Volume 8, Number 3, 2015. pp. 157-163

Jordan Journal of Physics

ARTICLE

Non-Destructive SR-XRF Analysis of Ancient Mamluk-Ayyubid Glazed Pottery Fragments from Karak Castle, Jordan

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Received on: 5/1/2015; Accepted on: 11/6/2015

Abstract: Sixteen Ayyubid-Mamluk glazed pottery sherds were analyzed in order to identify and characterize the elemental composition to determine their provenance. The tested sherds were collected from the historical site of Karak Castle, southern Jordan. Chemical analysis for the sixteen samples has been carried out using Synchrotron Radiation X-ray Fluorescence Spectrometry (SR-XRF) Technique. Furthermore, the semi-quantitative analysis of the elements Fe – Cu – Zn – Br – Rb – Sr – Y – Zr – Nb – Mo – Pd – Ag – Cd and Pb has been performed for the samples based on Principal Component Analysis (PCA) and hierarchical Cluster Analysis with Bray-Curtis in order to define grouping of different glazed pottery by obtaining information on their similarity and clustering. The results of chemical analysis provided persuasive evidence that the Karak Castle pottery sherds have at least three different sources of provenance.
Keywords: SR-XRF; Semi-quantitative; Karak Castle; Ayyubid-Mamluk pottery; Non-destructive, Multivariate statistical.

Introduction

During the past years, several studies have been carried out concerning the analysis of archaeological ceramics employing different techniques. Many studies dealt with the determination of chemical composition [1]. One of the most important questions asked by archaeologists is pertinent to the provenance of the excavated object. Provenance studies provide a more objective assessment of the movement of pottery as each vessel carries a chemical 'fingerprint' derived from the clay of which it was made. Thus, it becomes a simple matter to establish chemical compositional groups, using a suitable multivariate statistical procedure, in order to detect outliers or overlapping samples which could indicate imports or exports [2].

According to their analyzing ability, the Synchrotron Radiation X-ray Fluorescence Spectrometry (SR-XRF) has gained an increasing interest in the field of elemental analysis [3]. Several works showing the advent of technique based on XRF can be found in the literature during the past decade. This technique can be claimed as an instrumental key that has revolutionized the analytical scene in archaeometry, as in other fields [4-8].

Semi-quantitative procedures [9] are very well suited for the analysis of samples with various unknown chemical compositions and matrices. It should be noted that the term ‘semi-quantitative’ is contradictory and is not used in a uniform way. In certain cases, this may lead to misunderstandings and therefore the word ‘semi-quantitative’ is set in quotation marks [10]. As for glass and ceramic samples, the problem of quantitative XRF analysis does not arise

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normally from the irregular shape, but because of the difficulty of evaluating the auto absorption correction due to matrix low Z elements which in most cases cannot be detected by standard solid-state portable detectors [11].

Semi-quantitative analytical procedures are increasingly becoming popular among scientists. It is worth mentioning here that the accuracy of an analytical procedure depends to a great extent on the spectral resolution, counting statistics, matrix correction and analytical procedure which are especially optimized to provide fast analysis of metals and alloy composition [10]. The energy and intensity of the XRF spectral lines are not only in accordance with the corresponding element, but also with its abundance in the sample [12].

This study presents the characterization of a group of ancient pottery. The characterization focuses on the statistical methods of chemical composition based on semi-quantitative measurements in order to define grouping of different pottery sherds. The extracted information will help know more about the provenance sources of Ayyubid-Mamluk ceramic in the site, which will strengthen the information drawn from the elaboration of compositional data and shed new light on the importance of the region as an agricultural center and a trade link between the Mamluk centers in Egypt and Syria during the Ayyubid-Mamluk period.

Archaeological Site Settings and Sampling

Karak Castle is one of the largest crusader castles in the levant (Fig. 1). It is located in Karak town which is now the administrative center of Liwa Al-Karak. It is situated on a hilltop about 1000 meters above sea level and is surrounded at three sides by deep valleys. The town is located 130 km south of Amman the capital of Jordan. It is located on the King's Highway, east of the Dead Sea in the biblical land of Moab. The Castle, perched on an elevated escarpment, was laid out on a roughly trapezoidal plan which followed the contours of the ridge on the western and eastern sides (240m and 220m, respectively), while on the northern and southern fronts (130m and 85m, respectively) the castle was protected by deep dry moats [13].

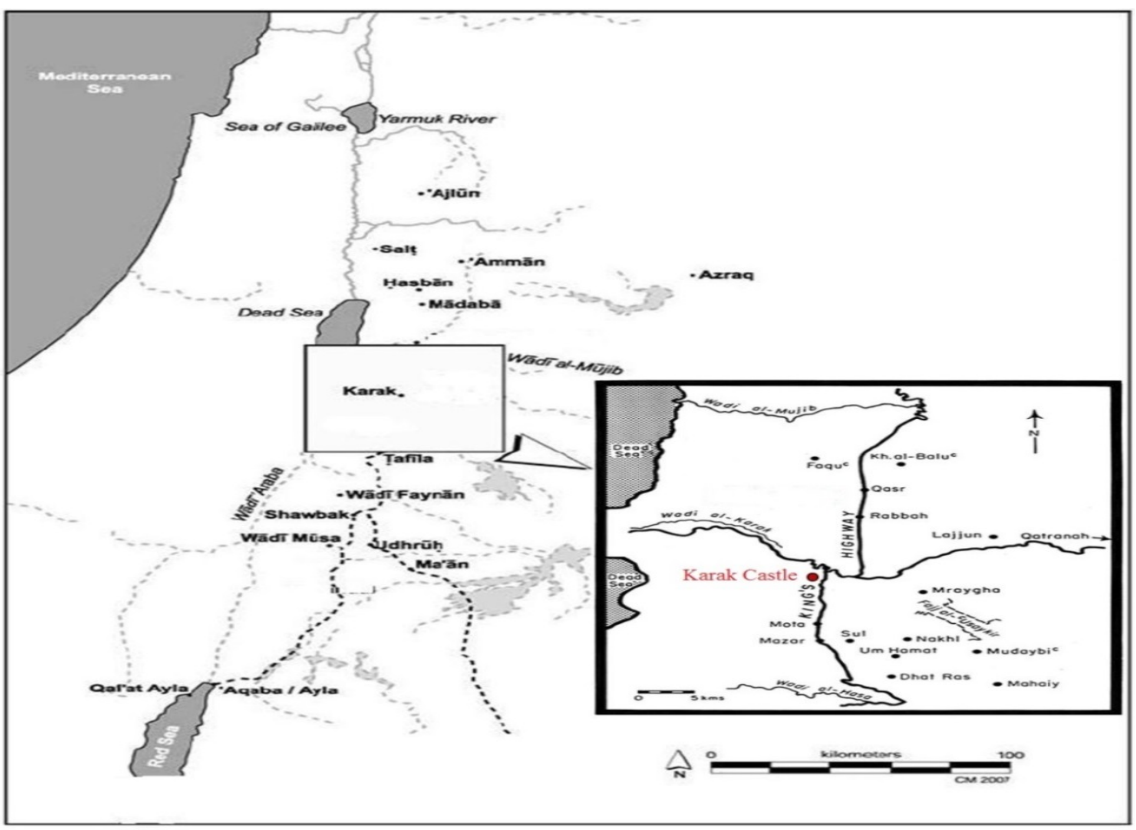

FIG. 1. Map of Jordan showing Karak Castle site and the Karak plateau.

FIG. 2. The ancient glazed ceramic sherds from Karak Castle.

Measurements and Analysis

To perform the analysis of the samples using SR-XRF, the inner part (core) of the samples was exposed to synchrotron X-ray Beam. All measurements were carried out in BAMLine at BESSY II Synchrotron light source in Berlin-Germany using 40 keV incident energy X-ray beam, focused to a (0.8x0.8) mm^2 spot size. From each tested sample, data have been acquired using an Si(Li) detector from two selected points on the core to be representative of the sample. The measurement time was 60 seconds for each sample. All measurements have been performed at room temperature. The spectra were processed by the AXIL-PC computer software program [14] based on IAEA standard program package QXAS. In order to be able to perform a semi-quantitative analysis, the elemental composition of the samples has to be identified. This task can be achieved by calculating the area under the XRF peaks. The used software in this analysis has the capability to perform the task. Semi-quantitative estimation can be a useful tool for determination of elemental concentrations, because the latter are proportional to the weight concentrations that can be measured using this technique.

The intensity of emission from each element can classify the elements. The area under the peak (counts) for a certain element in an XRF spectrum is used to calculate the abundance of the element in the sample, since the peak intensities are proportional to the concentration of the element present in the sample.

Statistical Methods

In the archaeological studies, Cluster Analysis together with Principal Component Analysis (PCA) are the most common methods used to classify items in subgroups. The PCA is a mathematical technique that allows n-dimensional identification of sample groups and is a very powerful method of exploratory multivariate statistical analysis. Also, it is often used in the interpretation of XRF artifact characterization for helping archaeologists to identify discrete compositional groups within a data set. This information may then be applied to formulate and test hypotheses on trade and exchange routes and socio-economic relationships. Cluster Analysis is a method which provides evidence for grouping the objects within the data set. The results are commonly presented as dendrograms showing the order and levels of clustering as well as the distances between individual samples [15-17].

In this work, the Bray-Curtis coefficient [18] was used to calculate similarity matrices for analysis. The Bray-Curtis coefficient is widely used in provenance determination of cultural heritage artifacts. The dendrograms were constructed using a group-average linkage hierarchical Cluster Analysis [19]. All data have been maintained and processed by the computer software package Unscrambler X Ver.10.1 (Camo ASA software, Oslo, Norway).

Results and Discussion

The SR-XRF results of Karak Castle samples are presented in Table1. The analysis results are represented by the net peak area data (in counts) for selected elements of the XRF spectra which reflect the abundance of these elements in the samples in order to perform a semi-quantitative analysis. Only 14 elements were analyzed: Fe, Cu, Zn, Br, Rb, Sr, Y, Zr, Nb, Mo, Pd, Ag, Cd and Pb. The final data set consists of 16 samples with 14 elements for ceramic pottery sherds from Karak Castle site with a total of 224 data entries. PCA and Cluster Analysis were performed. The multivariate statistical analyses have been carried out to verify the similarity between the samplings.

PCA and Cluster Analysis are routinely applied to analytical data for the purpose of group identifying of chemically similar sherds. Chemically similar sherds can be interpreted as representing, as they are made of the same raw materials or mixtures of raw materials. But this is not necessarily at the same time. Fig. 3 and Fig. 4 illustrate the Principal Component Analysis (PCA) and Cluster Analysis (CA) for the data presented in Table (1).

The data have been applied to the raw data matrix of dimensions 16×14 (samples × chemical parameters). Fig. 3 represents the scatter score plot of PC1 and PC2. The corresponding score plot suggests two large groups, while three samples; namely: CSL10, CSL12 and CSL16 do not belong to any of these two groups. Each of the two groups contains the samples that belong to the same pottery provenance source.

The two groups are characterized as follows:

(1) Group A (CSL1, CSL2, CSL3, CSL4, CSL5, CSL6 and CSL11). This group is characterized by high concentration of Iron and Strontium and low concentration of Lead as compared to samples of group B.

(2) Group B (CSL7, CSL8, CSL9, CSL13, CSL14 and CSL15). The samples belonging to this group are characterized by very high concentrations of Lead and medium concentrations of Zirconium compared to samples of group A. The samples CSL10, CSL12 and CSL16 do not belong to any of these groups as demonstrated by their different elemental composition. CSL10 shows average concentrations of Lead and Iron, while CSL12 contains high content of Lead. Sample CSL 16 contains high content of Iron and very little content of Lead. This differentiates them from groups A & B.

The hierarchical Cluster Analysis is based on Median linking and Bray-Curtis distances. The resulting dendrograms for 16 ceramic sherd samples (from Karak Castle site) were normalized as the area under the peak data as presented in (Fig. 4). The graph shows that the data set has two large distinguished groups: the 1st group consists of (CSL1, CSL2, CSL3, CSL4, CSL5, CSL6 and CSL11), and the 2nd group contains (CSL7, CSL8, CSL9, CSL13, CSL14 and CSL15). This result conforms with the PCA result. It is worth noticing that samples CSL10, CSL12 and CSL16 do not belong to any of these two groups. (CSL12 and CSL16 could to a lesser extent belong to Group B and Group A, respectively, but the verification of this result needs deeper interpretation).

TABLE 1. Net peak area (in counts) for selected elements of SR-XRF results for Karak Castle site samples.

	^{26}Fe	^{28}Cu	^{30}Zn	^{35}Br	^{37}Rb	^{38}Sr	^{39}Y	^{40}Zr	^{41}Nb	^{42}Mo	^{46}Pd	^{48}Cd	^{47}Ag	^{82}Pb
CSL 1	3005.2	59.2	113.3	90.1	217.6	4211.7	BDL	2069.0	98.0	BDL	BDL	BDL	BDL	201.3
CSL 2	4608.1	4109.8	122.0	109.0	BDL	2957.6	252.3	800.5	78.1	BDL	BDL	BDL	204.4	4778.2
CSL 3	4240.8	2842.5	131.7	BDL	BDL	3331.9	265.0	5675.8	95.5	BDL	BDL	BDL	BDL	388.5
CSL 4	3650.9	49.1	179.2	45.3	143.7	3483.8	189.0	1608.7	96.4	78.1	BDL	BDL	BDL	81.9
CSL 5	3649.0	6039.7	277.5	100.7	BDL	3871.3	274.6	2020.4	172.1	110.3	BDL	BDL	BDL	384.3
CSL 6	7452.9	85.3	143.9	BDL	381.2	3574.7	BDL	1603.4	165.2	74.0	BDL	BDL	80.3	6778.0
CSL 7	3262.1	1066.3	68.5	370.6	BDL	2039.4	BDL	3171.6	226.6	BDL	130.4	218.3	394.8	63574.6
CSL 8	3331.9	261.0	87.9	409.3	BDL	2309.8	BDL	2602.6	204.9	BDL	132.7	75.3	528.2	72693.6
CSL 9	4622.6	2736.5	92.5	519.5	BDL	2021.3	BDL	7606.1	321.3	BDL	172.4	BDL	616.2	87328.9
CSL 10	6057.9	BDL	BDL	87.5	BDL	2661.9	BDL	7908.00	540.6	BDL	BDL	119.4	BDL	33463.7
CSL 11	3767.5	41.7	81.1	BDL	193.8	2691.8	BDL	3479.1	241.6	161.4	BDL	BDL	BDL	3093.7
CSL 12	5337.9	1165.6	80.0	BDL	BDL	1400.2	BDL	3371.9	320.3	BDL	472.5	241.4	1548.9	137267.0
CSL 13	3393.1	832.9	BDL	BDL	BDL	2334.8	BDL	9379.1	577.3	BDL	122.9	108.2	411.5	38787.0
CSL 14	3345.6	1107.2	58.0	340.4	BDL	1159.0	BDL	2208.8	BDL	BDL	BDL	66.2	1304.7	60970.8
CSL 15	4687.7	1166.7	153.4	BDL	BDL	2601.1	BDL	7947.4	447.8	BDL	143.6	97.3	485.1	44800.5
CSL 16	13853.6	BDL	87.2	80.4	310.9	1442.5	BDL	15229.3	1155.1	BDL	BDL	75.4	BDL	432.2

* BDL: Below Detection Limit.

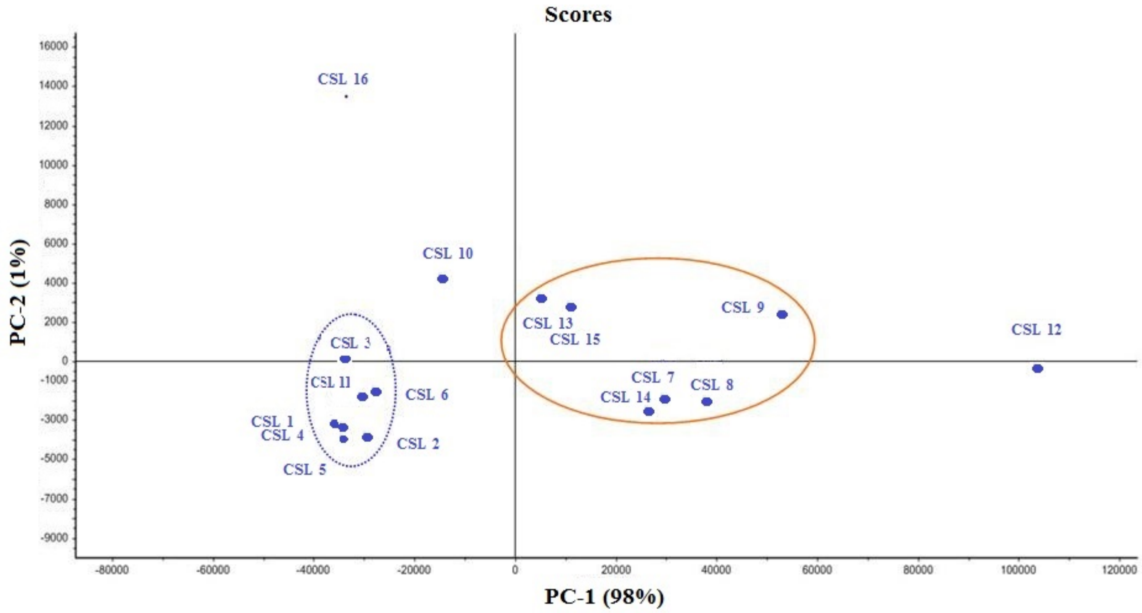

FIG. 3. Score plot of PCA of the area under the peaks of SR-XRF results for Karak Castle samples. PC1 vs. PC2 data matrix of dimensions 16x14 (16= number of samples from the site; 14= number of elements).

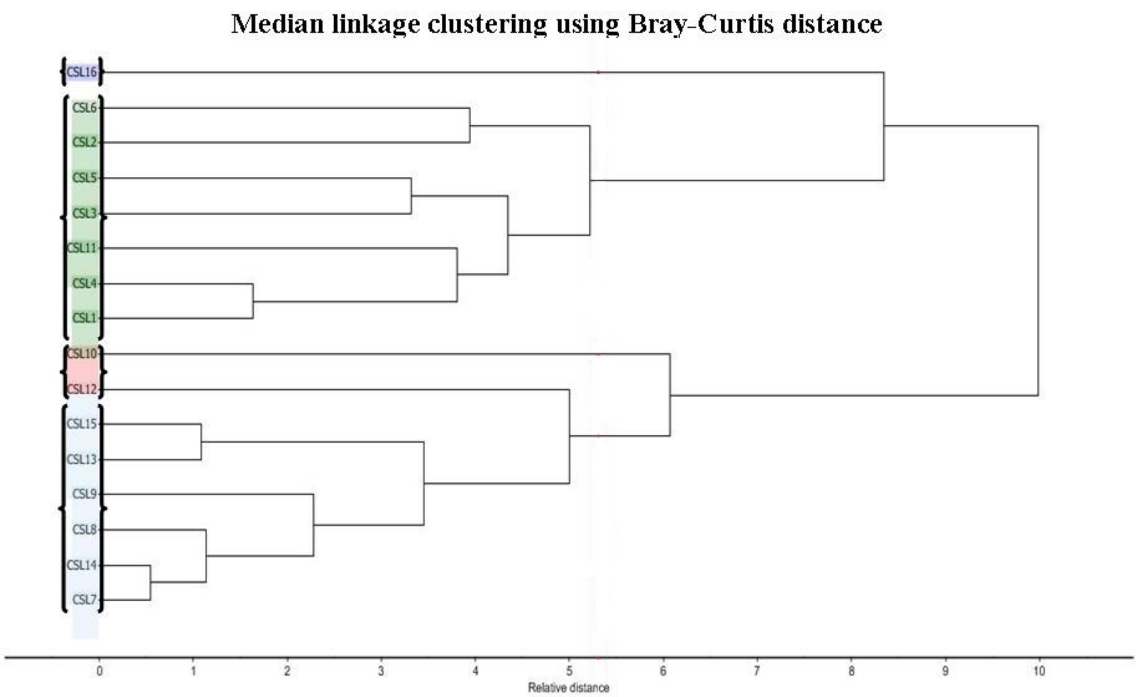

FIG. 4. Hierarchical clustering dendrograms by Median linking and Bray-Curtis distance for 16 ceramic sherd samples from Karak Castle site (area under the peaks of SR-XRF results).

Conclusions

This study demonstrates the growing importance of interdisciplinary research, particularly the importance of using SR-XRF in archaeological investigations. The increasing importance of non-destructive techniques manifests itself in archaeometry. This work investigates the chemical characterization of sixteen glazed pottery sherds dated to Ayyubid-Mamluk period from Karak Castle site in southern Jordan, in order to extract information about their original provenance. Multivariate statistical analysis gives good results concerning the fabric characterization of clay (matrix and colour) conforming to results coming from archaeologists. It is possible to confirm the use of chemical characterization of pottery sherds and statistical techniques of data handling to complete and integrate the work of archaeologists in provenance studies.

The ceramic sherd samples showed two large groups representing two different provenance regions. Also, it is evident that some samples do not belong to any of the two identified groups.

Unfortunately, the few studies available from Karak Castle site did not discuss or mention the ceramic, which were excavated from the site. Therefore, the significance of the present investigation stems from the fact that it will help archaeologists explain the cultural contacts and behaviors during the Islamic period and contribute to an understanding of human behaviors, especially when results are integrated with those of typological and technological studies, among others.

Acknowledgments

The authors would like to thank Ivo Zizak for her valuable help and discussion on the measurements and XRF analysis of the samples. They also acknowledge the synchrotron radiation source BESSY II for provision of SR. Thanks are also extended to all staff members at the BAMLine beamline for their scientific and technical support in obtaining the experimental data at Beamline. This work was supported by the IAEA/SESAME training project grant (CODE: BEAMUSER6MO).

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