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ED-XRF analysis for Cultural Heritage: is quantitative evaluation always essential?

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Abstract. Energy Dispersive X-Ray Fluorescence (ED-XRF) is a very suitable tool for examination of Cultural Heritage materials because of its simplicity, with no requirement for any sample preparation and the possibility of operating with portable instruments, and it can probably be considered the most useful non-destructive analytical technique for ancient valuable objects of archaeological, historical or artistic interest. As regards the possibility of getting quantitative analysis in archaeometric applications, the problems arising from the limited sensitivity in detecting low Z elements, the irregular shape or the non-homogeneous composition of the sample have generated a widespread opinion that only semi-quantitative analyses are possible in XRF applications to archaeometry. In fact, this is always true for non-homogeneous samples as, typically, painting layers. On the contrary, the problems deriving from limited sensitivity in detecting matrix light elements as well as from irregular surface under analysis can be solved in most cases. Notwithstanding, working on unique and not standardized objects requires to pay attention on details and to know how to choose correct parameters and calculation algorithms to obtain reliable results. Indeed opportunities to deal with these objects are very limited and results have implication in other fields, so that each information about materials and production technique is of great interest. Two typical materials of archaeological interest showing particular features are considered - namely high corroded metallic artefacts and ceramics - revealing that, even if in cultural heritage field detailed quantitative analysis is the goal, it is not always necessary as also qualitative information by XRF spectra increase the knowledge of artefact.

1. Introduction

Although the analyses using X-rays do not represent the only application of radiation to the study of cultural heritage, those based on the detection of characteristic X-ray fluorescence are surely the most used, involving also PIXE (particle induced X emission) and SEM (scanning electron microscope). XRF acronym refers to the analysis of material obtained through X-ray fluorescence excited by X-rays; this technique, multi-elemental and non-destructive, enables in situ analysis on a high measuring points, as no actual sample collection is needed [1].

As is well known, rather complicated mathematical manipulations are required to estimate the quantitative elemental composition accurately from intensity data [2]. Two conditions simplify the problem: if the exciting radiation is monochromatic and if the object presents a flat surface so that the angle of incidence of the exciting radiation and the direction of the emitted radiation can be determined.

Yet, archaeological, historical or artistic objects in general have irregular shapes, or non-geometric reliefs on their surface, and often inhomogeneous composition, both due to degradation processes or to



execution technique. During the years, various methods were developed to overcome the former difficulty [3]. Yet, hypotheses to get the equation for the quantitative determination of detected elements include also the microscopic homogeneity of samples and this means that any surface change or layering, both due to ageing or to original production, prevent us from getting reliable quantitative results.

2. Hypothesis and limits for quantitative ED-XRF analysis

The main limits to get quantitative analysis when using the energy dispersive version for X-ray spectroscopy - EDXRF - are ascribable to the limited detector sensitivity in revealing low Z elements, to the irregular shape or the non-homogeneous composition of the sample. For this reason, semi-quantitative analyses are sometimes preferred [4] in applications to archaeometry, even if the problems deriving from limited sensitivity in detecting matrix light elements as well as from irregular surface under analysis can be solved in most cases [5]. The mathematical procedures to get equations for quantitative XRF analysis show various complexity degrees depending on thickness, geometry and composition of the considered sample. Different algorithm are present in literature [2, 6] and more recently computer programs [7] allow the transformation from intensity peaks in the spectrum to concentration of detected elements. Basing on the fundamental parameter method [6], it is possible to clearly understand how to overcome the intrinsic limit of the technique.

Considering n elements in a sample, and supposing they all are detectable by XRF, we get

$$I_i = I_0 P \varepsilon_i G C_i \phi_1 \left[\frac{\mu_{ph}^i(E_0)}{\mu^M(E_0)\phi_1 + \mu^M(E_i)\phi_2} \right] \quad (1)$$

where:

I_i is the intensity of the considered element i

I_0 is the intensity of incident monochromatic radiation

P includes the atomic factors

ε_i is the detector sensitivity for the considered emission of the element i

G is a geometrical factor

C_i is the weight concentration of element i , to be detected

Φ_1 and Φ_2 are the cosecants respectively of incident and detection angle

$\mu_{ph}^i(E_0)$ is the photoelectric mass absorption coefficient at incident energy

$\mu^M(E_0)$ and $\mu^M(E_i)$ are the total mass absorption coefficients respectively for incident energy and characteristic energy of considered element I for the sample matrix, being M the weighed sum of the

weigh concentration of all the present chemical elements, i.e. $\mu^M(E_i) = \sum_{j=1}^n c_j \mu^M(E_i)$.

The above formula for characteristic X-ray intensity can be easily deduced under the hypothesis of exiting monochromatic radiation, infinite thickness of the sample with respect to X-rays penetration depth, no secondary excitation effects, collimated X-ray beams and well defined angles, homogeneous sample. But while the three first circumstance have been used here only for sake of simplicity – and more complex equations can account for different situations [2, 6] – the last two are absolutely necessary to the reliability of analytical results. For samples with irregular shape, for which angles are in general not well defined, some mathematical expedients can be applied [8]. In the case of samples with coating or surface alteration, quantitative analysis is surely not possible with traditional spectrometers, preventing form the possibility to get elemental concentration for both corroded or by nature layered samples. In these cases, the quantitative analyses is almost forbidden; nonetheless, as it will be shown later, interesting information on cultural heritage materials can anyway be deduced.

What is clearly stated by equation (1) is that the intensity of emitted X-rays in a sample is a function of the concentration of the element i itself and of the concentration of all the elements present in the sample, through the μ^M . This last dependence is referred to as matrix effects.

Usually, to ease calculation and improve results, the ratio with a reference standard analysis, in the experimental conditions, is considered, obtaining

$$c_i = \frac{I_i}{I_i^S} \frac{\sum_{j=1}^n c_j (\mu_j(E_0)\phi_1 + \mu_j(E_j)\phi_2)}{\mu^S(E_0)\phi_1 + \mu^S(E_i)\phi_2} \quad (2)$$

where the summit index S refers to the same parameters of eq. 1 for the reference standard.

Being the concentrations of each chemical element in the sample present in the formula, no calibration curve is possible unless the samples in study are very similar. Indeed, this is a system of homogeneous equations that must be solved adding the closing condition

$$\sum_{j=1}^N c_j = 1 \quad (3)$$

Moreover, if light non detectable elements are present, equations (1) and (2) state that also detected element cannot be quantified. Evaluation of self-absorption is needed to take into account the contribution of non-detected elements; this allows to quantify the detected elements, considering the effect of the light matrix in terms of absorption of x-rays. In the cultural heritage field, this is the case, for instance, of glasses and ceramics. Many papers have been published, resolving this problem [5, 9] in various ways, yet all of them consider the intensity of Rayleigh and Compton scattered peaks to get self-absorption evaluation of the light matrix.

3. Application to Cultural Heritage materials: case studies

Notwithstanding the intrinsic limits, expressed above, of ED-XRF application on cultural heritage materials, this technique is one of the most used in the field due to its non-destructivity, rapidity, portability that allows to work also in hostile location such as on scaffoldings, platforms or places where no electricity is supplied. This is particularly valuable when artistic objects cannot be moved for practical, conservative or economic reasons and an accurate qualitative elemental characterization can however increase the knowledge of the artefact. From experience, in fact, we learn that it is possible to extract essential information already from qualitative or semi-quantitative XRF analysis whenever the quantitative evaluation of chemical elements detected is not possible in an easy way, for instance in the case of glasses or gold gildings. In this cases, a semi-quantitative analysis can be applied, based on the ratio between significant detected elements corrected by their self-absorption coefficients.

When working on cultural heritage materials, the overview on the objects has to be as large as possible, always keeping in mind the necessity of portability and non-destructivity. So, one technique alone is hardly enough to get a complete picture on the artefacts: also XRF greatly advantages from the support of some other chemical and physical techniques. The most suitable and commonly used techniques are Raman, Fourier Transform Infrared Spectroscopy (FTIR) and UV-vis-NIR spectroscopy that can give different point of view to be related [10].

In the following, two examples on different materials will be considered. The former, showing how the qualitative information get from XRF spectra are good enough to obtain important information on the artefact, giving hints to historians and archaeologists; the guess is to obtain the provenance classification of ceramics without passing through the quantitative analysis. The latter example shows how the use of a complementary analytical technique can help XRF to give good results for quantitative evaluation even if the object conditions seem to be out of reach. In both cases, the focus will be mainly on the analytical method to get the most from qualitative XRF analysis, while archaeological or historical conclusions will be left aside.

3.1. *Comparison between quantitative XRF analysis and portable XRF spectra for provenance classification of archaeological bricks*

Pottery and earthenware are the most abundant tracers in archaeological excavations: they can account for ancient commercial trades and roads, besides being indicators for technological progress; for this reason, archaeologists are highly interested in the provenance of shards. The analytical tool widely used to find out different geographical proveniences among the sets of archaeological pottery is the examination of the elemental chemical composition, mainly focused on trace elements, in association with chemometric analysis [11]. In the following, the classification results on a set of bricks from the medieval Chartusian monastery of Certosa di Pavia, in the Po valley, northern Italy, is obtained both exploiting both a traditional XRF laboratory set up (on untreated taken samples) and a portable XRF spectrometer (in situ, directly on the charterhouse walls).

The study aims at verifying if a correct classification is possible even if the quantitative determination of minor and trace elements is abandoned, allowing a faster response when a large amount of data is concerned [12]. To this aim, weight concentration was determined from laboratory XRF measurements only while entire spectra were considered for the in situ campaign. Data were then submitted to different statistical data treatments to obtain provenance classification [13].

Twenty six bricks were considered, pertaining to different periods of original building. Nondestructive EDXRF analysis in the laboratory was performed in the fracture areas of sampled fragments to avoid external contamination. A Bruker spectrometer (Artax 200) was used, equipped with a Mo anode X-ray tube with the beam collimated down to 0.65 mm in diameter. The characteristic X-ray radiation emitted by the sample is passed to a silicon drift detector. A Mo transmission filter (12.5 mm thick) has been used for incident radiation and the working conditions were 25 kV and 0.7mA with an acquisition time of 100 s for each measurement. Weight concentrations were obtained using the AXIL-QXAS software and the National Institute of Standards and Technology (NIST) standard reference material 679. Eleven elements were considered, namely K, Ca, Ti, Mn, Fe, Cu, Zn, Rb, Sr, Zr, and Pb. For each sample, three measurement points were considered to check the homogeneity of the artifact; then, elemental concentration for homogenous samples was averaged and close to 100% for multivariate analyses and classification [14]. Measurements for three samples (namely 10b, 15a, and 15c) were rejected as they turned out not to be homogeneous. Normalizing the sample concentration to 100% is necessary to eliminate the differences among samples due to different silicate presence or firing temperatures, which could induce a varying weight loss also in samples with similar raw materials. This procedure is particularly advisable whenever samples contain indefinite amounts of extraneous material. For archaeological ceramics, the basic constituent of which is clay, an extraneous substance such as crushed shell or crushed stone, called temper, could have been added to the original raw material to improve the properties of the manufactured products. Classification has been obtained by principal component analysis (PCA), exploiting the correlation matrix, which permits to compare variables on different scales standardizing data [15].

Score and loading plots for the first two principal components (captured variance is 83.7%) are shown in figure 1. We note that most of the samples form a big, not very compact ellipse-shaped group, whereas a few samples act as outliers, namely 12a and 14b (higher Ca content and lower K and Fe content), 10a and 14a (higher Ca content and lower K content), and 11d. This result will be the reference point to check the classification obtained by the spectra classification.

In situ nondestructive EDXRF analysis was carried out using Bruker's Tracer III SD portable spectrometer equipped with a Rh target X-ray tube and a silicon drift detector. Working conditions were 20 mA at 40 kV and a spot size on the sample of 4 mm radius. Measuring time was set to 100 s.

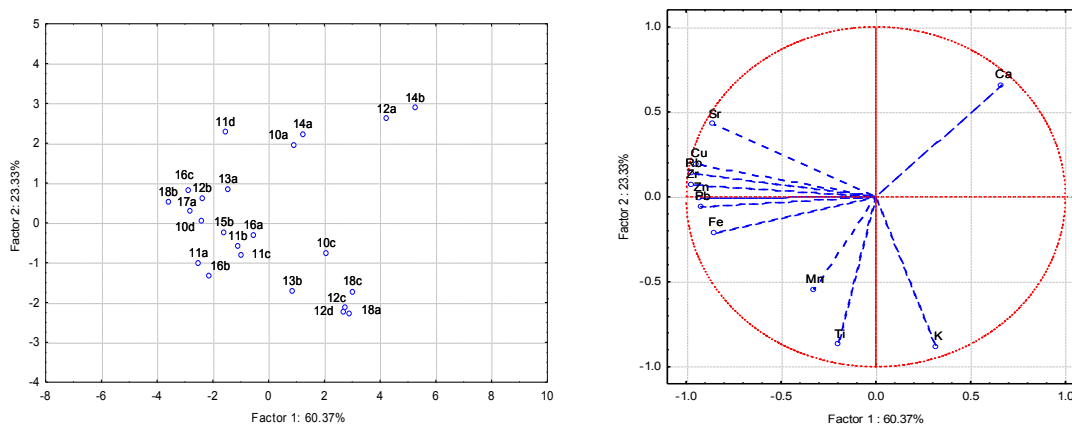


Figure 1: Score and loading plots (PC1 and PC2) from quantitative EDXRF analysis for the 23 bricks from Certosa di Pavia.

Analyses were performed directly on the monastery walls, in the same zone where samples had been previously taken, but because of the size of the instrumentation, spectra acquisition was not possible for all the sampled areas: two samples (12b and 17a) were thus left out. Our target is to obtain a correct classification directly applying multivariate analysis on the remaining 24 XRF spectra. For classification, we considered only the range of the spectra between 3 and 15 KeV (i.e. between K and Sr Ka peaks). Moreover, before performing PCA, spectra acquired on 2048 channels have been expressed in counts per second, smoothed (average on two nearest neighbors through LabVIEW software) and then rescaled so that the coherent scattering peaks have the same intensity value.

For the spectra analysis, the covariance matrix was considered [16]. In fact, the correlation matrix would standardize data, and in this case, it could confuse background noise with lower signals. On the other hand, the problem in using the covariance matrix is that the variables with the highest variance will dominate the first Principal Component. As in the samples some elements are present in a few percent while others in traces (i.e. ppm), XRF peaks in spectra highly differ in intensity and the highest peaks would dominate the first principal component, causing a loss of information. To avoid this problem, a logarithmic scale was used, getting the advantage of comparable peak heights [17].

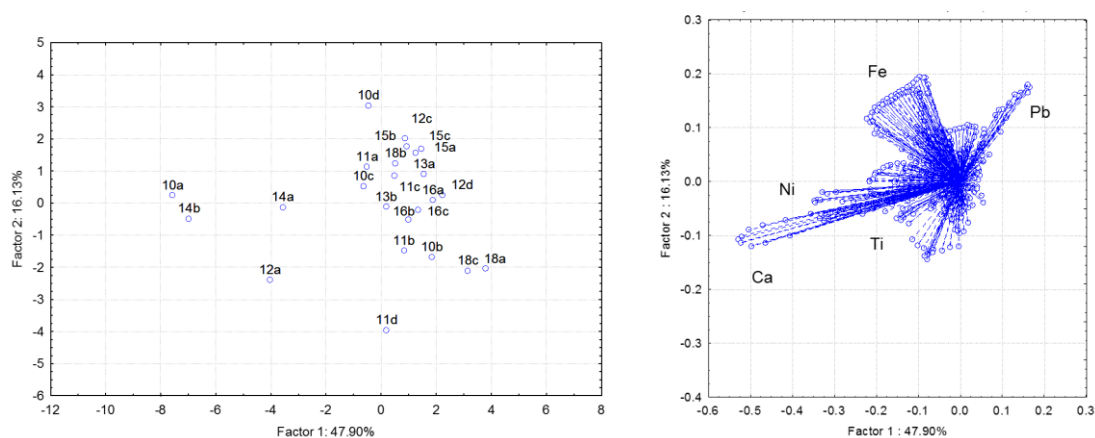


Figure 2: Score and loading plots (PC1 and PC2) from portable XRF spectra analysis for the 23 bricks from Certosa di Pavia.

The score and loading plots from PCA (covariance matrix) on the 24 in situ acquired spectra (smoothed, cut, and in logarithmic scale) is shown in figure 2. It is noticeable that a few channels (corresponding to some characteristic peaks, as indicated in the figure) weigh more on the principal components. Moreover, principal components with non-zero eigenvalues are only 23. From the PC1 and PC2 plot, it is evident that the considered samples form a compact group apart from samples 10a, 12a, 14a, and 14b, still to be distinguished on the basis of their Ca and Fe peaks, as well as sample 11d. From this results, we can say that is possible to get a reliable provenance classification of pottery avoiding quantitative analysis. Even if spot analysis can be misleading when we deal with non-homogeneous samples, we can apply multivariate analyses on entire spectra, paying attention to eventual geometry problems. This suggest to acquire more than one spectrum each sample when using handheld spectrometers.

3.2. Getting help from other techniques: quantitative EDXRF analysis of highly corroded metal artefacts

When dealing with highly mineralised historical objects, the quantitative EDXRF analysis cannot be applied due to the non-homogenous nature of the corrosion layer. Yet, combining EDXRF analysis with micro-Raman spectroscopy gave successful results in the identification of elements characterising the alloy of highly corroded metal samples and the patina surface and make it possible to determine the characteristic elements of the alloy [18].

The samples considered are from the grave goods of the Royal Tomb 14 (Sipán, Peru), found in the Lambayeque region, north of the Peruvian coast, in 2007 and pertaining to the one of the most remarkable among pre Inca civilisations, the Moche culture [19]. The crafts of metalworking was highly developed in the Moche society [20]; the metal smiths developed alloys of copper with either silver or gold and some silver, used to produce hammered sheet metal to serve as raw material for the manufacture of silver- or gold-looking objects by depletion gilding and electrochemical replacement plating [21].

Most of the scientific works published about Sipán artefacts analyses [22] are dealing with well-preserved object while the two fragments analysed in this work (metal foils about 1 mm thick reported in figure 3) are highly corroded and no polishing at all was possible. Due to deterioration of the original alloy, in fact, the artefacts analysed in this work were rather fragile and could not resist hard polishing aimed at cleaning off corrosion products. They were hence characterized through XRF, using both a portable instrument and a capillary collimated spectrometer to investigate details, and micro-Raman spectroscopy, to get mineralogical data on the green corrosion patina, formed during their long burial. It was composed mainly by copper oxides and copper sulphites, such as malachite, atacamite and magnetite.

Quantitative XRF analysis was performed starting from the data acquired using the same set up (Bruker Artax 220) described in paragraph 3.1; the working conditions were 50 kV and 0.6 mA with an acquisition time of 300 s for each measurement. Detected elements were Cl, Ca, Fe, Cu, Au, Hg, Ag for each measurement point in both samples. Being Cu, Au and Ag the elements of the alloy (likely tumbaga), Fe, Ca and Cl were supposed to derive from Cu reactions with the environment. Hg presence, instead, should be explained with the tradition of painting object and corpse with cinnabar, a red pigment composed of Hg and S [23] and not linked to metal extraction techniques. Knowing that complete copper mineralisation in malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) would leave 57% Cu [24], quantitative analysis has been conducted bearing in mind that there are significant amounts of non-detectable elements (as C, O and H) and that and that the concentration of some elements like Fe, Al, Si, Ca and Na is increased selectively by corrosion processes in copper artefacts by comparison with relative Cu concentration with respect to the original alloy composition.

To perform quantitative analysis, only gold, copper and silver were then taken into account as they were supposed to be part of the original alloy. Setting the normalisation condition and forcing copper to be present only as atacamite and malachite the weight concentration of selected elements was evaluated.

Reliability of obtained results was proved comparing analytical results former compositional analyses on some other Moche handworks belonging to the same period [24], considering, for our

samples, each measurement points as a freestanding [25]. The overall compositional data have been treated by means of cluster analysis, a multivariate method which allows to highlight groups of objects within the data set. In our application similarity between objects has been measured by Euclidean distance and the objects have been clustered by complete linkage using the statistical package SCAN (Software for Chemometric Analysis. Minitab Inc., State College, PA, USA, 1995).



Figure 3: The two sample from Sipan graves considered in the reported analyses: Sample 1Cu22-1 (on the right) and Sample 1Cu22-3 (on the left).

The dendrogram reported in figure 4 shows the similarity between the 24 measurement points on our metal sheets (code from 1 to 24) and the 28 Moche artefacts from literature [24] (codes from 25 to 53). The very large group contains all our samples which show a similarity with sub-groups from literature data higher than 90%. Two other groups are formed by objects with a high content of silver and gold and by the three objects belonging to a different historical period, respectively from left to right.

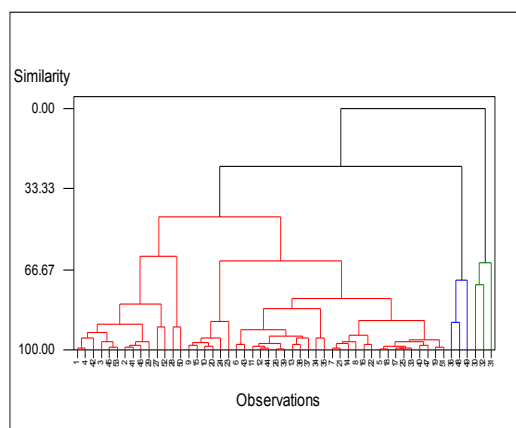


Figure 4: The two sample from Sipan graves considered in the reported analyses: Sample 1Cu22-1 (on the right) and Sample 1Cu22-3 (on the left).

This indicates that, even if our data surely lack of accuracy, they are still reliable and the result opens the possibility to perform EDXRF non-invasive measurements in situ on highly mineralised sample.

4. Conclusions

Cultural heritage field is very peculiar due to the unicity and preciousness of the artefacts involved in the analysis. For this reason, particular attention must be paid when performing scientific examinations, both when working directly on the objects and when analysing the spectra and data. Clearly, the quantitative analysis is the goal, but it is not always necessary as also reliable qualitative information increases the knowledge of artefact itself. Different experimental set-up are advisable in this cases to enlarge the amount of information obtained, such as the help of different analytical techniques that can give a larger and more complete view on the artefact.

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References

- [1] Mantler M and Schreiner M 2000 *X-Ray Spectrom.* **29** 3
Dran J C Calligaro T and Salomon J 2000 in *Modern Analytical Methods in Art and Archeology* (New York: Wiley)
José-Yacamán M and Ascensio J A 2000 in *Modern Analytical Methods in Art and Archeology* (Wiley, New York)
- [2] Lachance G R and Claisse F 1994 *Quantitative X-Ray fluorescence Analysis* (New York: Wiley)
- [3] Milazzo M and Cicardi C 1998 *Archaeometry* **40**, 351
Milazzo M 2004 *Nucl. Instr. and Meth. in Phys. Res. B* **213** 683
Bonizzoni L, Maloni A and Milazzo M 2006 *X-Ray Spectrom.* **35** 390
- [4] Moioli P and Seccaroni C 2000 *X-Ray Spectrom.* **29**, 48
- [5] Milazzo M 2004 *Nucl. Instr. and Meth. in Phys. Res. B* **213** 683
He F and Van Espen P 1990 *NIM A* **299** 580
Wobrauschek P Halmetschlager G Zamini S Jokubonis C Trnka G and Karwowski M 2000 *X-Ray Spectrom.* **29** 25
Confalonieri L Crippa R and Milazzo M 1987 *Appl. Radiat. Isot.* **38** 139
Bui C Milazzo M and Monichino M 1987 *NIMB* **28** 88
Bonizzoni L Galli A and Milazzo M 2000 *X-ray Spectrom.* **29** 443
- [6] Tertian R and Claisse F 1982 *Principles of Quantitative X-Ray Fluorescence Analysis* (London: Heyden)
- [7] He F and Van Espen P 1990 *NIM A* **299** 580
Van Espen P Janssens and K Swenters I 1994 *Manual for AXIL Software*. Canberra-Packard
XRF Q 6.0 ASSING LITHOS 3000, user handbook
Solé V A Papillon E Cotte M Walter Ph and Susini J 2007 *Spectrochim. Acta Part B* **62** 63
- [8] Milazzo M and Cicardi C 1997 *X-ray Spectrom.* **26** 211
Avaldi L Bui C Milazzo 1985 *M X-ray Spectrom.* **14** 159
- [9] Bui C Confalonieri L and Milazzo M 1989 *International Journal of Radiation Applications and Instrumentation. Part A. Applied Radiation and Isotopes* **40** 375
- [10] Rosia F Burnstockb A Van den Berge K J Miliania C Brunetti B G and Sgamellotti A 2009 *Spectrochimica Acta A* **71** 1655
Hocquet F P Calvo del Castillo H Cervera Xicotencatl A Bourgeois C Oger C Marchal A Clar M Rakkaa S Micha E and Strivay D 2011 *Analytical and Bioanalytical Chemistry* **399** 3109
Bonizzoni L Caglio S Galli A Poldi G 2008 *Applied Physics A* **92** 203
- [11] Jones R A 1986 *Greek and Cypriot Pottery* (Athens: The British School)
- [12] Freitas R P Calza C Lima T A Rabello A and Lopes R T 2010 *X-Ray Spectrom.* **39** 307
- [13] Bonizzoni L Galli A Gondola and M Martini M 2013 *X-Ray Spectrom.* **42** 262
- [14] Bonizzoni L Galli and A Milazzo M 2010 *X-Ray Spectrom.* **39** 346
Aruga R 1998 *Talanta* **47** 1053
- [15] Marengo E Aceto M Robotti E Liparota M C Bobba M and Pantò G 2005 *Anal. Chim. Acta* **537** 359
- [16] Massart D L Vandegiuste B G M Deming S N Michotte Y and Kaufman L 1988 *Data handling in science and technology vol.2* (Netherlands: Elsevier)
- [17] Baxter M J Buck C E in *Modern Analytical Methods in Art and Archaeology* 2000 (New York: Wiley)

- [18] Galli A Bonizzoni L Sibilia M and Martini M 2011 *X-Ray Spectrom.* **40** 74
- [19] Lechtman H Erlij A and Barry E J Jr 1982 *Am. Antiq.* **47** 3
- [20] Hoèrz G and Kallfass M 2000 *Mater. Character.* **45** 391
- [21] Donnan C B Scott D A and Bracken T 2008 in *The Art and Archaeology of the Moche* (Eds.: S. Bourged, K. L. Jones), University of Texas Press
- [22] Cesareo R, Rizzutto M A Brunetti A and Rao D V 2009 *Nucl. Instr. Meth. Phys. Res. B* **267** 2890
Cesareo R Brunetti A and Ridolfi S 2008 *X-Ray Spectrom.* **37** 309
Cesareo R Bustamante A Fabian J Calza C Dos Anjos M Lopes R T Elera C Shimada I Curayd V and Rizzutto M A 2010 *X-Ray Spectrom.* **39** 122
- [23] Cesareo R Bustamante A Fabian J Calza C Dos Anjos M Lopes R T Elera C Shimada I Curayd V and Rizzutto M A 2010 *X-Ray Spectrom.* **39** 122
- [24] Chapdelaine C Kennedy G and Ulceda Castillo S 2001 *Archaeometry* **43** 373
- [25] Bonizzoni L Galli and A Milazzo M 2010 *X-Ray Spectrom.* **39** 346