

# Chapter 6

## Portable XRF of Archaeological Artifacts: Current Research, Potentials and Limitations

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### Introduction

Nuclear beams and lasers are becoming increasingly important as analytical tools in art and archaeology for dating and characterization studies. Their portability and multifunctional mode, however, is the main concern as it requires particular instrumentation and software development. This development is triggered by the need to study the materials of cultural heritage, whether in situ or in the museums, in a non-invasive, rapid manner so as to acquire the maximum possible information in one operational action. The portable X-ray fluorescence (PXRF) instrumentation is aligned along this leading research trend.

For rapid, non-destructive detection of chemical elements, portable or desktop XRF devices are available, either in normal mains power or battery-operated. They are rugged, and highly sensitive for performing in-the-field non-destructive elemental analysis. Such system designs are compact, low weight, consume less power, and can operate at varying voltages of 40 to 60 kV and variable currents in the range of microamps, obtaining accurate results quickly.

This XRF technology can generally detect amounts of major, minor, and trace chemical elements. In particular, it is uniquely capable of detecting trace amounts of heavy elements, such as barium (Ba), antimony (Sb), lead (Pb), and strontium (Sr). The technology can be used wherever rapid, non-destructive, in situ analysis of chemical elements is needed.

To rapidly determine the identity and quantity of elements and distinguish them from background radiation, the analysis process can divide the spectrum into energy sub-bands, reducing the algorithmic complexity of analyzing the entire spectrum at once. As a result, the system obtains accurate, virtually real-time results

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for hundreds of material classes. These algorithms also could be applied to neutron and gamma spectroscopic analysis. Such a system with a low-flux, micro-focused X-ray tube operates using a high-voltage, low-power, miniaturized, and regulated power supply.

These apparatuses are developed for many investigations, including archaeology and culture materials culture in general (Potts and West 2008). The benefits encompass: *Sensitivity*: This technology can detect materials at the parts-per-million (ppm) level. *Advanced analytics*: Using software algorithms, the technology detects the relative amounts of elemental constituents, which can be used to identify the possible presence of surface traces. *Automated, remote operations*: They can be fully automated and operated remotely if required.

Especially, the systems designed with an X-ray tube that can operate up to 60 keV provide the ability to complete measurements to the ppm-level in a shorter time and to identify heavier elements more easily than with the 40 keV tubes typically found in portable XRF systems. The cost of a portable XRF systems that uses radioisotopes or X-ray generators ranges between 15,000 and 60,000 € (\$20,000–\$80,000).

The non-destructive advantage of the PXRF should be emphasized parallelly with their portability because other non-destructive methods of analysis are available with even superior capabilities that measure a large number of elements (e.g., particle induced X-ray emission [PIXE], NAA, IRPAS, FTIR, SIMS), but they are not portable. The portability coupled with the non-invasive capability makes the PXRF systems more favored by archaeometrists and, especially, archaeological scientists.

XRF spectrometry typically uses a polychromatic beam produced from radioisotopes X-ray tubes or synchrotrons of short wavelength/high-energy photons to induce the emission of longer wavelength/lower energy characteristic lines in the sample to be analyzed (see Chap. 2). X-ray spectrometers may use either the diffracting power of a single crystal to isolate narrow wavelength bands (wavelength-dispersive XRF [WDXRF]) or an energy-selective detector to isolate narrow energy bands (energy-dispersive XRF [EDXRF]) from the polychromatic radiation (including characteristic radiation) that is produced in the sample. Because the relationship between emission wavelength and atomic number is known, isolation of individual characteristic lines allows the unique identification of an element to be made, and elemental concentrations can be estimated from characteristic line intensities. WDXRF instrumentation is mainly used for (highly reliable and routine) bulk analysis of materials, e.g., in industrial quality control laboratories and destructively in geological research. In the field of EDXRF instrumentation, next to the equipment suitable for bulk analysis, several important variants have evolved in the last couple of decades. EDXRF became commercially available in the early 1970s with the advent of high-resolution solid-state detectors (see Chap. 2). In principle, the high-geometrical efficiency of the semiconductor detector (usually silicon drifted detector) in EDXRF instruments, permits a great variety of excitation conditions. The final

analytical capabilities and in particular the detection limits that can be attained by the instrument strongly depend on the sophistication of the detector electronics.

Types of X-ray sources used in portable/desktop XRF:

- (a) *Sealed X-ray tubes.* Most commercially available X-ray spectrometers utilize a sealed X-ray tube as an excitation source, and these tubes typically employ a heated tungsten filament to induce the emission of thermionic electrons under high vacuum. After high-voltage acceleration, the electrons are directed toward a layer of high-purity metal (e.g., Ag, Cr, Rh, W, Mo, Rh, Pd, etc.) that serves as the anode. In the metal layer, the bremsstrahlung continuum is produced upon which the characteristic lines of the anode material are superimposed. The shape of the emission spectrum can be modified by changing the electron acceleration voltage. The broad band radiation is well suited for the excitation of the characteristic lines of a wide range of atomic numbers. The higher the atomic number of the anode material, the more intense the beam of radiation produced in the tube, and the more effective is the acquisition of lower atomic numbers.
- (b) *Radioactive sources* are the most commonly employed in PXRF systems. Generally, these sources are very compact compared to X-ray tubes;  $\alpha$ -sources are suited for the analysis of elements of low-atomic number. Frequently used sources are the  $^{244}\text{Cm}$ , with a half-life ( $t_{1/2}$ ) of 17.8 years that emits 5.76 and 5.81 MeV  $\alpha$ -particles, and  $^{210}\text{Po}$ , having a half-life of 138 days and emitting 5.3 MeV or the  $\gamma$ -rays emitting isotopes of  $^{55}\text{Fe}$  ( $t_{1/2} = 2.7$  years),  $^{241}\text{Am}$  ( $t_{1/2} = 433$  years), and  $^{57}\text{Co}$  ( $t_{1/2} = 0.74$  years).

With regard to detection systems in XRF technology in general, several detectors have been constructed, aiming at higher energy resolution and high count rate efficiency. A review of PXRF, including gamma- and X-ray detectors, by Knoll (2000) and Potts et al. (2001) presented the full chronological history of all the types of detectors since 1950 that have been used for these spectroscopic regions (see also Potts and West 2008). The authors included the latest trends in portable, thermoelectrically cooled and silicon drift X-ray detectors and the more recent high-resolution cryogenic X-ray detectors.

Of interest is the work of Langhoff et al. (1999) that promotes the combination of a high brilliance, a low powered X-ray tube, a capillary optical system, and a non-cryogenic X-ray detector for applications in the analysis of works of art. Useful frequently updated information on PXRF can be found in the biannual Newsletter of the International Atomic Energy Agency's (IAEA) Laboratories in Seibersdorf, Austria.

Here we present a brief outline of the available portable XRF devices for some archaeological applications, refer to the detected trace elements, discuss the comparison with other desktop and analytical methods, introduce some prominent applications with various cultural materials, and weigh the potentials, limitations, and future growth and prospects, with emphasis on Aegean and World obsidian provenance.

## Applications in Art and Archaeology

Based on the new advancements on both the nuclear technology and the commercially available portable systems, the collection of quantitative data from archaeological samples is becoming one of the most trusted and widespread methods in archaeology.

The non-destructive capabilities of XRF are indeed particularly suited to research in art and archaeology, where the sample is unique or its integrity has significant technical or esthetic value. This is perhaps best exemplified in the examination of works of art, where the forensic aspects of the measurement may provide historical insight (Longoni et al. 1998; Spoto et al. 2000).

For example, if one assesses that the surface of archaeological and historical materials has deteriorated and differs in composition from the bulk, the quantitative measurements may require surface abrasion or even sampling, depending on the material; on the other hand, when a measurement has to be strictly non-invasive, one cannot expect reliable quantitative data. However, for each experimental situation, the choice of one approach over the other depends on the type and intrinsic value of the object, the aim of the investigation, the instruments available, and, last but not least, the scientist's or conservator's personal assessment of the acceptable damage.

Nonetheless, PXRF analyzers have shown during the last 30 years that they are ideal tools to aid in a variety of applications in cultural heritage, archaeology/geoarchaeology, and in archaeometry research in general (Rotondi and Urbani 1972; Hall et al. 1973; Cesareo et al. 1996, 1999; Longoni et al. 1998; Langhoff et al. 1999), including:

1. *On-site material characterization* with hand-held systems. Within the framework of a large scale geoarchaeological project in the area of eastern Crete, Greece, sediments from five drilling boreholes were analyzed using a PXRF; based on the resulted quantitative data, distinguishing of the fluvial or the marine character of the successively deposited sediments in all studied cores became feasible (Zacharias et al. 2009). In general, direct and in situ material characterization is a triggering task, and conclusive answers may come to light only with the use of a combination of calibrated portable sets that perform within an interdisciplinary environment of material scientists and geo-archaeologists.
2. *Museum analysis* using both hand-held and laptop systems. The PXRF can identify components of pigments in paintings and glazes, metal alloy content, provide the characterization of objects such as jewelry, silverware, and weaponry; thereby assisting conservators in the preservation and restoration of artifacts, as well as aiding in constructing databases from analytical data available for the scientific community.
3. *Provenance studies* based on the identified elements and their concentrations and by comparing sources and artifacts.
4. In *Conservation science* aimed at matching pigments in a rapid and accurate manner, helping to identify how objects have been preserved in the past, and



**Fig. 6.1** Spectrace 9000 TN PXRF measuring mural paintings of modern artist Spyros Papaloukas from the Amfissa Cathedral, near Delphi, Greece

provide the necessary knowledge in order to better conserve them for the future by examining elemental compositional data (Fig. 6.1).

5. In *art fraud or authentication testing*, the use of PXRF analysis performed on a variety of artifacts based on elemental data is extremely useful (Appoloni et al. 2007; Guerra 2008). Authenticating pieces helps prevent fraud, and can ensure that a returned artifact is the same one that a museum loaned or that donated pieces are identical in composition.
6. XRF has been used in combination with Raman spectroscopy in the identification of mineral pigments in modern art (Vandenabeele et al. 2000a; Liritzis and Polychroniadou 2007) and binding media and varnishes used in medieval paintings and manuscripts (Vandenabeele et al. 2000b).
7. *Ceramics*. Similarly, EDXRF was used for the examination of decorated shards of Neolithic pottery from Northern Greece (Papadopoulou et al. 2007). Using elemental concentrations for the painted and the non-decorated surface areas, the study revealed the main characteristics of each decoration, indicating the use of different techniques and exploitation of various clay deposits.
8. *Coins*. A comparison of PIXE and XRF for the elemental analysis of Japanese coins has been reported (Haruyama et al. 1999). It was found that selective

filtering was necessary to achieve successful PIXE analysis, and that XRF was the preferred approach. The relative concentration of low-level elements was found to be associated with their place of manufacture. The relationship between elemental composition of coins and their historical or geographical origin was the subject of a number of studies. These included the examination of Japanese medieval coins, 280 ancient Dacian coins from Romania (Cojocaru et al. 2000), Hungarian coins from the fifteenth century (Sandor et al. 2000), Ayyubid and Mamluk dirhams (AlKofahi and AlTarawneh 2000), and silver coins from the time of Alexander the Great (KallithrakasKontos et al. 2000). In the last case, the effect of the silver corrosion layer on the surface of the coins on the analytical results for 12 elements was studied before and after removal of the corrosion product.

9. *Manufactured glass.* Analysis of two sets of seventh to fourth century BC glass bead collections from Greece using a benchtop EDXRF set resulted in the characterization of the collection (Zacharias et al. 2008); in a subsequent step, the same collection was re-examined with the addition of one more calibrated EDXRF set and the introduction of the ion beam of PIXE, PIGE (particle induced gamma-ray emission), and RBS (Rutherford back scattering spectrometry) (Sokaras et al. 2009) provided good consistency and overall agreement between XRF and PIGER/PIGE for the detected major and minor elements. Application of radioisotope-excited XRF on eighth century Polish, Brandenburg, and Saxon glassware (Kunicki-Goldfinger et al. 2000), as well as EDXRF of Celtic glasses (Wobrauschek et al. 2000) has been reported. Furthermore, in porcelain analyzed by Wu et al. (2000), different compositional patterns were found for samples from various Chinese dynasties and for different usage. It was claimed that the method employed produced a highly efficient method of classification. In a similar study by Leung et al. (2000a), the use of principal components analysis of EDXRF data derived from 41 pieces of Dehua porcelain indicated that most of the samples were distributed in three areas, corresponding to the source of production.

## PXRF Instrumentation

Following the increased demand for non-destructive XRF analysis, there are a number of options, depending on intended use. Within the family of solid state detectors, one has two main groups: (a) cryogenically (liquid N<sub>2</sub>) cooled detectors and (b) thermoelectrically (Peltier effect) cooled detectors. Group (a) includes Si(Li) and HPGe detectors that provide good energy resolution (about 150 eV at 5.9 keV) and thick depletion layers, which means intrinsic efficiencies close to 100% for all the energies of practical interest (Knoll 2000) and large surfaces, that in turn mean high-detection efficiency. Typical figures for planar HPGe's are 13 mm and 200 mm<sup>2</sup> for thickness and surface, respectively. However, the need for liquid N<sub>2</sub> obviously reduces their portability and autonomy, and furthermore, due to large dimensions, the detector is positioned relatively far from the measurement point.

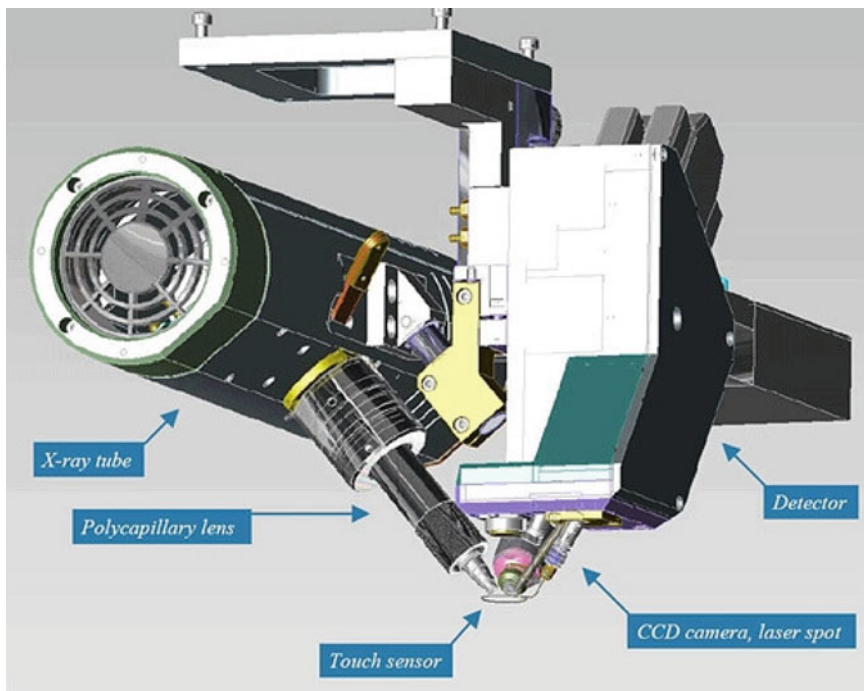
On the other hand, the detectors of group (b) do not need liquid N<sub>2</sub> and have small dimensions, which allow the detector to be placed very close to the measurement point; nevertheless, they have, with the exception of HgI<sub>2</sub> detectors, thin depletion layers – about 300 μm, corresponding to about 5% intrinsic efficiency for the Sn K-line – and small surfaces (less than 10 mm<sup>2</sup>) that create poor detection efficiencies; the group includes HgI<sub>2</sub> detectors, with good energy resolution (about 200 eV at 5.9 keV) and intrinsic efficiency; SiPIN detectors, with poor energy resolution (about 250 eV at 5.9 keV) and detection efficiency; and Si drift (SD) detectors, with good energy resolution (about 160 eV at 5.9 keV, even for high count-rates) and poor detection efficiency (see Cesareo et al. 1992, 2008).

A brief review of some of these portable XRF equipments operating in the energy or wavelength mode is given below:

The EDXRF field portable analyzer Spectrace 9000 TN is operated with a mercuric iodide (HgI<sub>2</sub>) detector, which has a spectral resolution of about 260 eV FWHM at 5.9 keV, and three excitation sources of radioisotopes within the probe unit – Americium <sup>Am-241</sup> (26.4 keV K-line and 59.6 keV L-line) measuring Ag, Cd, Sn, Ba, Sb; Cadmium Cd-109 (22.1 K-line, 87.9 keV K- and L-line) measuring Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Zr, Mo, Hg, Pb, Rb, Th, U; and Iron Fe-55 (5.9 keV K-line) measuring K, Ca, Ti, Cr. The wide range of excitation X-ray energies theoretically can measure all chemical elements from Z = 16 (sulfur) to Z = 92 (uranium); however, a variety of limiting factors produce a lower threshold of detection and in practice 26 simultaneous elements are measured.

The performance of the portable Spectrace 9000 TN EDXRF instrumentation in the laboratory has been reported (Potts et al. 1995; Liritzis 2007), while the entire concept of most investigations may apply to any available portable XRF instrument that requires an irradiated area rather than a point focus. Reference samples included rhyolites, metals, clays, soils, and low radioactivity reference samples. Several studies showed the capability of the instrument to determine major and minor elements (K, Ca, Fe, Ti, Mn) and selected trace elements (Rb, Sr, Zr, Mo, Ba, Pb) in typical silicate (rhyolitic) rocks. Other trace elements are not measured because their lower counting sensitivities mean that the concentrations were near to or below detection limits. The disadvantage of such PXRF with radioisotope sources is the need for replacement of the excitation sources that provide the primary X-rays every few years due to limited half-lives, which may become a serious problem when the production company no longer provides such sources.

Bruker company provides the Artax benchtop system that performs a simultaneous multi-element analysis in the range of Na(11) to U(92), by operating in two filtered modes using tungsten and molybdenum. In the latter, the X-ray tube generates 2–5 times larger peak areas for K-line elements above 20 keV for a better detection of light elements. The set is a micro (μ) XRF system since it provides a spatial resolution of down to 70 μm with the use of a CCD camera for a magnified digital image of the sample region under investigation, a white LED for illuminating the sample and to optimize the image quality and a laser diode to control the exact position of the beam on the sample and the exact distance between object and spectrometer.



**Fig. 6.2** Bruker handheld portable  $\mu$ -XRF device Artax – second generation (<http://www.bruker-axs.de/artax.html>)

The *handheld Tracer (turbo-SD) option from Bruker* incorporates silicon drift detector technology, thus additionally providing the concentrations of Mg, Al, and Si without vacuum or helium attachments (Fig. 6.2).

*Thermo scientific* provides a series of analyzers either for metal alloys or for multi-elemental archaeological applications: The extremely light (1.3 kg) battery operated NITON XL3t with a X-ray tube (Au anode at 50 kV) also provides the concentration of ca. 25 elements from sulfur to uranium, plus Mg, Al, Si, and P when connected via helium flush.

*NASA Goddard Space Flight Center PXRF* unit operates at variable voltages of up to 60 kV and variable currents of up to 100  $\mu$ A, obtaining accurate results quickly. This unit uses a metal-ceramic X-ray tube and a cadmium tellurium (CdTe) detector. Calibration can be automated, and the unit can be designed to include data accumulation, processing, storage, and transmission systems.

*Oxford Instruments (X-MET5000), Innov-X, and Spectro xSort*, all specialize in mining and metals operation solutions by providing handheld and benchtop sets for an effective measurement of the above-mentioned range of elements.

In contrast to the given information for some of the above systems that can reliably detect concentrations of light elements ( $Z \leq 13$ ), this still has to be



exploited in more archaeological applications and to be supported with published reference data.

In many XRF research laboratories, portable XRF spectrometers are built from commercially available components and in-house patents; such a  $\mu$ -XRF set has been developed at N.C.S.R. Demokritos (Athens) and is described in Karydas (2007).

A portable XRF spectrometer with polycapillary optics and vacuum chamber has also been constructed at the IAEA's XRF laboratory in cooperation with the Atomintitute Technical University, Vienna, operated up to 50 keV and a focal size of 100  $\mu$ m and a Silicon drift detector, for elements from Na upward (Wegrzynek, 2005).

The quantification procedure of intensity to concentration is based on the so-called fundamental parameter (FP) approach in XRF analysis (Ebel 1999; Kitov 2000). In general, the quantification of the spectral peaks to concentration is not simple, and care should be exercised. In fact, the FP correction technique is usually employed to calculate the true element intensity from the measured data. The efficiency model incorporates the bulk detector efficiency and the contributions from metal contact layers, dead layer and the beryllium entrance window. But the choice of which *calibration and matrix correction expression* to use has always been the subject of discussion. Thus, the assertion that the fundamental algorithm really was the most sufficient and the one from which all other theoretically valid expressions could be derived was the debatable issue (Willis and Lachance 2000, 2002). These authors questioned the original conclusions and strongly defended the use of the expression whose correctness had been called into question. Needless to say, such discussions will continue, while practitioners continue to use successfully the expression and software that they have validated for their own application.

Finally, the important topic of matrix correction using the FP approach continues to generate interest both in desktop and portable XRF applications. The detailed mathematics and calibration features of the FP method and some of the practical approaches that can be adopted for the solution of the FP correction equations were reviewed in detail by Kitov (2000). It is normally the case for FP correction algorithms that the excitation spectrum is either measured or calculated and calibrated.

Overall, the features of different portable XRF spectrometers are considered with special regard to the choice of X-ray tubes and detectors; this choice affects both portability and analytical performances. Moreover it has been shown that good detection limits are essential to investigate archaeological and historical materials since in most cases trace elements provide more information than the major ones.

## Detected Elements and Clustering Techniques

The chemical elements usually measured by PXRF are K, Ca, Ti, Mn, Fe, Zn, As, Rb, Sr, Zr, Ba, Hg, and Pb. For cluster processing, only concentrations well above the detection limit and thus low error are used.

Two of the most popular multivariate statistical techniques used in archaeometry are cluster analysis (CA) and principal component analysis (PCA) (Baxter 1994). The application of CA should be applied to more or less homogeneous samples regarding origin and time.

Hierarchical CA were among the earlier multivariate approaches to be systematically deployed by archaeologists, and Pollard (1986) gives a brief discussion of applications to the provenance of pottery using chemical compositions. CA inheres a wide range of techniques (Baxter 1994; Mantzourani and Liritzis 2006).

At any rate, a common problem with all methods is the assessment of cluster validity, for example, to decide how many “real” groups are in the data; not an easy issue, as no generally applicable solution to determining the appropriate number of clusters exists. Complementary methods that contribute to this problem include PCA, correspondence and discriminant analysis, and model-based multivariate mixture of normals (Papageorgiou and Liritzis 2007).

The CA results are commonly presented as dendrograms showing the order and level of clustering, as well as the distance between individual samples. Statgraphics 5 Plus (Manugistics, Inc. 2000) and Splus packages are used. However, it is shown that simpler scatter plots corroborated by CA are sufficient to differentiate at least several obsidian sources from the World, with a high confidence (see below).

## Comparison with Other Benchtop Methods: Elemental Differences

When comparing PXRF with other methods in the determination of similar major and trace elements, several issues must be taken into account:

1. About  $\pm 10\text{--}15\%$  and for some elements  $20\text{--}30\%$  differences already are reported between the different desktop methods used on same samples. This can be explained in different ways. First, in the comparison of measurements obtained by two methods on aliquots of a single sample, one has to consider both the precision but also the accuracy of each one. About precision, one has a certain number of repeats on different samples. About accuracy, it may depend on the standards used in each method (i.e., U.S.G.S. standards are powdered, not satisfactory for PIXE or EMP-WDS).
2. The mass/volume of sample analyzed. Typically 100 mg by ICP; “punctual measurement” by EMP-WDS (“defocused” beam, to a diameter of about 5  $\mu\text{m}$ , to avoid volatile elements losses); but a larger volume by SEM-EDS (scanned surface area of about 1  $\text{mm}^2$ ); even more by PIXE (scanning surface of about 1  $\text{mm}$  square but a penetration depth within the sample by the proton beam of about 50  $\mu\text{m}$ ).
3. The glass composition homogeneity.
4. The nature, size, relative, and absolute frequencies of mineral phases.

5. Certain elements (a) are more precisely analyzed by one method than by another, and (b) in some cases for a given element one can be near detection limits (hence derive a larger error in content determination) for one method but not by another one, etc. The latter is an obvious issue for U and Th in PXRF.
6. For different samples, internal variability of a given source composition occurs. Moreover, internal variability within one single source is of significance too. This, for example, especially applies in the case of pottery analysis. Here, clay's inhomogeneity, caused either by the presence of non-normally distributed inclusions (Buxeda i Carrigos et al. 2003) or simply incomplete refinement processes, results in distribution issues. In pottery studies, it is also the high- or over-firing that can occur on a sub-set of artifacts produced at the same kiln that is responsible for alteration effects in the rare earth element concentrations (Schwedt et al. 2004) and therefore severely affects the compositional groups resulting from the chemical analysis (Tite 2008) and, naturally, any comparison between PXRF with other analytical methods.

Another cause of variability is the grain size of the ground powder as well (see below for obsidian); but if inter-source differences are large, there may be no problem in source assignment.

Thus for sourcing, absolute element contents are not necessary, for example, see the works by Acquafredda et al. (1999, and Chap. 2) on XRF, where they use only peak intensities.

A past review of the relative merits of PIXE, XRF, and ICP-MS in the analysis of archaeological artifacts (Pillay 2001) and of EDXRF and X-ray microanalysis (Linke and Schreiner 2000) may also be of interest in this context.

## Worldwide Examples

### *Pigments*

The identification of pigments and inorganic materials used in works of art is fundamental to further the understanding of an object's history or an artist's technique, and may provide evidence for dating or attribution of artifacts. Characterization of the artist's original materials as well as materials applied later (by artist, conservator or forger) is useful for providing criteria for conservation decisions.

The onsite XRF technique is, however, subject to some intrinsic limitations. The so-called matrix emission intensity of each element is a function not only of its concentration but also of the overall composition of the larger area under investigation. Moreover, the technique is capable of detecting only the elements and not the compounds to which they belong, and an unambiguous identification is not possible for numerous copper, lead, cobalt, and chromium containing pigments. These limitations can be particularly important when XRF analysis is applied to the study of the modern artists' palette that may comprise natural and synthetic

pigments as well as complex mixtures, either mixed by the artist or used as readymade tube paint-formulations. Indeed, from the nineteenth century onward, paintings have become more complex in terms of the number and mixtures of materials used for a single work. Newly invented pigments became available, which were sold already mixed in tubes allowing artists to free themselves from traditional studio practice and to render their subject matter more vividly.

Desnica et al. (2008) investigated the pigments from the painted wooden inventory of the pilgrimage church of Saint Mary of Jerusalem in Trski Vrh – one of the most beautiful late-baroque sacral ensembles in Croatia. It consists mainly of two painted and gilded layers (the original one from the eighteenth century and a later one from 1903), partly overpainted during periodic conservation treatments in the past. The approach was to carry out extensive preliminary in situ pigment investigations using PXRF, and the problems not resolved by this method on site were further analyzed ex situ using  $\mu$ -PIXE (particle-induced X-ray emission) as well as  $\mu$ -Raman spectroscopy. Therefore, the XRF results acted as a valuable guideline for subsequent targeted sampling actions, thus minimizing the sampling damage.

In Agnoli et al. (2007), the analysis of samples of Roman Age mural paintings was carried out by using energy dispersive X-ray spectroscopy, XRF, and PIXE, resulting in the identification of the pigments used; in Capitan-Vallvey et al. (1994), the technique was used to identify the various pigments that appear in the decorations of the “Corral del Carbon” in Granada a fourteenth century restored monument.

Another comparison study on pigment identification was that of Perez-Arantegui et al. (2008) where PXRF performance was compared with laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) for the characterization of cobalt blue pigments used in the decoration of Valencian ceramics. Qualitative data on the elemental composition of the blue pigments obtained using both techniques show a



**Fig. 6.3** Anthivolo, preparatory drawing of pinched paper used by modern artist Spyros Papoloukas to paint Amfissa Cathedral

good agreement. Moreover, the results clearly illustrate that potters utilized different kinds of cobalt pigments in different historical periods.

Another interesting application of PXRF has been made on the wall paintings (hagiography) and preparation drawings (*anthivolo*) of the Amfissa Cathedral (Central Greece) by early twentieth century artist Spyros Papaloukas (Fig. 6.3).

Sampling locations ranged from the ceiling to ground level and on various decorative motifs and compositions. Only minute samples (at millimeter scale) were permitted. Any perceptible invasive sampling was unacceptable. The non-destructive EDXRF measurements were performed on hagiographic representations in the pulpit, the women's gallery, and the left aisle (Liritzis and Polychroniadou 2007). Sampling was restricted in view of the value and the condition of the wall paintings. Pigments identified from elemental concentration included red and yellow ochres, iron oxides, and lead and titanium white. Stains of similar pigments were also found in the *anthivolon*. In particular, the paper support, red and black stains, were analyzed by EDXRF, FTIR, and Raman. The black stain contains mostly iron probably an unknown red paint poured accidentally on the tamping (tampon) layer of the prickled paper which contained sienna, chrome yellow, white of titanium, and others. The red stain contains much more iron identified as iron oxide (sienna). The rest of the paper contains faint yellow, traces of sienna, chrome yellow, and lead oxide (orthorhombic massicot). See Tables 6.1 and 6.2.

Non-destructive analysis for pigment identification of colors on two pieces of *anthivolo* using Raman and EDXRF methods indicates that EDXRF yields only chemical element concentrations, while Raman spectroscopy offers information about the structure (Liritzis and Polychroniadou 2007).

Sample location, color, method used, and pigment identification by different methods on minute samples from various points of the wall painting is shown in Table 6.2 (high barium contents as BaCO<sub>3</sub> white are present rather due to weight increase and thus higher cost). Portable EDXRF analyses focus in a non-destructive manner on a larger area on the surface mural painting. Chemical elements are reported that reflect known compounds, in contrast to the tiny samples detached and analyzed by Raman and FTIR. The compounds here are recognized from a data bank spectral library. Manganese and iron oxides (ochres) and minion were used in antiquity.

**Table 6.1** The results of combined EDXRF and Raman analysis for the identification of colors on two pieces of *anthivolo*, drawing paper

Anthivolo sample reference	Color	Pigment	Method
AMFA-1 (26 × 56.5–59 cm)	Yellow	Lead chromate sulfate	Raman, EDXRF
	Black	Carbon	Raman
	Black stain	Contains iron (sienna)	EDXRF
	Red stain	Iron oxide (sienna)	Raman
		Iron oxide + titanium dioxide white (TiO <sub>2</sub> )	EDXRF

**Table 6.2** Sample data, color description, pigments identified and the techniques applied

Sample reference	Description	Color	Pigment	Method
AMF2	ΓΔ3, women gallery, right aisle third apse, yellow flaked pigment	Yellow	In four successive painted layers: chrome yellow + yellow ochre + ultramarine + red ochre (yellow ochre=kaolinite by FTIR) High content: Pb and Fe (mainly yellow from similar pigments as above)	Raman, FTIR EDXRF
AMF3	ΓΔ2, women gallery, right aisle, second apse, red flaked pigment	Red	Iron oxides + Ca + Sr. Red ochre	EDXRF
AMF4	Pulpit, red decoration	Red	High Fe, Ca, Sr, Ba. Red ochre	EDXRF
AMF5	Left aisle, internal side of column	Blue	High Fe, Ba, CaCO <sub>3</sub> , K, Prussian blue	EDXRF, FTIR, IRPAS
AMF12	ΓΔ3 Women gallery, right aisle, third apse )	Blue	High Fe and CaCO <sub>3</sub> . Red ochre	EDXRF
AMF14	Pulpit, part of surface, flaky pigment on paper with lettering	Yellow	Yellow of Pb-Sn + PbO, K, F (a surprising result which cannot at present be justified)	EDXRF
AMF17	ΓΔ3, women gallery right aisle, third apse red from the vault	Red	Red lacquer + Red ochre Iron oxides + MnO <sub>2</sub> + Clay. Red ochre	Raman EDXRF
AMF18-AMF26	Local shop	Various colors (modern pigments)	Gypsum, minium, oxides of manganese and iron, high barium	EDXRF

PXRF can assist in archaeometric issues when studying decorated surfaces of archaeological pottery fragments (Papadopoulou et al. 2006; Romano et al. 2006) and in Cathedrals (Ferretti et al. 1991).

However, limitations due to X-ray attenuation by absorption make the technique ideal for smooth surface analysis. Care must be taken to avoid any secondary products from weathering/erosion or corrosion effects; for very thin layers, such as the painted layers, the obtained data always provide semi-quantitative results, while in cases of multi-layered compositions, the recorded spectra are composite from all the layers in the vessel.

## *Metals*

Portable and micro-XRF operations are critical in ancient metal studies for the identification, characterization, mapping, and thickness determination of both alloys and, more important, the corrosion products; these products, usually distributed within small areas of the artifact surfaces, are strongly associated with the archaeological environment as well as some indoor conditions (Ferretti and Moiola 1998; Ferretti et al. 1997).

Thus, in archaeometallurgical studies, chemical analysis should work in line with metallography, and the conservation knowledge and background of the artifact. In the event that any corrosion or patina product is removed, the X-rays should be directed to the pure metal phase. When only the surface coatings are analyzed, the results are suspect.

In fact in quantitative EDXRF analysis of ancient metallic objects, two main difficulties emerge: (1) determining the correction factors for the irregular shape or relief effects, and (2) measuring the true composition of the bulk metal under the surface patina. In the case of coins, taken as a typical example, point (1) could, in principle, be by-passed by casting pure metal copies of specimens and comparing XRF intensities with the ones from regularly shaped standards. The interest in examining coins, however, mostly depends on the possibility of the analysis method to be applied to several pieces, and XRF analysis should prove to be impractical in this case. Gold alloy objects do not normally present a patina on the surface, so by choosing proper geometric conditions during irradiation and by resorting to XRF line intensity ratios, it is possible to eliminate the problem of evaluating geometric factors. Chemical analysis of metals and metal alloy collections provides information on the manufacturing process, the provenance of raw materials, the geographical distribution of the ancient metallurgical technology, etc.

PXRF was used for the *in situ* study of gold and silver jewels (seventh to first century BC) from the Benaki Museum of Athens (Karydas et al. 2004). For the gold objects, the use of two distinctive sources was revealed - a, native and of high purity gold alloy and for the silver jewels analysed the copper content was evaluated as a technological, parameter of the materials while the presence of some minor elements like Pb, Bi, and Au, was attributed to an argentiferous galena used for the silver production and thus confirmed the authenticity of the jewels. Within the frame of the same study, parallel use of PIXE and PXRF spectrometers was made for three red gemstones on jewels (fourth century BC to first century AD)

exhibited at the same museum (Pappalardo et al. 2005). The analysis showed that one out of the three red stones analyzed was a pyrope-type garnet and the other two were the almandine type. The use of PXRF enabled the determination of trace elements, such as Cr and Y, which turned out to be the decisive factor in the classification of the red garnets into different types; India and Sri-Lanka were then proposed to be the geographical provenance for the analyzed red garnets.

In authenticity testing of gold jewelry, the analysts should consider a number of difficulties that arise mainly from the non-destructive examination to be applied. Initial observations using microscopy techniques, such as optical microscopy, scanning electron microscopy and X-ray radiography, are used to determine manufacture techniques. Then, the in situ elemental analysis using portable  $\mu$ -XRF devices are inevitably used to provide the concentrations of the major elements of gold alloys including gold, silver and copper. Moreover, technological changes can be attributed to economic and seasonal differentiations while the ratios of some characteristic elements of gold (Pd, Sn, Sb, Pt, and so on) are straightforwardly correlated to the geological origin.

### ***In Vivo PXRF Analysis***

Another interesting application of PXRF can be found in Rebocho et al. (2006). In this work, the post-mortem lead concentration in human bones of the Middle Age was measured by means of a PXRF system based on  $^{109}\text{Cd}$  radioactive source consisting of a Ge hyper-pure detector. This system, conceived for in vivo Pb analysis in bone, is portable, non-destructive, and based on lead K lines detection in contrast to the common ones based on the L spectra, in the usual X-ray fluorescence techniques. The drawback of this technique is that only elements of high atomic number are detected with enough efficiency and resolution, while the other technique allows simultaneous detection of most of the sample elements. Furthermore, this work has highlighted that diagenetic alteration in bone depends mostly on the physical and chemical properties of the burial place and the structure of the bone.

### ***Combined Portable XRF with XRD and $\mu$ RAMAN***

Since the beginning of this century, instrumentation allowing both chemical and compound analysis appeared in scientific literature. In Uda et al. (2005), a portable X-ray diffractometer equipped with an X-ray fluorescence spectrometer was set up so as to get a diffraction pattern and a fluorescence spectrum simultaneously in air from the same small area on a specimen. Diffraction experiments were performed in two modes, i.e., an angle rotation mode and an energy dispersive mode. In the latter, a diffraction pattern and a fluorescence spectrum were simultaneously



recorded in a short time, 100 s or less, on one display. The diffractometer was tested in the field to confirm its performance. Targets chosen for this purpose were a bronze mirror from the Eastern Han Dynasty (25–220), and a stupa and its pedestal which are part of the painted statue of “Tamonten holding a stupa” from the Heian Period (794–1192 AD), enshrined in the Engyouji temple founded in 996. The performance of the diffractometer equipped with XRF should be improved in the near future by installing a two dimensional scanning stage and by introducing computer software for quantitative analysis.

Another promising combined facility is that of a mobile micro-analytical  $\mu$ Raman and XRF set up that was built within the PRAXIS European project (Andrikopoulos et al. 2006); the instrument permits structural characterization of the pigments incorporated in a painting under study by evaluation of the Raman spectra, together with elemental analysis of the same materials provided by XRF spectra. The validation of the instrument’s in situ and non-destructive capabilities was performed after its in vitro application on an experimental icon (painted with traditional Byzantine techniques). The data acquired by the two techniques from the same areas on the painting offer complementary results, which enable the identification of almost all pigments even in the case of over-painted art objects.

## *Ceramics*

Ceramic and similar material, such as bricks and clay deposits, were usually exploited analytically with the use of standardized multi-elemental techniques like NAA, ICP, and laboratory XRF infrastructures. But nowadays due to the improvement in the elemental range measured by PXRF, the use of portable applications can be increasingly seen in the literature. PXRF has been applied extensively to archaeological materials such as ceramics, clays, soils, focused on clay provenance, clay fabric similarities, and trade exchange issues processing the data by clustering techniques, for example, Mantzourani and Liritzis (2006), Papadopoulou et al. (2006), Papageorgiou and Liritzis (2007), Liritzis et al. (2002, 2007), Liritzis (2005), Pappalardo et al. (2003).

## *Other Applications*

1. Uda et al. (2000, see also Uda et al. 2005) analyzed some pigments on the Funerary Stele of Amenemhat (ca. 2000 BC) exhibited in the Egyptian Museum, Cairo, and on the walls of a rock-cut tomb in Thebes, Egypt. Measurements were made with a home-made XRD instrument and a commercial PXRF under touch-free conditions. Hunite (a white Ca–Mg carbonate pigment) and an As-bearing yellow pigment were detected.

2. In another archaeological application, a portable EDXRF instrument incorporating a calcium or lead-anode X-ray tube was used by Cesareo et al. (2000) to determine Cl and S in frescoes and stone monuments. Detection limits were reported to be 0.04% m/m for Cl and 0.03% m/m for S.

## Provenance Studies of Obsidians by PXRF

Provenance studies of the raw materials used by prehistoric lithic industries are of key importance in research on ancient man. They provide basic information on the extension of the territory exploited by small groups of hunter-gatherers during the Paleolithic age. With respect to the Neolithic period ((seventh century to fourth millennia BC), provenance studies contribute to the knowledge of long-distance circulation and exchanges of raw materials, using *chaines operatoires* of lithic artifacts. Indeed, reconstructing mobility strategies is a major goal of researchers interested in prehistoric hunter-gatherers, and the use of geochemical source characterization of obsidian found at sites in a region offers a way to reconstruct the procurement range, or distance traveled to obtain resources of prehistoric groups (Roth 2000; Leslie et al. 2007; Craig et al. 2007; Shackley 2005; Tykot 2001).

Obsidian, due to its often remarkable knapping properties and esthetic qualities, was frequently used by prehistoric people. It is also one of the preferred materials in provenance studies. This is because of its mode of formation in volcanic events and its glassy matrix; in addition, the physico-chemical properties of an obsidian are most often similar even at a micro scale.

Early obsidian provenance studies were based on bulk physical properties, such as, color, density, refractive index, etc., as well as on petrography. Although useful for sample description, these observations generally do not provide valuable criteria for provenance studies (Gopher 1983).

However, for archaeological obsidian artifacts, which generally have to be studied non-destructively, X-ray fluorescence has proved effective in analyzing large numbers of artifacts in a short time for characterization and provenance (Davis et al. 1998; Potts et al. 1995, 2001, and for provenancing British stone axes (Williams-Thorpe et al. 1999).

For example, recent analytical, dating, source, and trade studies within the western Mediterranean, central and Eastern Europe, the Aegean, and Anatolia and the Near East reviewed by Williams-Thorpe (1995) and De Francesco et al. (2007), have increased the use of PXRF on obsidian characterization and analysis in the region. Results of these studies have shown that distributions are mainly separate in the four regions examined, and that obsidian was traded for distances up to 900 km in the prehistoric period.

As chemical sourcing is becoming an increasingly important component of archaeological investigation, PXRF leads in this field of research. As discussed in Chap. 2, Craig et al. (2007) used the technique with laboratory EDXRF on 68

obsidian artifacts from the Formative site of Jiskairumoko, in southern Peru. Both techniques arrived at substantively similar conclusions.

Although a powerful approach, a geochemical characterization does not in all cases allow one to discriminate obsidians from different volcanoes or from different lava-flows within a single volcanic field, so the choice and measurement of particular elements is vital.

The classification of Aegean obsidian sources and artifacts (see below) by well calibrated portable EDXRF and simple scatter plots, complemented by 3D plots and dendrograms, offers the advantages of portable XRF, for example, (a) swift counting time, (b) analysis of tools by a non-destructive measurement, (c) low cost, (d) versatile as a portable analyzer performing in situ, (e) groupings by simple elemental biplots, and (f) comparison with other methods.

In the following sections, sample mineralogy (size and distribution), but also the percentage covering over a 25 mm diameter analyzer window with solid flat artifacts, as well as, correction factors will be defined (Liritzis 2007), while determination of critical powder thickness in vial sample holder, for lighter and heavy elements, provides a test for correct concentration of certain elements.

## **Effect of Grain Size on Elemental Concentration**

The effect of grain size of ground obsidian on elemental concentration has been examined. The grain sizes of <32, 32–71, 71–90, 90–125, 125–150, 150–212, and 212–500  $\mu\text{m}$  were collected, through a mesh, from obsidian flakes of Melos island, Greece. The general trend is reduction of concentration as a function of increasing grain size. For the two sources (Adamas and Demenegaki) and the candidate location at Katsouli (may be a working location), in Melos, the obtained differences in the trends for some elements are the following: For K the differences between the extreme sizes are 15–20%, for Fe 25–30%, for Ti 18–30%, and for Ca for both sources are around 19%. Moreover, the elemental concentration for some obsidian powders was compared to data obtained by respective solid flat samples. Similar concentration values within  $\pm 5\%$  were observed for K, Ca, Sr, Zr, Rb of Demenegaki and Adamas sources, while for Ti powder is around 25% lower than solid, and for Fe around 20% higher than solid.

## **Dependence of Atomic Number (Z) of Elements on Critical Depth and Detection Limits**

It is well known that the sample thickness affects elemental precision, particularly at high energies (Davis et al. 1998, Chap. 3). Hence it is useful to have a measure of appropriate thickness for certain elements, particularly in case of having small amounts of powder samples or thin solid samples.

The data of critical depth  $D_c$  vs. atomic number ( $Z$ ) of eight elements were obtained from Potts et al. (1997). They calculated  $D_c$  (in  $\mu\text{m}$ ) for 99% of the secondary X-rays for the eight elements of three reference samples (basalt BCR-1, andesite AGV-1, and rhyolite RGM-1). These samples were measured by our Spectrace 9000 TN portable EDXRF too, for heavy elements K, Ca, Ti, Fe, Rb, Zr, Ba, and Ce which are mostly affected from sample thickness.

The aim was to construct a relationship between  $D_c$ , in which secondary X-rays reach within the sample, but for 25 elements detected, and their  $Z$ . For this, plots between  $D_c$  and  $1/Z$ , as well as, against  $1/Z^2$  per each of eight elements used by Potts et al. (1997) were made. The latter plots fit the eight data points much better than simply vs.  $Z$ . Table curve 2D was employed and various fitted curves produced, chosen the one with best  $r^2$  closest to one. Verification of the appropriate equation was made using well-known data through Mathcad 2000. The best equation is the  $1/Z^2$  dependence of  $D_c$  given in (6.1).

$$1/Z^2 = a + b \ln x + c \ln^2 x + d \ln^3 x + e \ln^4 x + f \ln^5 x + g \ln^6 x, \quad (6.1)$$

where  $x = D_c$  in  $\mu\text{m}$ , and  $a$ – $g$  numerical coefficients (see Table 6.3).

Figure 6.4 shows significant differences in  $D_c$  below 0.0012 ( $>Z = 29$ ) for these three rock types, implying the need for having thick samples of certain size per rock type. For example for  $Z = 38$  (Sr), the  $D_c$  between basalt and rhyolite differs by about 0.7 mm.

Following similar concept, a relevant curve was made for soil. The  $D_c$  values are taken from Operation Manual of Spectrace 9000 TN portable analyzer. Elements used are Na, Si, Ca, Fe, Rb, Nb, Rh, La, and Eu (Fig. 6.5). The derived relationship was:

$$1/Z^2 = (a + cx + ex^2 + gx^3)/(1 + bx + dx^2 + fx^3 + hx^4), \quad (6.2)$$

where  $x = D_c$  in  $\mu\text{m}$ .

Coefficients for (6.1) and (6.2) are given below in Table 6.3.

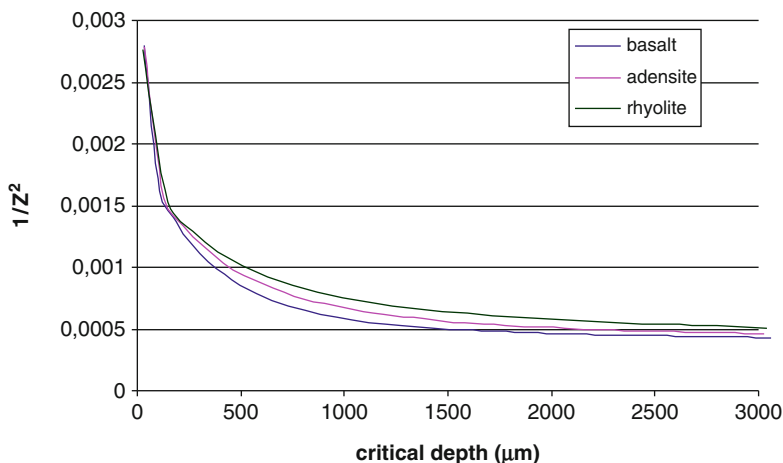
For soil and at the turn point of 0.001, the  $D_c$  increases significantly for measuring precisely elements with  $Z > 32$ . Therefore, for a particular rock type, construction of similar curves satisfies sample thickness and accurate concentration values.

Comparing  $D_c$  (99%) between basalt and soil, for say  $Z = 40$  or zirconium ( $1/Z^2 = 0.0006$ ), sample thicknesses are as follows: 0.946 mm for basalt, 1,784 mm for rhyolite, and 17.74 mm for the soil.

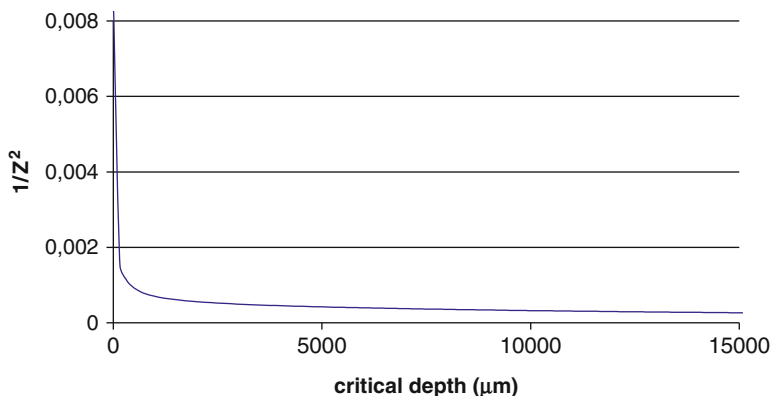
Application of this notion to actual concentration measurements has been made on reference radioactive sample BL4 (uranium ore, certified reference material CANMET, Canada) for K, Ca, Fe, Ti, Mn, Sr, Mo, Zr, Pb, Ba, U, Th as a function of sample thickness. Above 5 mm Basic elements above 5 mm are precisely measured. For heavy elements, e.g., Ba and Th, the  $D_c$ , and thus sample thickness, should be at least 13 mm for accurate results (Fig. 6.6).

**Table 6.3** Calculated coefficients of (6.2)

	$a$	$b$	$c$	$d$	$e$	$f$	$g$	$h$
Basalt	0.147	-0.141	0.056	-0.012	0.001	$-8.12 \times 10^{-5}$	$1.983 \times 10^{-6}$	-
Andesite	0.126	-0.117	0.046	-0.009	0.001	$-6.003 \times 10^{-5}$	$1.422 \times 10^{-6}$	-
Rhyolite	0.095	-0.0867	0.033	-0.0067	0.00074	$-4.274 \times 10^{-5}$	$1.0056 \times 10^{-6}$	-
Soil	0.01	0.00012	-0.00042	0.0019	$1.426 \times 10^{-5}$	$5.254 \times 10^{-5}$	$2.669 \times 10^{-8}$	$3.427 \times 10^{-6}$



**Fig. 6.4** Dependence of the atomic number ( $Z$ ) vs. critical depth ( $D_c$ ) for basalt, rhyolite, and andesite. This way, constructed family curves are made for particular element ( $Z$ ) in a rock (basalt: *lower*, andesite: *middle*, rhyolite: *upper*)



**Fig. 6.5** Dependence of  $Z$  as a function of  $D_c$  in soil

## Correction Factors for Measuring Small-Sized Obsidian Tools in Window-Type Apparatus

In window-type apertures of PXRF, the element concentrations derive from the total area, and the built-in software requires full counting geometry. In order to accommodate and measure accurately flat samples of size smaller than the window aperture, a procedure has to be devised (Bellot-Gurlet et al. 2000). For example, a procedure was devised relating the sample of variable sizes as percentage coverage of the window, of 25, 50, 75, and 100%, and the rest was covered with Perspex, the Spectrace 9000 TN portable EDXRF. Apart from the percentage coverage, the

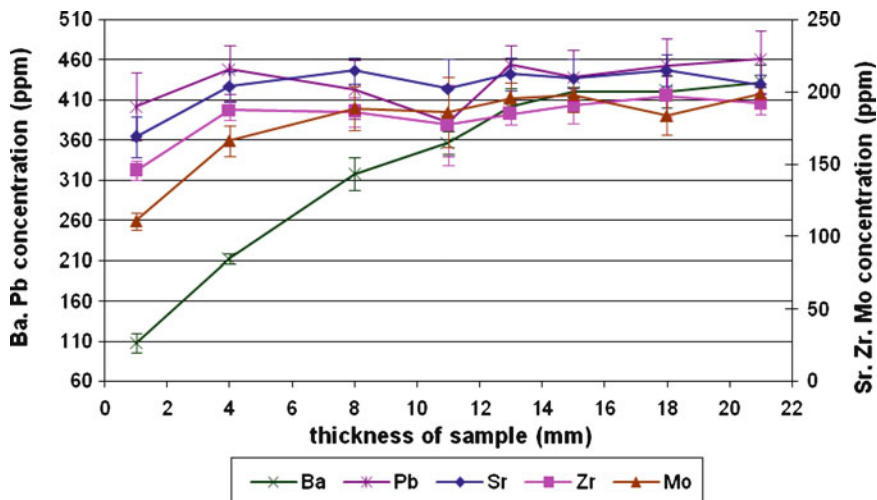


Fig. 6.6 Variation of K, Ca, Fe, Ti, Mn, Sr, Mo, Zr, Pb, Ba, U, Th, for standard sample BL4 as a function of sample thickness

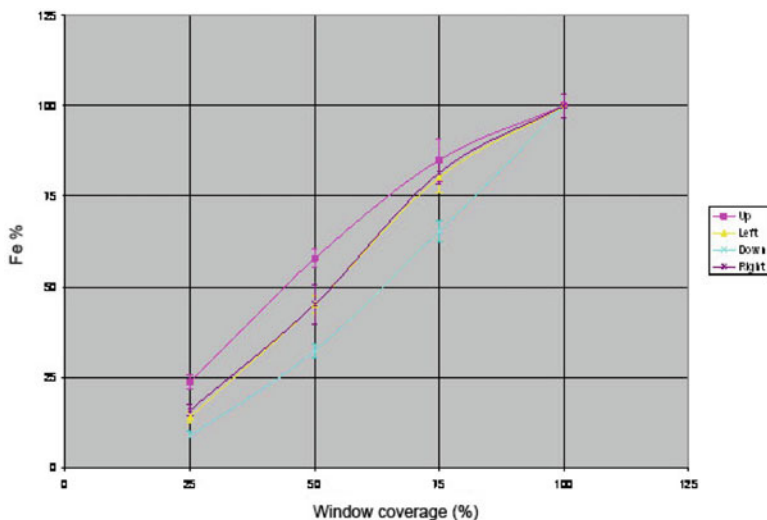
position of sample is important, that is, if the cover is on the left, right, up or down, looking on the window, due to the irradiation and counting geometry. Obsidian from Adamas (Melos Island) was cut flat, and six measurements were carried out for each data point for 200 s in each reading, with a repeated interval of 2 years. The repeat measurements were very similar to initial ones, and the average was used. It was found that for the two positions, forward as we look at it (up) and toward the operator (down), there is a discrepancy with regard to the other two positions (left and right), which give similar results (Fig. 6.7). From these data, it was possible to produce correction factors for small-sized samples. These correction factors  $f$  ( $=\text{total coverage/partial coverage}$ ) for left and right positions per element form a set of family curves.

Figure 6.8a–c shows three correction curves for K, Ca and Ti, and Fe, Sr, Zr, Rb, Ba.

## Clustering Techniques of Aegean and World Obsidians

Any clustering technique is meaningful if the analysis is correct. PXRF may sometimes produce dubious results. This may happen in case of elemental biases, concentration values near threshold of detection, inappropriate calibration and lack of interlaboratory comparisons. When these parameters have been adequately controlled and secured, then data normalization or standardization is the choice and the use of some hierarchical cluster analysis techniques.

Figure 6.9 shows the clustering of prehistoric ceramic shards derived from several settlements from the Greek mainland and the Aegean, employing cluster



**Fig. 6.7** Dependence of Fe concentration as a function of percentage coverage for four positions for the Spectrace 9000 TN

analysis with model-based multivariate mixture of normals (i.e., of data with normal distribution) (Papageorgiou and Liritzis 2007).

However, the groupings can also be resolved using either 3D plots (Liritzis et al. 2007), biplots of elemental ratios, or simple biplots. A case study of simple biplots applies to obsidians and their elements Sr and Ti – a simple but effective and fast result of PXRF (Liritzis 2007).

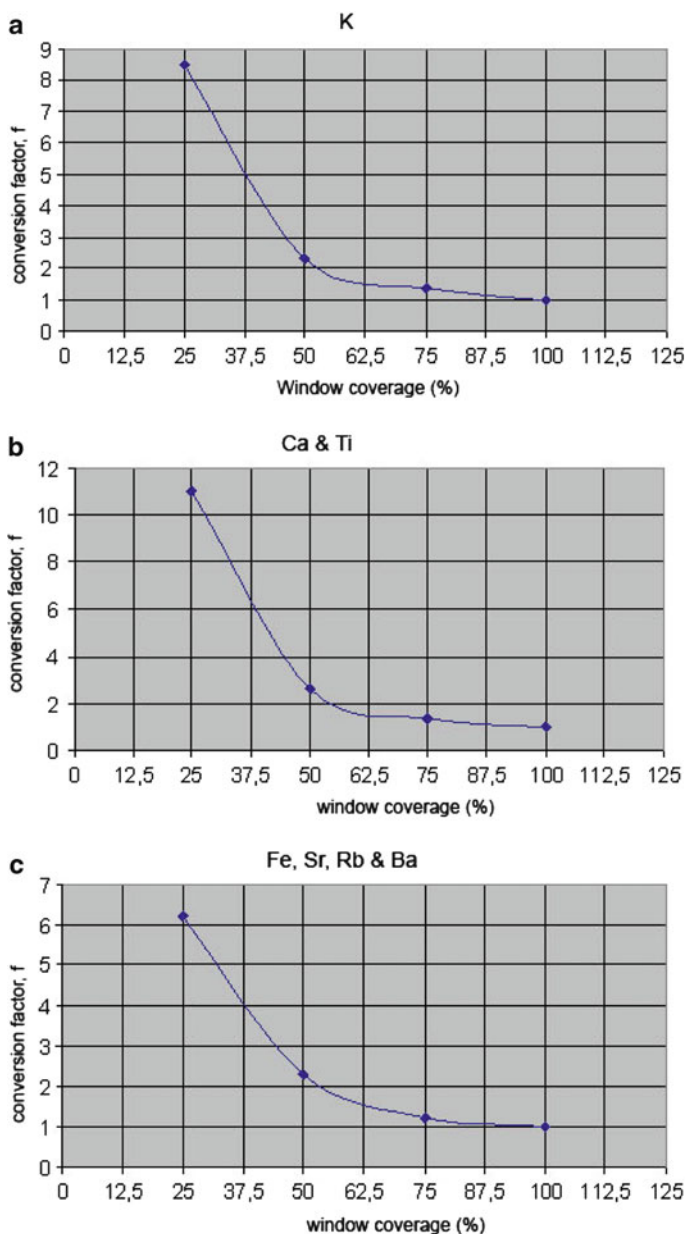
Figure 6.10 shows Sr vs. Ti (in ppm) of some Mediterranean sources and newly analyzed artifacts and Fig. 6.11 similar for some World obsidian sources acquired with our PXRF or by other desktop devices taken from the literature.

## Discussion of Advantages and Limitations

From the above outline of portable and non-destructive XRF analyzers, a summary of the advantages and limitations can be outlined.

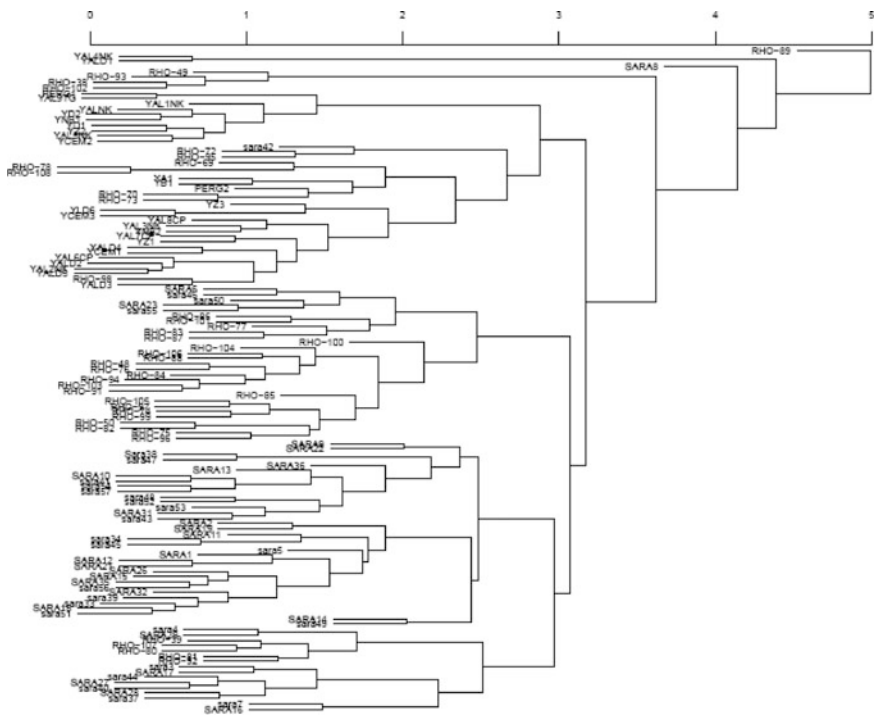
Limitations where particular attention is needed include: (1) PXRF cannot differentiate superimposed thin painting layers, (2) the presence of corrosion layers provides misleading results, (3) the thickness (infinite thickness) of sample is vital for some heavy elements, (4) flatness of sample. In fact, one of the well-known difficulties with in situ PXRF is that results are affected by surface roughness effects, more so than desktop EDXRF instruments. When analyzing whole samples, the effect of surface roughness usually introduces an additional air gap between sample and PXRF analyzer. In addressing this problem, Gauvin and Lifshin (2000) developed a Monte Carlo





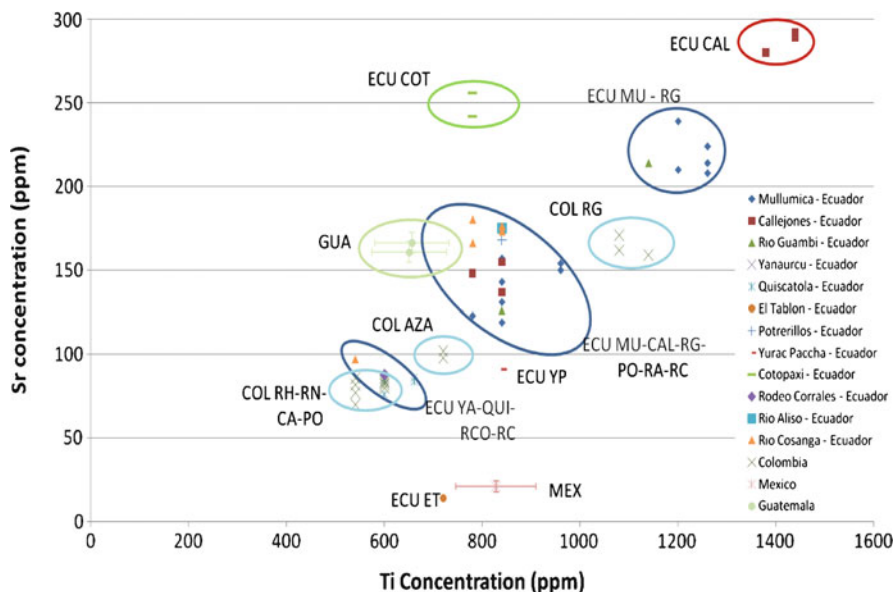
**Fig. 6.8** Correction factors (y-axis) as a function of percentage coverage of window (*left or right*) for (a) K, (b) for Ca and Ti, and (c) Fe, Sr, Zr, Rb, Ba

program that simulated the X-ray spectrum from samples having a rough surface. The shape and intensity of such X-ray spectra were shown to be strongly influenced by changes in the generation and absorption of X-rays as the beam was moved across the



**Fig. 6.9** A dendrogram of 188 ceramic and clay samples ranging from Neolithic to Bronze Age from Aegean, Cyprus, and Asia Minor of elements measured by PXRF. It is based on cluster analysis (hierarchical, average linkage). The main aim here was to compare Bayesian technique of Reversible Jump Markov Chain Monte Carlo with hierarchical clustering. They suggest the same number of main groups (except outliers/singletons) (Papageorgiou and Liritzis 2007)

sample. Bos et al. (2000) introduced a new calibration procedure for small samples of irregular shape based on conventional calibration samples and small modifications to existing procedures and software. Typical errors were of the order of 1.4–1.5%. A different approach to surface shape correction was applied to ancient ceramics by Leung et al. (2000b). These workers used Y as an outer marker by coating an appropriate solution on a Mylar membrane. Characteristic peaks of  $Y K\alpha$  and  $Y K\beta$  were then recorded with the piece of pottery covered with the membrane with correction coefficients calculated for elements of interest from test samples measured at discrete distances up to about 10 mm from the analyzer. (5) Detection limits near the limit threshold. Concentrations around this cut-off should be rejected. (6) Recording X-rays and converting to concentration: The processing of X-ray and gamma ray spectra poses its own particular problems. Stressed here is the tactic of using real peak shapes in the fitting function as there are typically large amounts of low-energy tails on peaks, which must be fitted accurately in order to get reliable peak area data. Similar findings on the importance of including peak distortions are reported by Kondrashov et al. (2000) who also recommended the use of least moduli rather than least squares



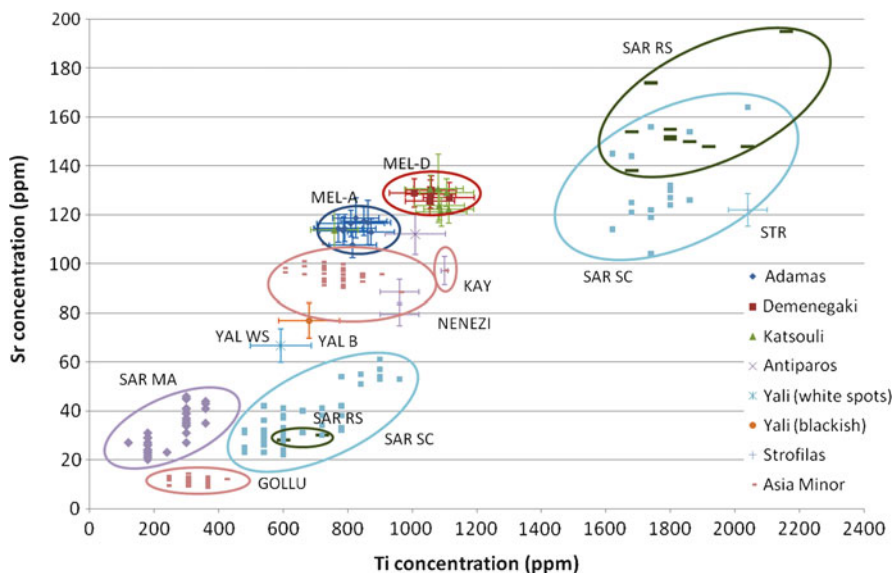
**Fig. 6.10** Biplots of Sr vs. Ti for Ecuador and Colombia measured by ICP-AES, ICP-MS, and PIXE (Bellot-Gurlet et al. 2002, 2008), Mexico and Guatemala by PXRF (Liritzis 2007). Error bars are assigned when available, and ellipses are indicatively drawn. *ECU* Ecuador; *CAL* Callejones; *MU* Mullumica; *RG* Rio Guambi; *YA* Yanaurcu; *QUI* Quiscatola; *ET* El Tablon; *RCO* Rodeo Corrales; *RC* Rio Cosanga; *RA* Rio Aliso; *POT* Potrerillos; *COT* Cotopaxi; *YP* Yurac Paccha; *COL* Colombia; *RG* R10 Granates; *AZA* Azafatudo; *RH* R10 Hondo; *RN* R10 Negro; *CA* Caclites; *PO* Popayan; *MEX* Mexico; *GUA* Guatemala

method when fitting peaks with high peak-to-background ratio. It is well known that, no matter how good the peak fitting algorithm, the overall performance can only be as good as the detector response function, and while detector function is improved, peak fitting algorithms are crucial in reducing error. Many of the desktop manufacturers have been perfecting the peak fitting software for many years, but this has not necessarily translated to the PXRF instrumentation.

We suggest caution to users of ready built software in PXRF devices, and suggest interlaboratory comparison and proficiency tests, preferably with established laboratories (see for example IAEA Report IAEA-CU-2006-06, CRP Project F.2.30.23, proficiency test on the determination of major, minor and trace elements in ancient Chinese ceramics).

Last but not least, the spectrum evaluation, matrix correction, and calibration procedures are most critical parameters, needing the attention of any PXRF user of applications in art and archaeometry, especially due to the wide range mineralogy of cultural materials studied.

Among the advantages are (1) the non-destructive/non-invasive procedure of measurement, (2) the portability (fieldwork, museums), (3) the fast processing, and (4) the satisfactory accuracy and precision in solving many archaeological issues.



**Fig. 6.11** Biplot of Sr vs. Ti. Aegean samples (Melos, Yali, Strofilas) were measured by portable EDXRF (Liritzis 2007), Asia Minor by ICP-MS, ICP-AES, LA-ICP-MS (Carter et al. 2006) and Sardinia by PIXE and SEM-EDS (Lugliè et al. 2006, 2007). Error bars are assigned when available, and ellipses are indicatively drawn. *MEL* Melos; *A* Adamas; *D* Demenegaki. Asia Minor, *GOLLU* Gollu Dag East; *NENEZI* Nenezi Dag; *KAY* Kayerli; *YAL* Yali; *WS* white spots; *B* blackish; *STR* Strofilas; *ANT* Antiparos; *SAR* Sardinia; *RS* Rio Saboccu; *SC* Su Carroppu; *MA* Monte Arci

## Conclusion

Chemical analysis by the portable WD- or EDXRF analyzers is efficient and accurate, and the equipment is versatile for in situ work and work in the laboratory. In the latter and window-type apertures, with appropriate calibration, smaller than the aperture size objects can be measured, using appropriately constructed set of curves per element, for which correction factors are devised per fractional coverage of the window. For other analyzers with focused X-rays beams particular surface points can be efficiently measured.

Grain size is essential for the evaluation of elemental contents, the fine grain size preferred and giving the highest values. If solid flat surfaces are used, the difference between those and the powdered samples is within counting errors, but not for some heavy elements such as Ti and Fe.

Sample thickness is essential in PXRF analysis of thin objects or unavailability of large quantities of powder. The critical depth  $D_c$  of the secondary X-rays depends upon the atomic number  $Z$  of the searched element, thus appropriate curves of  $D_c$  vs.  $Z$  may be produced for different rock types that assess this point.

The calibration as well as the interlaboratory comparison is essential .

PXRF instruments are extremely useful in a variety of applications in archaeology and history of art as they help to avoid destruction and conform to archaeologists' demand of non-invasive sampling. Many worldwide applications to cultural materials including ceramics, clays, soils, painted surfaces, and metals, enhance the value of PXRF and have produced useful results.

PXRF offers a unique opportunity for the non-destructive study of ancient materials, and portability is critical in making this technique effective. In this area, big steps forward have been taken: spectrometers weighing hardly a few kilograms have been built, thanks to the combined use of miniaturized X-ray tubes and thermoelectrically cooled detectors. Such advancement in portables rivals and, in most cases, acts independently of cumbersome laboratory instruments.

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## References

- Acquafredda, P., Andriani, S., Lorenzoni, S., Zanettin, E., (1999) Chemical characterization of obsidians from different Mediterranean sources by nondestructive SEMEDS analytical method. *Journal of Archaeological Sciences* 26, 315–325.
- Agnoli, A., Calliari, I., Mazzocchin, G.-A., (2007) Use of different spectroscopic techniques in the analysis of roman age wall paintings. *Annali di Chimica* 97 (1–2), 1–7.
- AlKofahi, M.M., AlTarawneh, K.F., (2000) Analysis of Ayyubid and Mamluk dirhams using X ray fluorescence spectrometry. *X-Ray Spectrometry* 29, 39–47.
- Andrikopoulos, K.S., Daniilia, S., Roussel, B., Janssens, K., (2006) In vitro validation of a mobile Raman-XRF microanalytical instrument's capabilities on the diagnosis of Byzantine icons. *Journal of Raman Spectroscopy* 37 (10), 1026–1034.
- Appoloni, C.R., Blonski, M.S., Parreira, P.S., Souza, L.A.C., (2007) Pigments elementary chemical composition study of a gainsborough attributed painting employing a portable Xrays fluorescence system. *AIP Conference Proceedings* 884, 459–464.
- Baxter, M.J., (1994) *Exploratory multivariate analysis in archaeology*. Edinburgh University Press, Scotland.
- BellotGurlet, L., Le Bourdonnec, F.X., Poupeau, G., Dubernet, S., Bos, M., Vrieling, J.A.M., van der Linden, W.E., (2000) Nondestructive analysis of small irregularly shaped homogenous samples by Xray fluorescence spectrometry. *Analytica Chimica Acta* 412, 203–211.
- BellotGurlet, L., Dorigel, O., Poupeau, G., Keller, F., Scorzelli, R.B., (2002) First characterization of obsidian from Colombian and Ecuadorian sources using ICPAES and ICPMS. *Proceedings of the 31st International Symposium on Archaeometry*, Jerem, E. and Biro, T. (eds.), Archaeopress Archaeolingua, BAR International Series 1043 (II), 678–684.
- BellotGurlet, L., Dorigel, O., Poupeau, G., (2008) Obsidian provenance studies in Colombia and Ecuador: obsidian sources revisited. *Journal of Archaeological Science* 35 (2), 272–289.
- Bos, M., Vrieling, J.A.M., Van der Linden, W.E., (2000) Nondestructive analysis of small irregularly shaped homogeneous samples by X ray fluorescence spectrometry. *Analytica Chimica Acta* 412, 203–211.
- Buxeda i Carrigos, J., Jones, R.E., Kilikoglou, V., Levi, S.T., Maniatis, Y., Mitchell, J., Vagretti, L., Wardle, K.A., Andrews, S., (2003) Technology transfer at the periphery of the Mycenaean World: the cases of Mycenaean pottery found in Central Macedonia (Greece) and the plain of Sybaris (Italy). *Archaeometry* 45 (2), 263–284.

- Capitan - Vallvey, L.F., Manzano, E., Medina - Florez, V.J., (1994) A study of the materials in the mural paintings at the "Corral del Carbon" in Granada, Spain. *Studies in Conservation* 39 (2), 87–99.
- Carter, T., Poupeau, G., Bressy, C., Pearce, N., (2006) A new programme of obsidian characterization at Catalhoyuk, Turkey. *Journal of Archaeological Sciences* 33 (7), 893–909.
- Cesareo, R., Gigante, G.E., Iwanczyk, J.S., Dabrowski, A., (1992) Use of a mercury iodide detector for Xray fluorescence analysis in archaeometry. *Nuclear Instruments and Methods in Physics Research A* 322, 583–590.
- Cesareo, R., Gigante, G.E., Canegallo, P., Castellano, A., Iwanczyk, J.S., Dabrowski, A., (1996) Applications of noncryogenic portable EDXRF systems in archaeometry. *Nuclear Instruments and Methods* 380, 440–445.
- Cesareo, R., Gigante, G.E., Castellano, A., (1999) Thermoelectrically cooled semiconductor detectors for nondestructive analysis of works of art by means of energy dispersive Xray fluorescence. *Nuclear Instruments and Methods A* 428, 171–181.
- Cesareo, R., Cappio Borlino, C., Stara, G., Brunetti, A., Castellano, A., Buccolieri, G., Marabelli, M., Giovagnoli, A.M., Gorghinian, A., Gigante, G.E., (2000) A portable EDXRF apparatus for the analysis of sulphur and chlorine in frescoes and stony monuments. *Trace Microprobe Technology* 18 (1), 23–33.
- Cojocar, V., Constantinescu, B., Stefanescu, I., Petolescu, C.M., (2000) EDXRF and PAA analyses of Dacian gold coins of "Koson" type. *Journal of Radioanalytical and Nuclear Chemistry* 246 (1), 185–190.
- Craig, N., Speakman, R.J., PopelkaFilcoff, R.S., Glascock, M.D., Robertson, J.D., Shackley, M.S., Aldenderfer, M.S., (2007) Comparison of XRF and PXRF for analysis of archaeological obsidian from southern Perú. *Journal of Archaeological Science* 34 (12), 2012–2024.
- Davis, M.K., Jackson, T.L., Shackley, M.S., Teague, T., Hampel, J.H., (1998) Factors affecting the energy dispersive X ray fluorescence (EDXRF) analysis of archaeological obsidian. In Shackley, M.S. (ed.), *Archaeological Obsidian studies, method and theory*, Plenum Press, New York, 159–180.
- De Francesco, A.M., Crisci, G.M., Bocci, M., (2007) Non destructive analytical method using XRF for determination of provenance of archaeological obsidian from the Mediterranean area: a comparison with traditional XRF method. *Archaeometry* 50 (2), 337–350.
- Desnica, V., Škarić, K., JembrihSimbuerger, D., Fazinić, S., Jakšić, M., Mudronja, D., Pavličić, M., Peranić, I., Schreiner, M., (2008). Portable XRF as a valuable device for preliminary in situ pigment investigation of wooden inventory in the Trski Vrh Church in Croatia. *Applied Physics A: Materials Science and Processing* 92 (1), 19–23.
- Ebel, H., (1999) Xray tube spectra. *X-Ray Spectrometry* 28, 255–266.
- Ferretti, M., Moioli, P., (1998) The use of portable XRF systems for preliminary compositional surveys on large bronze objects. A critical review after some years' experience. In *Proceedings of the International Conference Metal 98*, Draguignan 2729 May 1998, Mourey, W. and Robiola, L. (eds.), 39–44.
- Ferretti, M., Guidi, G., Moioli, P., Scafe R., Seccaroni C., (1991) The presence of antimony in some grey colours of three paintings by Correggio. *Studies in Conservation* 36, 235–239.
- Ferretti, M., Miazzo, L., Moioli, P., (1997) The application of a nondestructive XRF method to identify different alloys in the bronze statue of the Capitoline Horse. *Studies in Conservation* 42, 241–246.
- Gauvin, R., Lifshin, E., (2000) Simulation of X ray emission from rough surfaces. *Mikrochimica Acta* 132, 201–204.
- Gopher, Z., (1983) Physical studies of archaeological materials. *Report Progress on Physics* 46, 1193–1234.
- Guerra, M.F., (2008). An overview on the ancient goldsmith's skill and the circulation of gold in the past: the role of Xray based techniques. *X-Ray Spectrometry* 37 (4), 317–327.
- Hall, E.T., Schweizer, F., Toller, P.A., (1973) Xray fluorescence analysis of museum objects: a new instrument. *Archaeometry* 15, 53–78.

- Haruyama, Y., Saito, M., Muneda, T., Mitani, M., Yamamoto, R., Yoshida, K., (1999). Comparison between PIXE and XRF for old Japanese copper coin analysis. *International Journal of PIXE* 9, 181–188.
- Kallithrakas-Kontos, N., Katsanos, A.A., Touratsoglou, J., (2000) Trace element analysis of Alexander the great's silver tetradrachms minted in Macedonia. *Nuclear Instruments and Methods in Physics Research B* 171 (3), 342–349.
- Karydas, A.G., (2007) Application of a portable XRF spectrometer for the noninvasive analysis of museum metal artefacts. *Annali di Chimica* 97 (7), 419–432.
- Karydas, A.G., Kotzamani, D., Bernard, R., Barrandon, J.W., Zarkadas, Ch., (2004) A compositional study of a museum jewellery collection (7th - 1st c. BC) by means of a portable XRF spectrometer. *Nucl. Instr. Meth. in Physics Res. B* 226, 15–28.
- Kitov, B.I., (2000) Calculation features of the fundamental parameter method in XRF. *X-Ray Spectrometry* 29, 285–290.
- Knoll, G.F., (2000) Radiation detectors for X-ray and gamma-ray spectroscopy. *Journal of Radio-analytical and Nuclear Chemistry* 243 (1), 125–131.
- Kondrashov, V.S., Rothenberg, S.J., SajoBohus, L., Greaves, E.D., Liendo, J.A., (2000) Increasing reliability in gamma and X-ray spectral analysis: least moduli approach. *Nuclear Instruments and Methods in Physics Research A* 446 (3), 560–568.
- Kunicki-Goldfinger, J., Kierzek, J., Kasprzak, A., Malozewska - Bucko, B., (2000) A study of eighteenth century glass vessels from central Europe by x-ray fluorescence analysis. *X-Ray Spectrometry* 29, 310–316.
- Langhoff, N., Arkadiev, V.A., Bjeoumikhov, A.A., Gorny, H.E., Schmalz, J., Wedell, R., (1999) Concepts for a portable X-ray spectrometer for nondestructive analysis of works of art. *Berliner Beiträge zur Archäometrie* 16, 155–161.
- Leslie, C., Matthew, G., Moriarty, D., Speakman, R.J., Glascock, M.D., (2007) Feasibility of field portable XRF to identify obsidian sources in Central Petén, Guatemala. In *Archaeological chemistry: analytical methods and archaeological interpretation*, Glascock, M.D., Speakman, R.J., Popelka Filcoff, R.S. (eds.), 506–521. ACS Publication Series 968. American Chemical Society, Washington, DC.
- Leung, P.L., Daze, S., Stokes, M.J., (2000a) EDXRF surface shape correction for thick sample measurement using an outer mark membrane. *X-Ray Spectrometry* 29 (5), 360–364.
- Leung, P.L., Peng, Z.C., Stokes, M.J., Li, M.T.W., (2000b) EDXRF studies of porcelains (800–1600 A.D.) from Fujian, China with chemical proxies and principal component analysis. *X-Ray Spectrometry* 29(5), 253–259.
- Linke, R., Schreiner, M., (2000) Energy dispersive X-ray fluorescence analysis and X-ray micro-analysis of medieval silver coins. *Mikrochimica Acta* 133, 165–170.
- Liritzis, I., (2005) Ulucak (Smyrna, Turkey): chemical analysis with clustering of ceramics and soils and obsidian hydration dating. *Mediterranean Archaeology and Archaeometry* 5(3), Special Issue, 33–45.
- Liritzis, I., (2007) Assessment of Aegean obsidian sources by a portable EDXRF analyzer (grouping, provenance and accuracy). In *Proceedings of the 4th Symposium of the Hellenic Society for Archaeometry*, Facorellis, Y., Zacharias, N., Polikreti, K. (eds.), Archaeopress, BAR International Series 1746, 399–406.
- Liritzis, I., Polychroniadou, E., (2007) Optical and analytical techniques applied to the Amfissa Cathedral mural paintings made by the Greek artist Spyros Papaloukas (1892–1957). *Revue d'Archaeometrie (Archaeosciences)* 31, 97–112.
- Liritzis, I., Drakonaki, S., Vafiadou, A., Sampson, A., Boutsika, T., (2002) Destructive and nondestructive analysis of ceramics, artefacts and sediments of Neolithic Ftelia (Mykonos) by portable EDXRF spectrometer: first results. In Sampson, A. (ed.), *The Neolithic settlement at Ftelia, Mykonos*, University of the Aegean, Department of Mediterranean Studies, Rhodes, 251–272.

- Liritzis, I., Sideris, C., Vafiadou, A., Mitsis, J., (2007) Mineralogical petrological and radioactivity aspects of some building material from Egyptian Old Kingdom monuments. *Journal of Cultural Heritage* 9, 1–13.
- Longoni, A., Fiorini, C., Leutenegger, P., Sciuti, S., Fonterotta, G., Ströder, L., Lechner, P., (1998) A portable XRF spectrometer for nondestructive analyses in archaeometry. *Nuclear Instruments and Methods A* 409, 407–409.
- Lugliè, C., Le Bourdonnec, F.X., Poupeau, G., Bohn, M., Meloni, S., Oddone M., Tanda, G., (2006) A map of the Monte Arci (Sardinia Island, Western Mediterranean) obsidian primary to secondary sources. Implications for Neolithic provenance studies. *C R Paleo* 5, 995–1003.
- Lugliè, C., Le Bourdonnec, F.X., Poupeau, G., Atzeni, E., Dubernet, S., Moretto P., Serani, L., (2007). Early Neolithic obsidians in Sardinia (Western Mediterranean): the Su Carroppu case. *Journal of Archaeological Science* 34, 428–439.
- Mantzourani, H., Liritzis, I., (2006) Chemical analysis of pottery samples from Kantou Kouphouvounos and Sotira Tepes (Cyprus): a comparative approach. Reports of the Department of Antiquities, Cyprus, 63–76.
- Papadopoulou, D.N., Zachariadis, G.A., Anthemidis, A.N., Tsirliganis, N.C., Stratis, J.A., (2006). Development and optimisation of a portable microXRF method for in situ multielement analysis of ancient ceramics. *Talanta* 68 (5), 1692–1699.
- Papadopoulou, D., Sakalis, A., Merousis, N., Tsirliganis, N.C., (2007). Study of decorated archaeological ceramics by micro Xray fluorescence spectroscopy. *Nuclear Instruments and Methods in Physics Research A* 580 (1), 743–746.
- Papageorgiou, I., Liritzis, I., (2007) Multivariate mixture of normals with unknown number of components. An application to cluster Neolithic ceramics from the Aegean and Asia Minor. *Archaeometry* 49 (4), 795–813.
- Pappalardo, G., Karydas, A.G., La Rosa, V., Militello, P., Pappalardo, L., Rizzo, F., Romana, F.P., (2003) Provenance of obsidian artefacts from different archaeological layers of Phaistos and Hagia Triada. *Creta Antica* 4, 287–300.
- Pappalardo, L., Karydas, A.G., Kotzamani, N., Pappalardo, G., Romano, F.P., Zarkadas, Ch., (2005). Complementary use of PIXE-alpha and XRF portable systems for the nondestructive and in situ characterization of gemstones in museums. *Nuclear Instruments and Methods in Physics Research B* 239 (12), 114–121.
- Pérez-Arantegui, J., Resano, M., García - Ruiz, E., Vanhaecke, F., Roldán, C., Ferrero, J., Coll, J., (2008). Characterization of cobalt pigments found in traditional Valencian ceramics by means of laser ablation inductively coupled plasma mass spectrometry and portable Xray fluorescence spectrometry. *Talanta* 74 (5), 1271–1280.
- Pillay, A.E., (2001) Analysis of archaeological artefacts: PIXE, XRF or ICPMS?. *Journal of Radioanalytical and Nuclear Chemistry* 247 (3), 593–595.
- Pollard, A. M., (1986) Multivariate methods of data analysis. In Greek and Cypriot pottery: a review of scientific studies, (ed. R. E. Jones). Fitch Lab. Occas. Pap., 1, Brit. Sch. Athens, 56–83, Athens.
- Potts, J.P., West, M., (eds), (2008). *Portable Xray fluorescence spectrometry: capabilities for in situ analysis*. The Royal Society of Chemistry, Cambridge.
- Potts, J.P., Webb, P.C., Williams - Thorpe, O., (1995) Analysis of silicate rocks using fieldportable Xray fluorescence instrumentation incorporating a mercury (II) iodide detector: a preliminary assessment of analytical performance. *Analyst* 120, 1273–1278.
- Potts, J.P., Williams-Thorpe, O., Webb, C.P., (1997) The bulk analysis of silicate rocks by portable XRay fluorescence: Effect of sample mineralogy in relation to the size of the excited volume, Geostandards Newsletter. *The Journal of Geostandards and Geoanalysis* 21 (1), 29–41.
- Potts, J.P., Ellis, A.T., Kregsamer, P., Marshall, J., Streli, C., West, M., Wobrauschek, P., (2001) Atomic spectrometry update: Xray fluorescence spectrometry (The Royal Society of Chemistry). *Journal of Analytical and Atomic Spectrometry* 16, 1217–1237.



- Rebocho, J., Carvalho, M.L., Marques, A.F., Ferreira, F.R., Chettle, D.R., (2006) Lead postmortem intake in human bones of ancient populations by <sup>109</sup>Cd based Xray fluorescence and EDXRF. *Talanta* 70 (5), 957–961.
- Romano, F.P., Pappalardo, G., Pappalardo, L., Garraffo, S., Gigli, R., Pautasso, A., (2006) Quantitative nondestructive determination of trace elements in archaeological pottery using a portable beam stability controlled XRF spectrometer. *X-Ray Spectrometry* 35 (1), 17.
- Roth, B.J., (2000) Obsidian source characterization and hunter gatherer mobility: an example from the Tuscon basin. *Journal of Archaeological Science* 27, 305–314.
- Rotondi, G., Urbani, G., (1972) Non destructive analysis of chemical elements in paintings and enamels. *Archaeometry* 14, 65–78.
- Sandor, Z., Tolgyesi, S., Gresits, I., Kaplan - Juhasz, M., (2000) Qualitative and quantitative analysis of medieval silver coins by energy dispersive Xray fluorescence method. *Journal of Radioanalytical Nuclear Chemistry* 246 (2), 385–389.
- Schwedt, A., Mommsen, H., Zacharias, N., (2004) Postdepositional elemental alterations in pottery: neutron activation analyses of surface and core samples. *Archaeometry* 46, 85–101.
- Shackley, M.S., (2005) *Obsidian. Geology and archaeology in the North American Southwest*. University of Arizona Press, Tucson.
- Sokaras, D., Karydas, A.G., Oikonomou, A., Zacharias, N., Beltsios, K., Kantarelou, V., (2009) Combined elemental analysis of ancient glass beads by means of ion-beam, portable XRF and EPMA techniques, *Analytical Bioanalytical Chemistry* 395, 199–2209.
- Spoto, G., Torrisi, A., Contino, A., (2000) Probing archaeological and artistic solid materials by spatially resolved analytical techniques. *Chemical Society Reviews* 29 (6), 429.
- Tite, M.S., (2008) Ceramic production, provenance and use: a review. *Archaeometry* 50, 216–231.
- Tykot, R., (2001) Chemical fingerprint and source tracing of obsidian: the central Mediterranean trade in black gold. *Accounts of Chemical Research* 35, 618–627.
- Uda, M., Sassa, S., Taniguchi, K., Nomura, S., Yoshimura, S., Kondo, J., Iskander, N., Zaghoul, B., (2000) Touchfree in situ investigation of ancient Egyptian pigments. *Naturwissenschaften* 87 (6), 260–263
- Uda, M., Demortier, G., Nakai, I., (eds.), (2005) *X rays in archaeology*. The Netherlands, Springer.
- Vandenabeele, P., Moens, L., Edwards, H.G.M., Dams, R., (2000a) Raman spectroscopic database of Azopigments and application to modern art studies. *Journal of Raman Spectroscopy* 31 (6), 509–517.
- Vandenabeele, P., Wehling, B., Moens, L., Edwards, H., De Reu, M., Van Hooydonk, G., (2000b) Analysis with microRaman spectroscopy of natural organic binding media and varnishes used in art. *Analytical Chimica Acta* 407, 261–274.
- Wegrzynek, D., (2005) (Trans) portable XRF spectrometer with polycapillary optics and vacuum chamber. XRF Newsletter, IAEA, Issue 10, December.
- Williams-Thorpe, O., (1995) Obsidian in the Mediterranean and Near East: a provenancing success story. *Archaeometry* 37, 217–248.
- Williams-Thorpe O., Potts, P.J., Webb, P.C., (1999) Field portable non destructive analysis of lithic archaeological samples by X ray fluorescence instrumentation using a mercury iodide detector: comparison with wavelength – dispersive XRF and a case study in British stone Axe provenancing. *Journal of Archaeological Science* 26 (2), 215–237.
- Willis, J.P., Lachance, G.R., (2000) Resolving apparent differences in mathematical expressions relating intensity to concentration in Xray fluorescence spectrometry. *The Rigaku Journal* 17 (1), 23–33.
- Willis, J.P., Lachance, G.R., (2002) Debate on some algorithms relating concentration to intensity in XRF spectrometry. *The Rigaku Journal* 19 (1), 25–34.
- Wobruschek, P., Halmetschlager, G., Zamini, S., Jokubonis, C., Trnka, G., Karwowski, M., (2000) Energy dispersive xray fluorescence analysis of Celtic glasses. *X-Ray Spectrometry* 29, 25–33.

- Wu, J., Leung, P.L., Li, J.Z., Stokes, M.J., Li, M.T.W., (2000) EDXRF studies on blue and white Chinese Jingdezhen porcelain samples from the Yuan, Ming and Qing dynasties. *X-Ray Spectrometry* 29, 239–244.
- Zacharias, N., Beltsios, K., Oikonomou, Ar., Karydas, A.G., Bassiakos, Y., (2008) Thermally and optically stimulated luminescence properties of an archaeological glass collection from Thebes, Greece. *Journal of Non Crystalline Solids* 354, 761–767.
- Zacharias, N., Bassiakos, Y., Hayden, B., Theodorakopoulou, K., Michael, C.T., (2009) Luminescence dating of deltaic deposits from eastern Crete, Greece: geoarchaeological implications. *Geomorphology* 109 (1–2), 46–53.