Provenance studies of archaeological ceramics from Mar-Takla (Ain-Minin, Syria) using radioisotope X-ray fluorescence method

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Abstract The radioisotope X-ray fluorescence method was applied to studies of the provenance of the ceramics fragments originated from the Mar-Takla site in Syria. The samples were irradiated 1000 s by a ^{109}Cd radioisotope source and 13 elements (Ca, Ti, Mn, Fe, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, and Pb) were determined in 35 samples. The data were subjected to two multivariate statistical methods, cluster and principal components analysis (PCA). It was shown from the combination of the statistical techniques and the determination of elemental composition of the samples that 94% of the ceramic samples analyzed can be considered to be manufactured using two sources of raw materials.

Keywords X-ray fluorescence, Ceramics fragment, Provenance, Multivariate analysis

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1 INTRODUCTION

Archaeologists have been, for many years, interested in the provenance of pottery fragments, since the pottery is one of the fundamental tools used to derive archaeological information. Studies of archaeological sites in Syria have been made a reply on typology based on ceramic style to extract some information about the possible exchange between communities, as it is known that communities, which produced these wares, did not live in isolation from each other. A classification of the samples according to their physically characteristic decoration and style is one of the techniques utilized to put these material into particular groups. Another methods were based on the determination of the elemental composition of the samples. In this purpose different modern analytical techniques, such as neutron activation analysis[1~3], inductively coupled plasma (ICP)[4], particles induced X-ray emission (PIXE), and X-ray fluorescence (XRF)[5~7], were applied to determine the elemental composition of archaeological material. In the present study the radioisotope X-ray fluorescence spectrometry was applied for determining the elemental

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composition of the samples come from the excavation at the site of Mar-Takla of Ain-Minin village located at 20 km north east of Damascus city. Thirty-five samples were analyzed and at least four different physical styles were found in the selected samples. The samples fairly represent Romanian, Byzantine and Islamic ceramics made between the 3rd century B.C. and the 11th century A.D.

2 EXPERIMENTS

2.1 Sample preparation

The surface deposit was physically removed from the fragments by using nickel and Teflon coated tools. The remaining clay material was ground for 10~15 minutes using an agate motor and the resulted powder was dried in an oven at 105°C for 24 h.

2.2 Instrumentation and measurements

The analyses of the powder-pressed pellets were performed. The weighing of the samples is not needed because only relative values of the measurements are required for the radioisotope X-ray fluorescence technique. The samples were irradiated by a ^{109}Cd radioisotope source (~9×10^8 Bq) for 1000 s and the measurements of the X-ray fluorescence outgoing from the samples were carried out with an X-ray spectrometer mounting a Si(Li) detector with an energy resolution (Full-width-half-maximum) of about 180 eV at 5.9 keV for the Mn-Kα X-ray. The X-ray fluorescence data were collected and analyzed using a personal computer (Pentium 400) based multi-channel analyzer (MCA) and a quantitative x-ray analysis system (QXAS) program from the International Atomic Energy Agency (IAEA). Soil-7 (IAEA), SL-1 (IAEA) and rock GSR-3 (China) were used as the standard for testing the accuracy of sensitivity curves and the repeated analyses of several samples showed that in each case the relative standard deviation (RSD) was less than 5% for each element under investigation.

3 RESULTS AND DISCUSSION

Table 1 shows the mean and the minimum, the maximum concentration values for the determined elements in the 35 samples and their standard deviations. As listed in Table 1, a total of 13 different elements in at least several of the samples were measured. It is observed from the data in this Table that there are large variations in the elemental concentrations.

Table 1 Mean, minimum and maximum concentration values and standard deviations for the ceramic samples from Mar-Takla archaeological site. All concentrations are in $\mu g/g$ except those stated elsewhere

Element	Mean	Minimum	Maximum	Std. Dev.
%Ca	10.41	0.65	27.5	7.87
%Ti	0.614	0.30	1.20	0.32
Mn	315.9	115	715	191
%Fe	3.439	0.27	7.10	1.12
Zn	112.1	28.7	183	33.6
Ga	20.87	19.0	28.5	2.64
As	14.20	12.0	29.9	4.09
Rb	41.99	3.60	59.5	10.0
Sr	265.7	90.9	455	104
Y	25.84	5.0	54.3	15.6
Zr	322.8	54.8	703	247
Nb	22.97	4.0	48.6	17.8
Pb	82.11	10.0	656	160

In order to further determine the provenance characterization of the materials, various statistical techniques have been combined with the determination of elemental composition of the material[8~10]. In this study the cluster and principal components analysis were used as multivariate statistical methods and before subjecting the data to the multivariate methods, some criteria should be taken into account. It is important to include only the samples with few missing elemental concentration values in the data set. It is also important to take into account the precision with which the elements were measured. Based on these criteria the elements of Mn, Ga, and As were not included in the final data set used for multivariate analysis, because their concentration values are missing for more than 50% of the samples analyzed. Although the measured values for Pb have only a relative standard deviation of around 5%, they were not included in the data set because the variation of concentration values between samples was very big, this may be due to the migration of Pb from the surface into the clay paste. For this reason we found that it could introduce errors to use Pb as variable in the cluster and PCA when assigning provenance in Mar-Takla ceramics. The statistical package Statistica (version 6.0) was used to perform the multivariate analysis. Before analyses, the elemental concentration data were converted to base 10 log to normalize the element distribution and to reduce the impact of differences in magnitude for some of the major elements. The cluster analysis, which allocates samples into distinct groups, is often used in the initial inspection of data. The results are communally presented as dendrogram showing the order and levels of clustering as well as the distance between individual samples. From the resulted dendrogram showed in Fig.1, which obtained using the single linkage as grouping rule according to the Euclidean distance, it is evident that there are three groups, i.e., the first group containing 7 samples (12, 2, 23, 24, 3, 21, and 8), the second group containing

8 samples (25, 30, 28, 34, 13, 15, 1, and 26) and the third one containing the remaining samples except one sample (case 20). It is not clear from Fig.1 if the first two groups can be considered as separated or as one group. In order to confirm the last assumption the data were submitted to a principal components analysis (PCA). We report the results for the first and second principal components (PC1 and PC2) in the scatter plots since they were sufficient for our purpose as they account for 91.1% of the total variance (see Table 2). It is seen from the plot presented in Fig.2 that the samples of group 1 and group 2 except sample 26 are grouped in one group, respectively. On the other hand it is clear that sample 20 is very well separated whereas sample 26 that is included in group 2 deviates from this group. This result suggests that the two samples are outliers of the two groups or perhaps are of other provenances. Finally, the results have provided a persuasive evidence that Mar-Takla ceramics used at least two different clay sources. A systematic analysis of the local clay will confirm whether these sources are local or not.

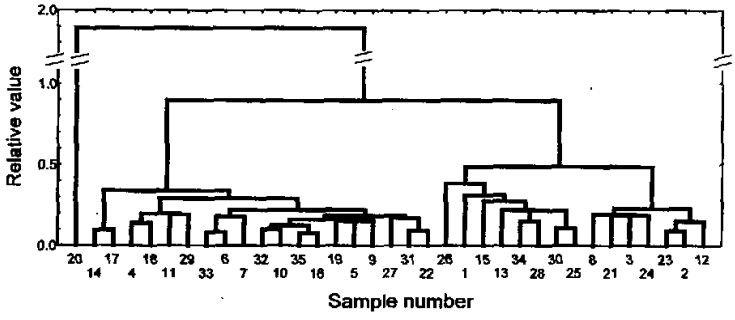

Fig.1 Grouping of the ceramic samples from Mar-Takla site by the cluster analysis

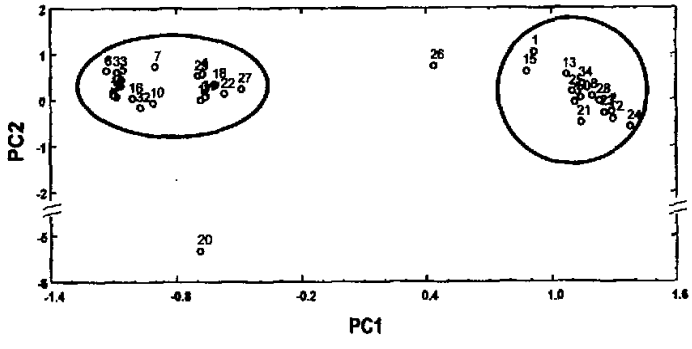

Fig.2 PC plot (first two PCs, 91.1% of total variance) resulted from the principal components analysis of chemical composition data of the samples

Table 2 Factor loading for the samples data set (nine elements, principal component analysis, varimax rotation)

Elements	Factor 1	Factor 2
Ca	-0.857*	0.331
Ti	0.972*	0.119
Fe	0.269	0.900*
Zn	-0.401	0.811*
Rb	0.244	0.899*
Sr	-0.820*	0.493
Y	0.942*	0.305
Zr	0.964*	0.187
Nb	0.963*	0.188
Variance explained by factors, %	60.1	31.0

Note: The marked loading is >0.700

4 CONCLUSION

Combination of the XRF analysis and statistical analysis is helpful for archaeologists in Syria, who now work on typology classifying material in fragmented conditions. In this study, by resorting to the cluster analysis and principal components analysis, of the concentration of 13 elements, quantitatively measured by the radioisotope X-ray fluorescence technique, most of the 35 pottery fragments could be divided into two large categories which are characterized by different concentration levels of particular elements. The two categories suggest that the two groups of samples that came from the same archaeological site belong to different geo-chemical historical origins.

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