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Research Article

Provenance Study of Archaeological Ceramics from Syria Using XRF Multivariate Statistical Analysis and Thermoluminescence Dating

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Thermoluminescence (TL) dating and multivariate statistical methods based on radioisotope X-ray fluorescence analysis have been utilized to date and classify Syrian archaeological ceramics fragment from Tel Jamous site. 54 samples were analyzed by radioisotope X-ray fluorescence; 51 of them come from Tel Jamous archaeological site in Sahel Akkar region, Syria, which fairly represent ceramics belonging to the Middle Bronze Age (2150 to 1600 B.C.) and the remaining three samples come from Mar-Takla archaeological site fairly representative of the Byzantine ceramics. We have selected four fragments from Tel Jamous site to determinate their age using thermoluminescence (TL) method; the results revealed that the date assigned by archaeologists was good. An annular ^{109}Cd radioactive source was used to irradiate the samples in order to determine their chemical composition and the results were treated statistically using two methods, cluster and factor analysis. This treatment revealed two main groups; the first one contains only the three samples M52, M53, and M54 from Mar-Takla site, and the second one contains samples that belong to Tel Jamous site (local).

1. Introduction

Analysis of archaeological ceramics can confirm the information recorded in historical documents, such as trade routes linking populations of different areas, and help to find out the chronology of events. Establishing databases of Syrian ceramics, by using many techniques, was started a few years ago.

The classification of ceramics based on typology is one of useful methods, but only when applied to whole or reconstructed objects [1, 2]. The chemical composition of the made ceramics is unique and related to sources identification of provenance [3–5], from which they were fashioned. In order to classify ceramics, we need to determine the chemical composition of a large number of samples and they should be from a single site and from a single period.

To reach this goal many techniques were applied, since the initial ceramics study by Sayre and Dodson [6], such as X-ray fluorescence (XRF) [7, 8], proton induced X-ray emission (PIXE) [9, 10], and neutron activation analysis (NAA) [3, 5, 11, 12]. We applied in our laboratory most of these techniques to study archaeological objects. The main aim of our study was to prove to archaeologists the advantage of applying physical techniques and present the effectiveness of the combination of some methods in their studies such as dating of the sites and the provenance studies of ancient ceramics. The other aim was providing new additional data to the Syrian database.

In the present study we applied

(i) thermoluminescence (TL) dating for the age determination of ceramics sherds. This technique is the only available today to determine the age of ceramics. See [13, 14] for principles and mechanism of TL;

(ii) radioisotope X-ray fluorescence spectroscopy for determining the elemental composition of the ceramics, where fourteen chemical elements were determined.

XRF is nondestructive methods and allows fast multielemental analysis.

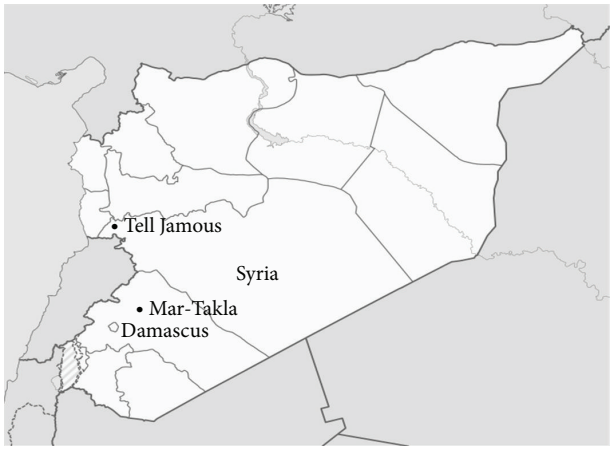

Figure 1: Map of Syria with the area considered.

Fifty-four samples were analyzed in this study. Fifty-one of them labeled 1–51 come from the excavation at the site of Tel Jamous in Sahel Akkar region located at the west of Syria (see Figure 1), which fairly represent ceramics belonging to the Middle Bronze Age (2150 to 1600 B.C.) according to archaeologists. The remaining three samples labeled M52–M54, set as "control" samples, come from excavation at the site of Mar-Takla, already studied in [7], located at 20 km north east of Damascus city (see Figure 1) and they are fairly representative of the Byzantine ceramics.

Four samples (samples J-A, J-B, J-C, and J-D) were chosen randomly among the 51 samples from Tel Jamous site, to be analyzed by thermoluminescence for age determination.

The data which consisted of the concentration of fourteen chemical elements have been treated statistically using two methods, cluster and factor analysis, to establish a categorization of the ceramics raw material source from Tel Jamous archaeological site. The chemical groups are assumed to present sources which could present the use of local material or production workshops.

2. Experimental

2.1. TL Experiment

2.1.1. Sample Preparation. The fine grain technique [14] was used, and the preparation procedure was carried out in subdued red light to avoid bleaching effects. We removed about 3 mm of the pottery's outer surface to eliminate the beta dose contamination from the soil.

The next step is to obtain a quantity of powder, about 250 mg, through the drill within the sample; after that we added acetone, about 60 cm^3, to the sample and waited for 2 min. We left the precipitant and took the solution. We added acetone again and waited for 20 min. In the next step, we took this time the precipitant with a small amount of acetone. We put, using micropipette, 3 mL of the solution in each of the glass tubes (1 cm of diameter and 6 cm of height). Finally we leave the tubes for the next day in an oven at 50°C. The separated grains then are allowed to deposit on aluminum discs in a thin layer of a few microns thickness which are placed at the bottom of individual flat-bottomed glass tubes. We prepared twenty discs for each sample, the whole discs were placed on the tray, using tweezers [15], which contain 48 holes, before measurement.

2.1.2. Instrumentation and Measurements. The age of the ceramics can be calculated by the absorbed dose or Paleodose (ED) in Gy unit divided by the dose rate (DR) in mGy/a or in Gy/ka. The absorbed dose, which is called equivalent dose (ED), is related to the time in which the samples are exposed to natural radiation, and the dose rate is the dose received from natural radiation by the sample for one year (annual dose). The measurements were performed using RISØ TL/OSL reader model DA-20 at atomic energy commission of Syria. The additive dose procedure was used to determine the absorbed dose [15]. Strontium-90 (emitting beta particles) was used as the radioactive source, with a dose rate of 0.135 Gy/s. The annual dose was estimated from measurements of the radioactive elements U, Th, and K within the sample and soil and from cosmic rate. Alpha spectrometry system was used to determine uranium and thorium while atomic absorption spectrometry was used to determine the radioactive element potassium.

2.2. XRF Experiment

2.2.1. Samples Preparation. The sherds were ground, after removal of the surface deposit, using an agate mortar; this step is important to have good homogeneity of the analyzed sherds. The obtained powders were dried at 105°C for 24 hours; after that the powders were converted into pellets with a hydraulic press [16].

2.2.2. Instrumentation and Measurements. The pellets (25 mm diameter) were irradiated for 1000 sec. live time by an annular ^{109}Cd radioactive source, which has the following specifications: activity (~9 10^8 Bq), outer diameter of 2.54 cm, active diameter of 1.9 cm, and thickness of 5 mm. An X-ray spectrometer mounting a Si(Li) detector was used for the measurements of the X-ray fluorescence and the distance between sample and detector was 3 cm. The energy resolution of the detector (full-width-half-maximum) is 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 based on the multichannel analyzer (MCA) and a quantitative X-ray analysis system (QXAS) program from the international atomic energy agency (IAEA). The subprogram AXIL [17] was used to fit the spectra in order to calculate the net peak intensities of the Kα and Lα lines. For testing the accuracy of sensitivity curves, Soil-7 (IAEA), SL-1 (IAEA), and rock GSR-3 (China) were used as standards. The repeated analyses of several samples reveal that the relative standard deviation (RSD) was less than 5% for each determined element.

2.3. Statistical Treatment. The final data which consist of observations (samples) and variables (elements) have been treated using two statistical methods, cluster analysis (CA) and factor analysis (FA), by using Statistica 8.0 package.

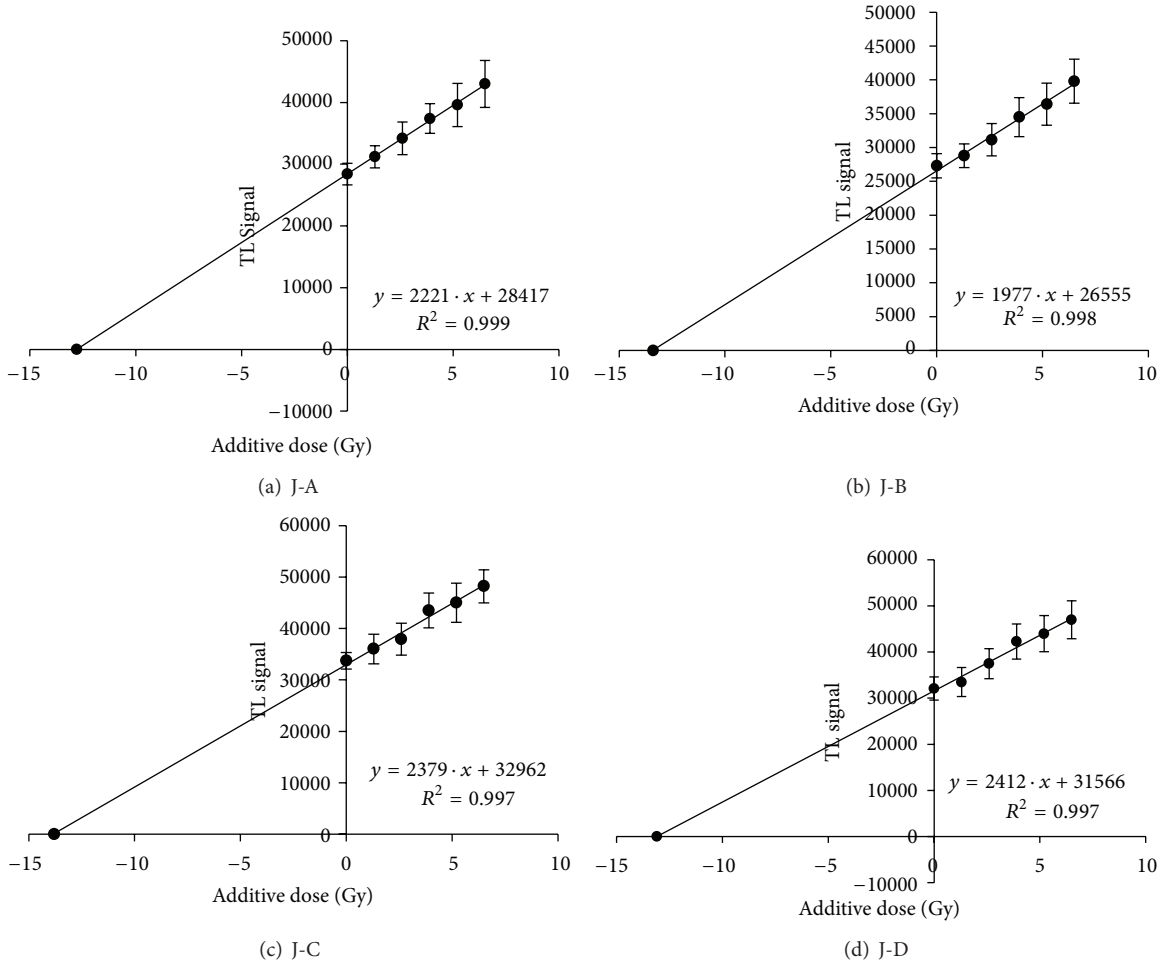

Figure 2: Luminescence counts versus additive dose for the four samples J-A, J-B, J-C, and J-D.

Cluster analysis (CA) classifies samples into distinct groups by calculating distance measures between the samples [18]. The results are commonly presented as dendrogram. We used single linkage as a grouping rule, according to Euclidean distances.

Using factor analysis (FA) we can extract a minimum number of factors which explains an acceptable amount of total variance of the data set. In general the two or three first factors are sufficient to reach this goal.

3. Results and Discussion

3.1. TL Results

3.1.1. Accumulated Dose (Paleodose). A growth curve was built on the basis of four additive beta doses using three discs for each dose. The graphs of additive dose versus luminescence counts were plotted. They are shown in Figure 2. The fitting-line of the graphs was as follows: $Y = 2221X + 28417$ (sample J-A), $Y = 1977X + 26555$ (sample J-B), $Y = 2379X + 32962$ (sample J-C), and $Y = 2412X + 31566$ (sample J-D). As it is known the intercept with the dose = 0 axis (X-axis) gives the absorbed dose. The values of the absorbed dose are presented in Table 1 (fifth column).

3.1.2. Annual Dose (Dose Rate). Alpha rays have the shortest range in geological materials (approximately 0.03 mm); beta rays traverse up to 3 mm in solid matter, while gamma rays penetrate about 30 cm, much greater than the dimensions of our pottery samples.

Before TL measurements are carried out on our sherds, the outer 3 mm of the sample is cut away. The remaining portion has therefore received its alpha and beta dose entirely from within the volume of the sherd. This dose, termed the internal dose, can be determined from an examination of the sample alone. Like the alpha and beta rays, gamma radiation derives from the decay of naturally occurring radionuclides present in the ground, such as potassium-40 and members of the uranium and thorium decay series.

The doses rates (annual doses) are presented in Table 1 (fourth column), where the internal contribution, Table 1 (second column), was calculated from alpha and beta activity measures coming from the samples taking into account the alpha correction factor (α-effectiveness, α-0.15) (Aitken, 1985) [14], while the external contribution, Table 1 (third column), was calculated from gamma activity coming from the soil. The conversion of alpha, beta, and gamma has been achieved according to Adamiec and Aitken [19] and the

Table 1: U, Th, and K concentrations with internal annual dose, external annual dose, annual dose, equivalent doses, and the ages obtained and ages assigned by archaeologists for the pottery sherds investigated.

Sample	Internal dose (mGy/a)	External dose (mGy/a)	Annual dose (mGy/a)	Archaeodose (Gy)	Age (a) B.P	Age assigned by archaeologists
J-A	2.67 ± 0.27	0.75 ± 0.06	3.42 ± 0.33	12.8 ± 0.3	3750 ± 240	1600–2150 B.C.
J-B	2.44 ± 0.26	0.75 ± 0.06	3.19 ± 0.32	13.4 ± 0.3	4200 ± 220	1600–2150 B.C.
J-C	2.76 ± 0.30	0.75 ± 0.06	3.51 ± 0.36	13.8 ± 0.5	3930 ± 270	1600–2150 B.C.
j-D	2.86 ± 0.29	0.75 ± 0.06	3.61 ± 0.35	13.1 ± 0.3	3630 ± 260	1600–2150 B.C.

The dose rate conversion factors used are given in Adamiec and Aitken [19].

cosmic rate was 0.18 Gy/ka. The calculated age before present (BP) of the sherds is presented in Table 1 (sixth column). The errors for the calculated age vary in the range of 5–10%.

We can notice from Table 1 (sixth column and last column) that the calculated ages are in accordance with the ages supposed by archaeologists.

3.2. XRF and Statistics Results. The statistical analysis was performed after elimination of the elements in the data set which have more than 25% missing values and then transform the data to base log.10. Only 12 elements were considered for the statistical analysis. The elements Cu and Ni were not included because their concentrations values are missing for more than 50% of samples analyzed.

The two elements niobium and lead have three and four missing values, respectively. The procedure used to estimate the missing values for them was to replace any missing value by the minimum detection limits (MDL) determined by XRF. The MDL are 15 ppm (niobium) and 10 ppm (lead). The final data set consisted of 54 observations (samples) and 12 variables (elements) for a total of 648 data entries.

The resulting dendrogram based on the analysis of 12 elements is shown in Figure 3. Two main clusters were found. Cluster 1 contains the three samples M52, M53, and M54 which are from Mar-Takla site and all the remaining samples, which are from Tel Jamous site, form only one group (cluster 2) except three isolated samples (2, 9, and 20).

The factor analysis (FA) was carried out on the same twelve elements used for cluster analysis. The three factors extracted in this study explain 63.8% of the total variance of the data set. Varimax method was used for rotation and maximum likelihood method was used for factor extraction.

Table 2 shows the factor loading for the three extracted factors. Factor scores quantify the relative intensities of factor strength on each sample. Samples with the same factor score patterns can be grouped together into particular categories. Figures 4 and 5 present plots of factor score 1 against factor scores 2 and 3, respectively, for each of the 54 samples. It is clear from Figures 4 and 5 that the classification is similar to the classification in the cluster analysis. Samples from Mar-Takla site identified as group 1 from the cluster analysis in Figure 3 follow a consistent pattern. The 48 samples from Tel Jamous site identified as group 2 from the CA in Figure 3 follow also a consistent pattern.

The results confirm, after statistical analysis using two methods, that there are one principal group which contains 48 samples derived from Tel Jamous site and another group which contains "control" samples, that is, samples M51, M52, and M53, derived from Mar-Takla site. The 48 samples of category 2 are thus considered to correspond to wares manufactured in Tel Jamous site.

Table 2: Factor loading for the samples data set, twelve elements.

Elements	Factor 1	Factor 2	Factor 3
Ca	−0.31	0.84	−0.25
Fe	0.32	0.29	0.52
K	−0.10	0.91	0.02
Mn	0.31	0.04	0.72
Nb	0.25	−0.77	−0.22
Pb	0.04	−0.64	−0.31
Rb	0.35	−0.20	0.51
Sr	−0.51	0.34	−0.09
Ti	0.81	−0.19	0.34
Y	0.94	−0.25	0.03
Zn	0.47	0.27	0.39
Zr	0.70	−0.15	0.38
Total variance %	25.0	24.8	14.0

Table 3: Mean values and standard deviation for the two chemical groups in the pottery. All values are in μg/g; n equals the number of samples in each category.

Elements	Group 1 (n = 3) Mar-Takla Mean ± SD	Group 2 (n = 48) Tel Jamous Mean ± SD
Ca	155000 ± 10000	75000 ± 11000
Cu	39 ± 10	45 ± 13
Fe	32000 ± 3000	49000 ± 10000
K	17000 ± 1000	11000 ± 1000
Mn	260 ± 16	600 ± 67
Nb	18 ± 2	20 ± 4
Ni	58 ± 10	77 ± 26
Pb	19 ± 3	19 ± 4
Rb	21 ± 3	47 ± 7
Sr	240 ± 28	170 ± 39
Ti	4000 ± 200	7600 ± 1200
Y	22 ± 2	32 ± 4
Zn	110 ± 13	133 ± 10
Zr	195 ± 9	310 ± 41

Finally Table 3 presents the average elemental concentration and standard deviation for the samples in categories 1 and

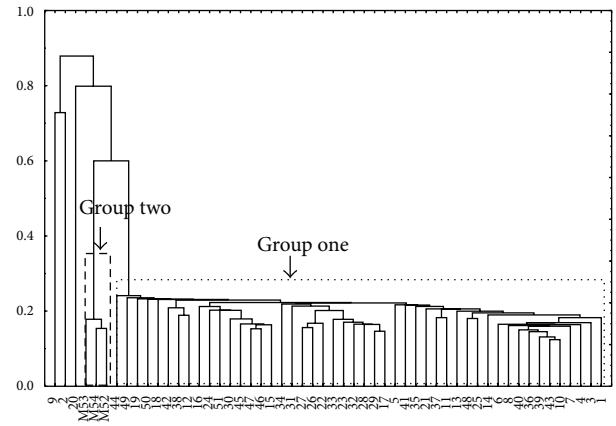

Figure 3: Grouping of pottery samples by cluster analysis.

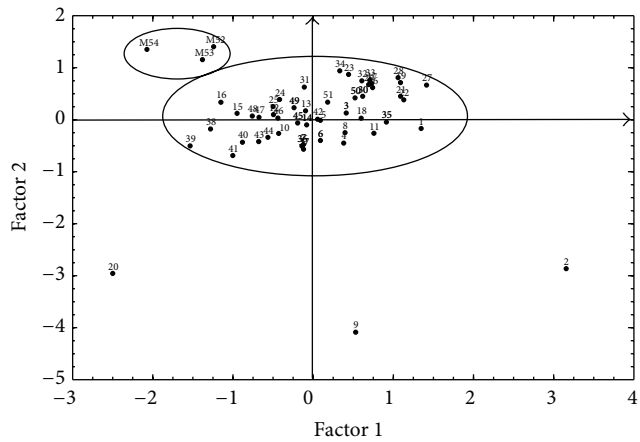

Figure 4: Factor score 1 against factor score 2 of ceramics samples.

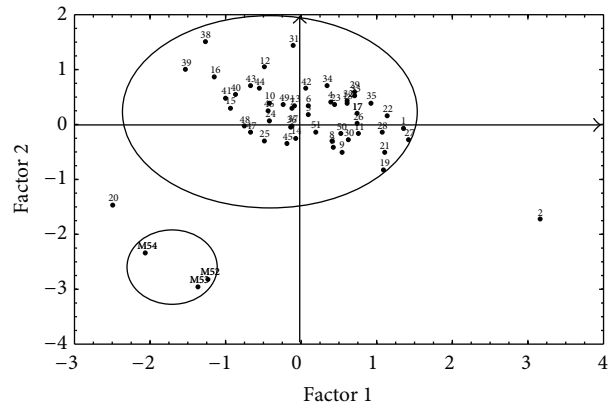

Figure 5: Factor score 1 against factor score 3 of ceramics samples.

2. It is clear from the standard deviation that there are large variations (scattering) in the elemental concentrations among the samples in the same category. It is clear from Table 3 that the concentrations of Ca, K, and Sr in Mar-Takla site are roughly 1.5 to 2 times higher than those for Tel Jamous site. It is also evident, from this table, that the concentrations of Fe, Mn, Rb, Ti, Y, and Zr in Tel Jamous site are higher than those in Mar-Takla site.

4. Conclusion

Thermoluminescence (TL) dating and X-ray fluorescence (XRF) analysis combined with multivariate statistical method have been utilized to analyze 51 ceramics samples from Tel Jamous site, Syria. Four samples among them were chosen for dating. Three additional ceramics samples from Mar-Takla archaeological site were used as "control" samples. The ceramics sherds of Tel Jamous date back to the Middle Bronze Age (2150 to 1600 B.C.) according to archaeologists. The date obtained by TL technique was in good agreement with the date assigned by archaeologists. Up to 14 elements were determined by XRF and the concentrations of 12 of them have been taken into consideration for statistical analysis where two methods were applied, cluster analysis and factor analysis, in order to classify the ceramic sherds. Statistical results separate samples 2, 9, and 20, put samples M52, M53, and M54 from Mar-Takla archaeological site in an isolated group, and confirm that there is one principal group of ceramics from Tel Jamous site. Application of XRF, TL techniques, and statistical analysis has proved to be very helpful for Syrian archaeologists to study ancient ceramics. This study could be beneficial in geological studies such as sediment studies where optically stimulated luminescence (OSL) technique is used in general instead of TL technique for chronological dating t of the sediments.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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