and that require additional investigation. We expect this could become routine in the future, but this is clearly not the case at present.

Another infrequently given reason (5%) is use of HHpXRF as an inexpensive and/or quick replacement for labXRF. While cost and time affect the choice of any analytical technique, they are not the primary factors that should determine which technique is used to address a specific problem. Nevertheless, archaeology does not operate outside financial realities, so time as well as expense are necessarily considerations in any research design. Additionally, as noted earlier, such pressures have likely aided the widespread adoption of HHpXRF in environmental testing and economic geology. Thus the use of HHpXRF as a “quick and cheap” analytical technique is not necessarily invalid, perhaps even in a large portion of the research. Such studies, however, follow the labXRF paradigm and, accordingly, take on its perspectives on method, theory, and research goals. We contend that novel applications of HHpXRF will be what can lead to methodological – and thus theoretical – changes within our discipline (that is, a new paradigm), so those applications interest us most. Furthermore, we note that, regarding XRF in archaeology, the discussion of balancing time and cost with data of adequate quality is nothing new (e.g., Olsen, 1962) and exists as part of the established paradigm.

The largest portion of the chart (33%) reveals that one third of the papers gave no reason for HHpXRF. In several cases, researchers also employed laboratory-based destructive analyses, so labXRF easily could have been used instead. We suspect that most of these studies are also cases of selecting HHpXRF as an inexpensive and/or

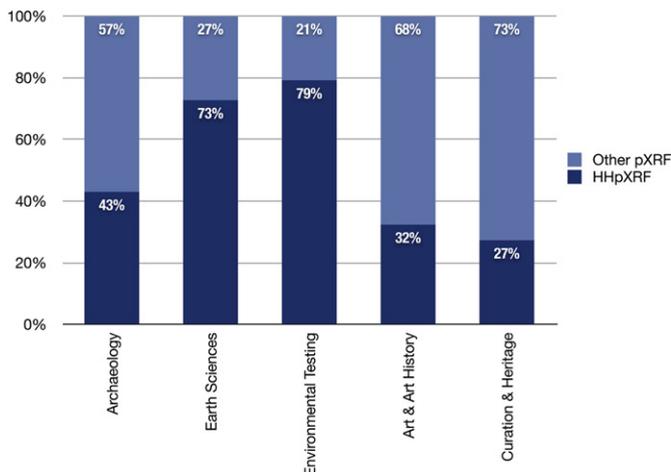


Fig. 2. Proportions of HHpXRF versus other pXRF types in archaeology and related fields.

quick alternative to labXRF, making this the most frequent reason archaeological studies use HHPXRF.

**Question #4 (Fig. 4):** Where are HHPXRF and pXRF instruments being used in archaeology?

The trends here are marked. The majority (43%) of HHPXRF in archaeological studies is conducted in laboratories, usually great distances from the sites, using it as a benchtop instrument. This gives a truer measure of how frequently HHPXRF is being used as an inexpensive and/or quick replacement for labXRF. The next most frequent setting is museums or other archive facilities, accounting for a fifth (20%) of the studies. Thus, nearly two-thirds (63%) of HHPXRF takes place in essentially laboratory settings. Presumably a large fraction of this work occurs under the auspices of trained analysts and competent archaeological scientists. Another fifth (19%) of the papers do not state (or even vaguely hint) where HHPXRF was used, but we suspect laboratory use in most cases. Altogether, more than four-fifths (82%) of HHPXRF may be conducted in laboratory settings far from archaeological sites. Consequently, a mere 18% of HHPXRF is conducted in a fieldhouse or on-site laboratory (3%) or at an excavation, on a survey, or inside a historic structure (15%).

If one has concerns archaeologists are running rampant with HHPXRF, this result should temper that belief. Only 43% of pXRF studies use HHPXRF, and of these, only 18% of studies involve taking the instrument into the field. Clearly it is not true in most cases that the first thing a HHPXRF-equipped archaeologist does is run in the field and zap anything at hand. The vast majority of such instruments never leave a museum or university laboratory. If most archaeologists are using HHPXRF as a lab-based technique, it follows their research operates within the labXRF paradigm. Those who are using HHPXRF with novel approaches (that is, the Kuhnian “anomalies” that operate outside of laboratory environments) are developing a new paradigm that, in turn, will lead to new methods, theories, and goals.

Despite our avoidance of performance issues, it must be noted there are attestations in the literature that HHPXRF data acquired in the field are less reliable compared to data acquired by an analyser used in benchtop mode. Consider the statement from Goodale et al. (2012) that the analyser “was placed in a test stand [rather than held in hand] in order to ensure the instrument was physically stable which in previous experience of the authors was found to be important for obtaining reliable results” (879). This suggests Mauss’

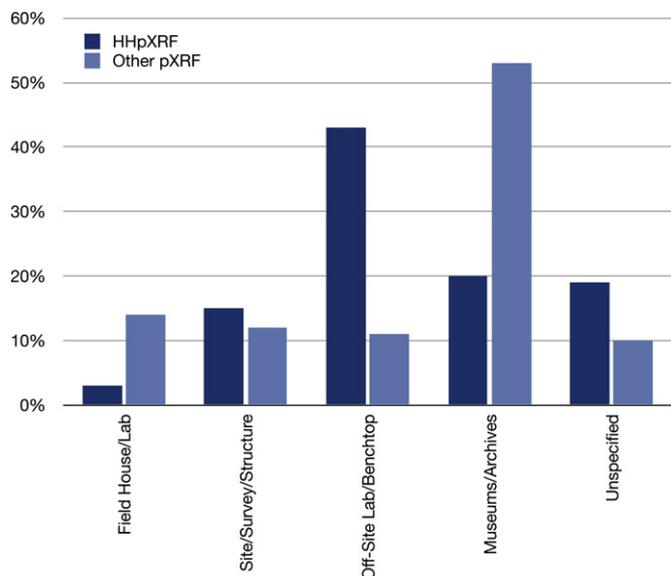


Fig. 4. Locations where HHPXRF and pXRF instruments are being used in archaeology.

(1934) “body techniques” and Lemonnier’s (1992) “gestures” become important for an analytical technique involving (potentially) handheld instruments. This issue is one that may be mitigated through method; however, it reinforces the importance of our questions: where are archaeologists using HHPXRF and why? The causality is not yet clear. Are more than four-fifths of archaeologists’ HHPXRF analysers used in the lab due to users’ discovery of performance issues related to field use, or because users are not yet engaging in research questions that require instrument use in the field? We suspect that prevalent use in labs far from archaeological sites, in large part, reflects the established laboratory-based paradigm.

**Question #5 (Fig. 5):** What archaeological materials are being analysed using HHPXRF, pXRF, and labXRF?

About 45% of HHPXRF is being done on obsidian and other rocks. There are three likely reasons for this. First, obsidian studies are almost always at the forefront when new techniques are brought to archaeology, due in part to the volcanic glass being so well suited to sourcing. Second, lithics are one class of artefact that cannot be easily exported or, given the importance of morphology in lithic analysis, altered or destroyed. Thus HHPXRF enables archaeologists to source obsidian and other lithic materials without biases imposed by export restrictions. Third, obsidian studies ideally involve extensive fieldwork to identify the raw-material sources, and HHPXRF can analyse geological specimens in the field rather than shipping as many as one can carry to a laboratory. This also explains why museum- and component-type pXRF systems are infrequently used: such systems can be transported to a fieldhouse but not up the flanks of a volcano.

Paints and pigments are logically most often analysed using museum- and component-type pXRF. Analyses of frescoes and other paintings typically must be done on-site and nondestructively, as must those of decorated ceramics in museums. It is not unusual for art museums to have conservation laboratories with a pXRF system at their disposal. Such systems are also used to study and conserve other types of artefacts in their collections, especially metal and glass objects. Ores and slags, in contrast, are often approved for export and destructive sampling and/or analysis. Archaeometallurgy is a field with many experts bringing analytical experience from outside archaeology but with interests in applying their expertise and instruments to ancient materials. Thus ores and slags represent a large portion of labXRF analyses.

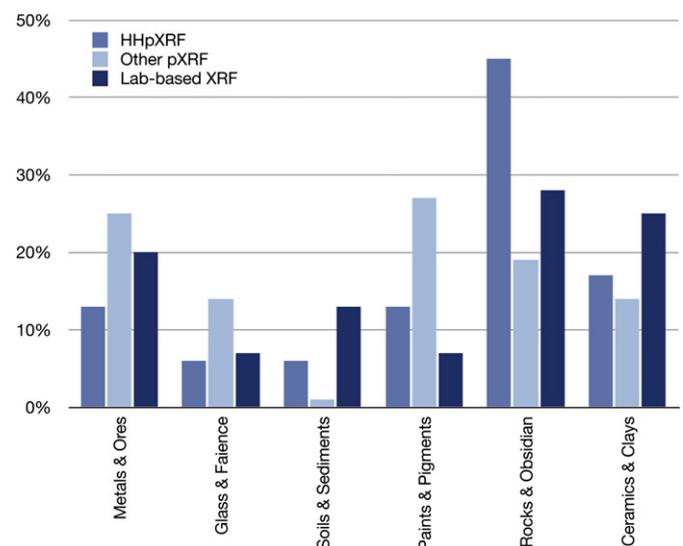


Fig. 5. Archaeological materials being analysed using HHPXRF, pXRF, and labXRF.

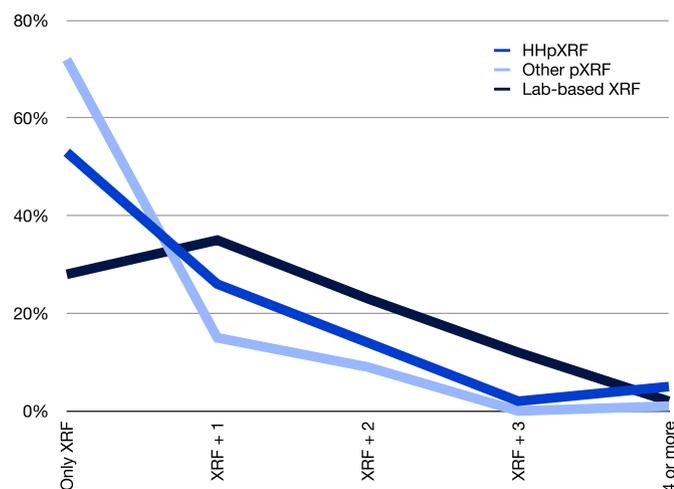
It makes sense that museum- and component-type pXRF are infrequently used to study soils and sediments. There are no issues with their destruction, and given the proper governmental licenses, there are few issues with their export. Unless their measurement can provide immediate on-site feedback using HHPXRF (see above), there is little motivation not to send them to a distant specialist laboratory for analysis at a later date. Thus most soils and sediments are exported for labXRF, and consequently specimens may also be studied with other techniques, for example, thin-section petrography.

The same is true for ceramics and other clay artefacts, another group that is still mostly analysed using labXRF but also fairly evenly distributed among the XRF varieties. Obviously ceramic artefacts, such as intact Greek red-figure vases, will be analysed non-destructively in a museum, whereas sherds are often capable of being studied destructively and either moved to a national research centre or exported to a more distant facility.

**Question #6 (Fig. 6):** Are HHPXRF, other pXRF types, and labXRF in archaeology being used alone or in conjunction with other techniques?

The differences among HHPXRF, other pXRF types, and labXRF reveal interesting trends. We expected museum- and component-type pXRF systems would most often be used in isolation because they are typically used for analysing collections or artefacts that can be studied no other way. We also expected labXRF to be used with complementary techniques, whether that be thin-section petrography or instrumental analysis like NAA or ICP-MS. If one uses labXRF, there are presumably few issues with export or destructive sampling. Indeed, labXRF is most frequently used with one other technique, but two or three additional techniques are also common.

HHPXRF falls between the curves for labXRF and other pXRF types. Roughly half the time HHPXRF is used in isolation; however, its use with one or two other techniques is also common. What does this mean? It may reflect researchers' caution and indicate an awareness of the criticisms regarding HHPXRF and, consequently, a choice to use additional techniques to corroborate their results and/or satisfy sceptical reviewers. It may also mean archaeologists view HHPXRF as only part of the analytical toolkit and best combined with other techniques. This trend further suggests HHPXRF is being used less frequently with artefacts that cannot be analysed any other way. This too implies that archaeologists largely have not yet formulated new questions best addressed using HHPXRF.



**Fig. 6.** Use of HHPXRF, other pXRF types, and labXRF in archaeology alone and in conjunction with other techniques.

**Question #7 (Fig. 7):** Where in the world (i.e., on what continents) are HHPXRF, pXRF, and labXRF being used in archaeology?

This question asks where HHPXRF is being used, not from where artefacts originated. Frankel and Webb (2012) used HHPXRF to analyse Cypriot ceramics in the Australian Institute of Archaeology, and thus count as Oceania. Similarly, Forster and Grave (2012) analysed Near Eastern obsidian artefacts using HHPXRF at the University of Sydney, so their work also counts as Oceania.

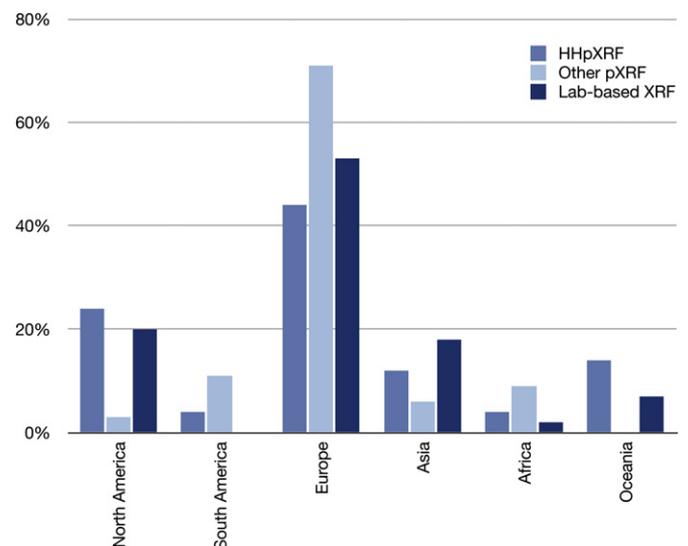
Clearly most XRF, regardless of type, is being used in Europe. Over half of labXRF is conducted in Europe, as is two-thirds of museum- and component-type pXRF. Furthermore, 44% of HHPXRF is conducted in Europe. We attribute this to the preponderance of research centres and museums. Furthermore, where there are archaeologists familiar with labXRF and there is an infrastructure for its archaeological use, there is also an existing compatibility with portable versions of the technique. We wonder, though, if such compatibility is more likely to lead to direct substitution of labXRF with HHPXRF.

Museum- and component-type pXRF are largely unknown in North America. We expect well known, dedicated archaeological XRF laboratories (for example, the Geoarchaeological XRF Laboratory) largely served the XRF needs of American archaeologists, and museum- and component-type systems were simply unnecessary or still considered the purview of specialists. We propose that American archaeologists, until recently, considered XRF a technique best done by experts in a laboratory; however, when presented with HHPXRF instruments, there is great interest in freeing the technique from the laboratory.

We also note that museum- and component-type pXRF also seem unknown in Oceania, where recent studies used HHPXRF to analyse museum collections. labXRF is largely, if not totally, absent in South America, which explains the relatively high proportion of studies using museum- and component-type pXRF: the archaeologists either had to export artefacts or bring XRF with them to museums and fieldhouses. We also observe that nearly all of the “Africa” studies took place in Egypt, where export of artefacts is extremely restricted and where pXRF studies frequently must take place in museums.

## 6. A revolution?

The potential for HHPXRF to bring about change in the routine analysis of diverse archaeological materials is great. We argue that



**Fig. 7.** Continents on which HHPXRF, pXRF, and labXRF is being used in archaeology.

this potential will not be realised simply as the result of technological innovations in hardware and software. Rather these instruments may initiate changes in the practice of archaeological science and its interfaces with wider bodies of archaeological theory and practice. With new possibilities of how and where to work, coupled with the ability to sample and analyse at unparalleled scales, we may perhaps see hints of a revolution roughly analogous to a Kuhnian “paradigm shift.” While we would not argue that HHPXRF will lead to changes in our discipline as profound as the Copernican revolution or Darwinian evolution, we might reasonably expect a period of development where archaeologists and scientists cultivate a number of approaches that our community previously would not have considered valid.

As the results of our literature survey show, most HHPXRF-based archaeological studies are currently based on the foundational XRF studies in archaeology, which are all laboratory-based. The current laboratory-based use of HHPXRF use is simultaneously surprising and understandable. Any emergent technology with the capability of functioning outside the traditional context of scientific practice, that is, the laboratory, is bound to raise challenging assumptions about its performance. The use of HHPXRF in the laboratory can therefore be seen as an attempt to gather confidence in the instruments’ performance during this introductory period. The laboratory, as a place for scientific practice, is held in esteem by scientists (and others), and it offers a calm and controlled environment where careful measurement can be undertaken objectively. What we now anticipate is the increased use of this instrumentation in novel contexts and with novel objectives.

The emergence of archaeological science as an increasingly specialised field of practice has paralleled the development of specialised archaeometric laboratories over the past five decades. These laboratories have garnered international reputations while defining a range of specific methods that are tied to particular instruments, ones that have been secured through significant and continued funding streams. Understood from this perspective, the relatively low capital cost of HHPXRF, coupled with its field abilities, may position pXRF as technology capable of disrupting the current hierarchies of practice. Such scenarios will be familiar to anthropologists of science. It has been clearly noted that the manner in which material, technical, and human resources are configured **in a laboratory** directly affects the kinds of challenges, facts, and counter-facts that are produced from that place (Latour and Woolgar, 1979). The prospect of working outside the laboratory could then directly challenge decades of intellectual and material investment in the now-established modes of practice. While the development of specialised archaeometric laboratories has led to incalculable contributions to archaeological knowledge, the increased specialisation and segmentation of archaeological practice has not been without controversy and debate (e.g., Clarke, 1973; Shanks and Tilley, 1987; Hodder, 1986).

This is an important issue as the continued separation between science-led archaeology and social-science/humanities-led archaeology has been a constructed crisis frequently revisited in recent decades (e.g., Andrews and Doonan, 2003). The repeated debates seem to focus on the epistemological foundations of particular types of knowledge and, ultimately, the location of practice (i.e., the laboratory or field). In our view, this debate appears to have more to do with disciplinary politics and funding than an actual rift in the practice of archaeology. Yet the portability of HHPXRF has a real role to play in bringing together scientists, scientific practice, and archaeologists in a common context of practice, one in which the varied rhythms of investigation, analysis, and interpretation become syncopated together in the field and within coherent project objectives.

The projected shift of HHPXRF into the field is one we would encourage since researchers working within an established lab-based paradigm only engage with the types of research questions and goals that this paradigm can most readily answer. Thus research following the paradigm is highly productive, as one can observe in the great successes of labXRF in archaeological research during the last fifty years, but such practice does not play to the obvious strengths of HHPXRF. HHPXRF cannot compete with the capabilities of labXRF within the lab-based paradigm but can be uniquely successful in novel applications. This change will be based, at first, in method. Theory, in turn, can change with new relationships among data.

We must emphasise the methodological revolution will be non-Kuhnian in an extremely important aspect: the new paradigm will be not “incommensurable” with the old one. That is, novel archaeological research approaches with HHPXRF can and will still occur alongside conventional XRF approaches. The novel and conventional approaches need not be incompatible rivals because both can be used to address the questions of archaeological interest. Both paradigms may operate side-by-side.

## 7. The future

The reasons for the desirability of HHPXRF to archaeologists are clear: the potential for high-quality compositional data acquired quickly in the field can transform the ways in which our discipline approaches questions requiring chemical information. Continuing advancements in hardware and software, particularly the addition of sophisticated FP calibrations to the mobile data-correction toolkit, enable analyses of a wide range of archaeological materials encountered in the field. Developing the traditional empirical calibrations using matrix-matched standards is fairly straightforward when, for example, sourcing obsidian artefacts in a region with a few well-known sources: their compositions will fall within an expected range as a result of the particular geochemical processes required for obsidian formation. That is almost certainly not true for the broad range of soil and sediment compositions one may encounter in the facies of a Pleistocene cave site or Bronze-Age coastal settlement, for instance. The technological capacity exists for in-field analyses to investigate a Mousterian living floor or to locate copper production areas. As we have shown, however, these types of studies are rarely published in comparison to research that could readily be done using labXRF with no change in method and theory.

We warn of sweeping generalisations regarding the performance of HHPXRF. Just as GPR does not generate archaeologically useful information for all landscapes, HHPXRF may not provide useful *in situ* analyses in all environments or for all research goals. Geophysicists have, empirically over time, identified the types of landscapes and questions for which their techniques may yield archaeologically useful results. Such knowledge regarding the utility of HHPXRF has yet to be generated by our discipline. This entails recognising the contexts – including physical, methodological, theoretical – in which HHPXRF may be archaeologically useful.

Regarding theoretical approaches best suited to the advantages of HHPXRF, we anticipate that those approaches most closely linked to space, context, and material culture patterning will most readily accommodate new ways of collecting chemical data on-site. For instance, existing methodological and theoretical frameworks to consider craft production and household organisation are conducive to using high-resolution geochemical surveying as a means to explore living and production spaces. Similarly, it is no coincidence, in our view, that the archaeological uses of pXRF in the 1980s involved locating metal production areas. The

organisation of space, from the household to landscape scale, lends itself to study with an instrument that can uniquely be moved through that space. Contextual analysis is another highly compatible approach. The understanding of an artefact in relation to its surroundings and the whole from which it is drawn can only be supplemented by chemical analyses of its associations, meaning that HHPXRF may give further structure for interpretation. In a discipline with the mantra “context is everything,” we predict some of the greatest potential for HHPXRF related to these aspects of our discipline.

The previously mentioned work of Davis et al. (2012) offers a glimpse of what is possible. We believe it likely that HHPXRF can change the scale of detailed, systematic studies of spatial patterning in archaeological data. Traditionally XRF has been used in archaeology, for example, to reconstruct regional-scale distribution maps linked with the concepts of exchange, contact, and diffusion. This methodology has enabled formulation and testing of archaeological theories such as central place theory and settlement hierarchy, and such studies have proven useful for regional chronologies. HHPXRF, as we have noted, may enable novel high-resolution studies involving occupation areas, households, and the use of space. The temporal, not just the spatial, scale may also change. Rather than informing regional chronologies, HHPXRF may permit new studies of, for instance, “living floors” versus sites’ occupational palimpsests. Novel methodologies, in turn, would ideally enable formulation and testing of new theories regarding cultural, behavioural, and cognitive aspects of humanity (and our recent ancestors) in the past. Developing new theories, at least at the “middle range” level, is likely, we argue, because HHPXRF brings a potential for new observations in the archaeological record to interpret and explain. Middle-range theoretical developments may eventually feed into “high” theoretical debates, but at this point, such speculations are perhaps best left to the aforementioned post-conference gatherings.

Clearly we agree with Shackley (2010) that HHPXRF “has the potential to make very real changes in our discipline” (18). To do so, we argue, the use of HHPXRF must move beyond the one-to-one replacement of labXRF. Since HHPXRF is uniquely suited to *in situ* analysis (that is, chemical analysis conducted in a specific place), we expect “very real changes” to occur linked to methodological and theoretical approaches involving space, context, and related frameworks.

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