

Analysis of Chemical Composition for Sasanian and Parthian Artwork Found in Various Regions of Garmian Areas with Micro-XRF and P-XRF

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ABSTRACT

The objectives of this paper are to use micro-X-ray fluorescence spectrometry (μ -XRF) and portable X-ray fluorescence spectrometry to specify the quality and element percent content of Sasanian and Parthian artwork samples: glasses, metals, and ceramics found in various regions of the Garmian area to determine and characterize the element and material compositions of the studied samples. The metallic models (L, M) are made of iron, (O) brass, (N.R) bronze, and (W, Y) silver, according to our findings. Soda ash makes up the majority of the glass samples (Si, Na, Ca>1%, MgO, K₂O>1%). Sample J might be soda-lime glass because of the low Mg and K content (<1% MgO, <1% K₂O). Six of the elements tested in the ceramic samples (Cl, Co, As, Mo, W, Bi) were not measurable (<LOD). The origination of the samples is also of importance, in addition to the material composition. As a result, lead isotope analyses on the samples will be performed to assess the source of lead and lead-containing raw materials. The next measurement campaign, on the other hand, has yet to be arranged and can only be carried out with a bigger number of samples on hand.

KEYWORDS: μ -XRF, XRF, P-XRF, Sassanian and Parthian Artworks.

الخلاصة

الهدف من هذه الدراسة هو تحديد وتشخيص العناصر المكونة لعينات الاعمال الفنية للساسانيين والبارثيين: المعادن، الزجاج و السيراميك التي تم استكشافها في مناطق مختلفة من ادارة كرميان و باستخدام الاشعة السينية الدقيقة. لتحديد جودة و محتوى النسبة المئوية للعنصر في العينات (P-XRF) والاشعة السينية المحمولة (Micro-XRF). استنتجنا أن النماذج المعدنية (L, M) تتكون من الحديد، نموذج (O) من النحاس الاصفر، نموذجي (N.R) من البرونز و النموذجان (W, Y) تتكونان من الفضة اما عينات الزجاج فاعليها هي رماد الصودا (Si, Na, Ca>1%. MgO, K₂O>1%). نظراً لانخفاض نسبة Mg، K (<1% MgO, <1% K₂O) يمكن أن تكون العينة J عبارة عن زجاج حجر الكلس بالإضافة إلى تكوين المواد، فإن منشأ العينات مهم أيضاً. لذلك يجب إجراء قياسات نظائر الرصاص على العينات لتحديد منشأ الرصاص والمواد الخام المحتوية على الرصاص. ومع ذلك لم تتم جدولة للقياس هذه النظائر بعد، ولا يمكن إجراؤها إلا بعد الحصول على عدد أكبر من العينات المتاحة.

INTRODUCTION

The administrative center of Garmian is Kalar. Its 140 kilometers southeast of Sulaymaniyah and 30 kilometers from the Iranian border. Kalar is proud of its historical past. Kalar has administrative links to several minor metropolises. Kalar is located on a large plain with many historical sites dating from different periods, including those that date back to the B.C. Islamic Times (AD) [1]. Historical landmarks include Shirwana Citadel, Pasha Citadel, and the Christian Canal. Because of its proximity to the Iraqi-Iranian border and the

presence of ongoing hostilities, this region did not experience peace until 2003. In addition, there was no way to conduct archaeological investigations or research. Due to sampling, sample preparation, and analysis, archaeological research is difficult. We were able to collect numerous samples of minerals, glassware, and pottery that were excavated in different parts of the Garmian administrative area with the help of the Directorate of Antiquities and Excavations in Garmian (see Figure 1).

Analysis of Artifacts by using XRF and μ -XRF

Analytical techniques established in the field of materials science are used. It assists art historians and archaeologists in obtaining information about the material composition of specific artefacts for art objects, and archaeology provides answers to inquiries about where, when, and by whom such an item was produced [2]. Furthermore, further research like this can aid in understanding how items are manufactured and, as a result, the civilizations under study's way of life. Scientific study is frequently necessary and, in some cases, indispensable for conservation initiatives to distinguish the original elements of an object from subsequent modifications, past restoration work, or even forgeries. Furthermore, our cultural legacy is headed to extinction due to ageing and the damaging impacts on the environment.

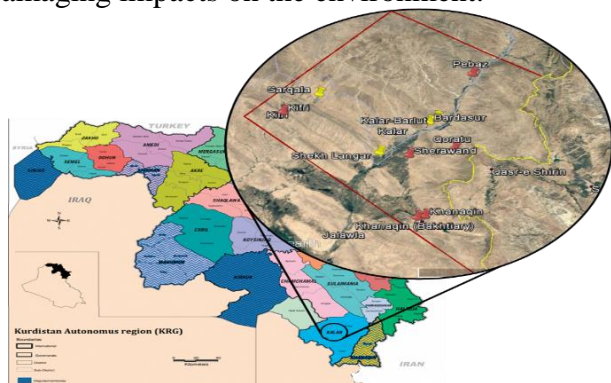


Figure 1. A map showing the sites that were excavated.

The deterioration of open-air monuments or metal sculptures is well-known. All of the objects can also be found on exhibits or in well-kept museums, archives, and libraries. They're in danger of deteriorating. To understand the dynamics of decay and create therapies and strategies to avoid or delay these processes, these phenomena must be researched in depth [3].

Two more data sources are provided for the systematic investigation of the material composition. The holistic method uses radiation from gamma rays to infrared to generate a picture of the complete item that can be seen with the naked eye. These procedures are non-destructive in the formal sense, meaning that no samples from an object are required, and the substance of an item is not affected throughout the analyses. This is appropriate for an art historian, archaeologist, or conservator interested in dealing with pieces of art. Techniques like X-ray radiography and computer

tomography for example used widely and approved. Data on the production line and the status of an object may be obtained using these approaches without having to touch the artefact. [4, 5]

Until World War II, the second source of information, which determines the material composition of tiny regions, relied mostly on chemical methods of analysis. However, because chemical and many instrumental analytical procedures are disruptive and need small samples to be removed from an item, their use to objects of art and archaeology is severely limited presently. X-ray fluorescence XRF as well as X-ray diffraction analysis XRD have gained growing interest in the last decades [6]. Both techniques are adequately nondestructive when used with attention and consideration for potential harm from high radiation doses.

X-ray fluorescence analysis (XRF) has been widely utilized for material analysis since, in principle, all elements except the first two (H, He) of the periodic table are applicable. Many light elements, on the other hand, are extremely difficult to compute and need specialist instruments, which frequently limit practical work to ordinary numbers greater than 11 (Na)[7]. Even in this case, it is impossible to detect the characteristic radiation of elements with atomic numbers between 11 and 16 (Na-S), because the majority of instruments for non-destructive object analysis must be air-path systems, and the characteristic radiation of elements must be Na-S absorbed by the atmosphere [5]. Furthermore, traditional instruments employ an X-ray beam with a diameter of several millimeters, which limits the use of XRF to certain applications like detecting pigments in tiny paintings or miniature decorating of glass, ceramic, or metal items.

Micro – x-ray fluorescence spectrometry

The development of micro X-ray tubes in combination with polycapillary lenses to focus the primary beam to less than 100 μ m and highly sensitive detectors for secondary X-rays is another step toward meeting the requirements for non-destructive investigation of art objects.

Adams et al.1997 published several examples of the application of (micro) analytical techniques appropriate for describing archaeological and artistic materials [8]. (Gem) stones, Ceramics, glass, aluminous, calcified materials, paper and

pigments use Proton Induced X-ray Emission (PIXE) and related techniques from Malmqvist [9]. Because XRF satisfies several of the aforementioned criteria, it is quite usual to utilize conventional XRF to analyze objects of artistic and/or archaeological interest. It is considered as one of the most frequent ways of obtaining qualitative and semi-quantitative data about the materials that make up these artefacts [10].

Traditional XRF, on the other hand, is severely limited in its ability to do accurate quantitative analysis because of the large exposed area. This stops those characteristics from studying the decorations' details on their own. The sample's radiation geometry and surface are frequently not perfect and/or poorly characterized, which can lead to systemic quantification errors. By employing smaller X-rays, some of these drawbacks can be eliminated. In this respect, the motorized sample mobility allows for the two-dimensional imaging of some components on the surface of objects, extending the capability of local analysis. Because many artistic and/or archaeological items are huge and voluminous (e.g., sculptures, oil paintings, vases, treasure chambers), it is much more convenient to utilize tools that can handle a variety of forms and operate in an open environment.

For radiation safety, they are usually equipped with tiny, well-shielded sample chambers. Depending on the sort of study and information needed, one of the μ -XRF types can be used.

μ -XRF may be used to do quantitative fingerprint analysis on materials to learn more about their origins, with detectability down to the ppm level for certain elements. [11]. The employment of a tiny beam allows us to do a detailed analysis of the processes that have changed the surface makeup of the material. Synchrotron micro beams' high primary strength makes them unsuitable for studying metallic compatible materials, but they're perfect for micro-analysis of organic materials (e.g., paper, pigments distributed in an organic binder) or silicate-rich materials like ceramics or glass at the trace level (e.g. artefacts of bronze, iron, silver, gold or alloys of these metals). However, laboratory μ -XRF may be utilized easily for this purpose. The Laboratory μ -XRF's strength is its ability to do local (quantitative) analyses on objects whose size, shape, or design are

incompatible with the vacuum and tiny sample housing employed by most classic micro analytical methods like EPXMA and μ -PIXE. μ -XRF offers similar options to PIXE with an external beam in this regard, but with a better lateral resolution [12]. Smaller objects (such as coins) that might be studied as a whole in standard XRF equipment benefit from employing a tiny blasting tool. To do so, the original content must be separated freely from only a small portion of the (altered) surface [13].

Choosing spots on an item that approximate the ideal is usually easier with a tiny beam. A smooth and polished surface is usually required for repeatable quantitative measurements. The current tendency in the manufacture of μ -XRF instruments is the fabrication of compact small-beam instruments consisting of an air-cooled mini-focus X-ray tube, a compact optical element for beam focusing/collimation, and a Peltier-cooled energy-dispersive detector [14]. The availability of such devices with 50-200 mm cross-section beams is particularly beneficial for in-situ assessment of historical and artistic objects, i.e. in the museum, gallery, or archaeological site where they are normally placed.

MATERIALS AND METHODOLOGY

A total of twenty-five glass, ceramic, and metal items were analyzed. The items were discovered in different parts of the Garmian area (see Figure 3) and should be classified according to their material composition. Micro-X-ray fluorescence analysis (μ -XRF) and portable X-ray fluorescence analysis (p-XRF) were used in this study.

For easier handling and optimal measurement methods, parts of all samples were embedded in epoxy resin, rubbed, and polished (Figure 2). This enables sample analysis without the interference of a corrosive layer, which would alter the results. Measurements were taken in the metal core of the metal samples in particular.



Figure 2. Left: Glass and metal samples embedded in epoxy resin. Right: Ceramic samples embedded in epoxy resin.

The parameter for characterization of parameters for the μ -XRF measurements and parameters for the XRF measurements are shown in table 1 and 2 respectively.



Figure 3. Samples of glass, Metals and Ceramic are collected during the excavations in Garmian.

Table 1. Parameters for the μ -XRF measurements.

Device description	Eagle μ -Probe II (company: EDAX, distributed by Röntgenanalytik Mess Technik GmbH)
X-ray tube	Rh tube with beryllium window, rhodium target
Accelerating voltage	10-40 [keV]
Cathode current	20-1000 μ A
Detector	Si (Li) detector
Evaluate software	Edax-Vision32. Version 3.999. Sys-Disk V3.38 Fund Param version 35
Analyzer unit	Phoenix. EDI-1
X-ray optics	Poly capillary from Kevex, type XOS 107 Length [mm]: 80.2; focus distance [mm]: 8.9; Diameter of output cross section [mm]: 4.6 (cover) Spot size: approx. 50 μ m at 5.9 keV

Table 2. Parameters for the XRF measurements

Device description	DELTA X Dynamic XRF Premium (DS 4000 CC as a premium-Version). model (company: Innov-X Systems)
X-ray tube	Rh tube with beryllium window
Acceleration voltage	10-40 [kV]
Cathode current	bis 100 μ A
Detector	SD detector with Peltier cooling
Evaluation software	Delta User Interface, factory-calibrated with pure element standards, manually optimized for mercury and arsenic
X-ray optics	Spot size 8 mm

RESULTS AND DISCUSSION

Metal samples

The qualitative and quantitative analyses of the metal samples were carried out utilizing μ -XRFA on the one-bed samples. The parameters used for the point measurements of the samples are listed in Table 3.

Table 3. Parameters used for the point measurement of the metal samples.

Parameter	Setting
Tube current	80 μ A
Tube voltage	40 kV
Spot size	50 μ m
Measuring time	150 sec
Atmosphere	Vacuum

For each sample, measurements were taken three times. In the case of sample S, substantially different contents were discovered, probably as a result of the sample's partly stronger corrosion. For each of the two regions, two measurements were taken. Table 4 lists the element contents determined by (μ -XRF) micro x-ray fluorescence analysis across a basic parameter model, along with the standard deviations.

The items constructed from various compositions. According to the results, L and M are iron metal samples. Brass is used in example O, whereas bronze is used in samples N, R, and S. The Sn concentration of sample S varies dramatically depending on the measurement location (see Figure 4). It's most likely a sample having a corrosive layer that is appositionally continuous. Because Sn

tends to collect in the corrosion layer. The two coins (examples W and Y) are definitely silver. The mean value of 3 measured values (S per 2), as well as the standard deviation, are given (see table 4). The X-ray lines used for quantification are indicated next to the element symbols. All element contents are given in % by weight. All data was standardized by the software to 100%. The <LOD elements were not quantifiable.

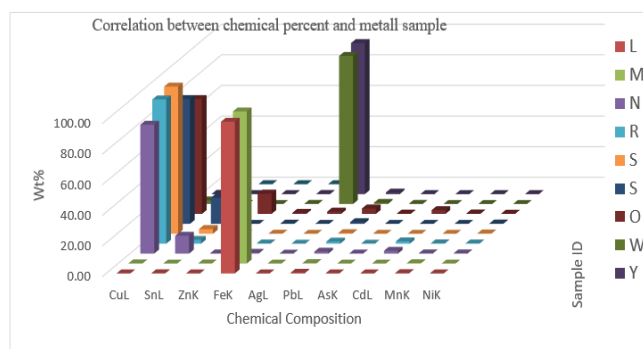


Figure 4. Correlation between element percent and metal samples.

Table 4. μ -XRF analyses of metal objects for 10 quantifiable elements.

ID	Origin	Dating	Metal type	CuL	SnL	ZnK	FeK	AgL	PbL	AsK	CdL	MnK	NiK
L	ShekhLangar (Kalar)	Parthian	Iron	0.06 ± 0.04	0.15 ± 0.22	0.05 ± 0.01	99.14 ± 0.66	<LOD	0.43 ± 0.43	0.01 ± 0.01	<LOD	0.17 ± 0.03	<LOD
M	Sarqala	Parthian	Iron	0.09 ± 0.06	<LOD	0.06 ± 0.03	99.38 ± 0.19	<LOD	0.25 ± 0.12	<LOD	<LOD	0.22 ± 0.01	<LOD
N	Bardasur	Parthian	Bronze	84.24 ± 1.02	11.67 ± 0.86	0.09 ± 0.15	0.52 ± 0.03	<LOD	1.28 ± 0.24	0.04 ± 0.04	1.85 ± 0.56	0.16 ± 0.04	0.14 ± 0.01
O	Qurato	Sasanian	Brass	75.07 ± 0.71	2.64 ± 0.23	13.28 ± 0.08	0.73 ± 0.02	1.5 ± 0.40	3.57 ± 0.41	0.23 ± 0.03	2.45 ± 0.80	0.31 ± 0.04	0.19 ± 0.01
R	Sarqala	Parthian	Bronze	94.23 ± 0.64	2.47 ± 0.95	<LOD	0.15 ± 0.05	<LOD	1.33 ± 0.51	0.01 ± 0.01	1.5 ± 0.63	0.18 ^v	0.13 ± 0.01
S	Kalar-Barlut	Parthian	Bronze	96.21 ± 0.23	3.08 ± 0.28	<LOD	0.09 ± 0.01	<LOD	0.42 ± 0.06	<LOD	<LOD	0.01 ± 0.01	0.21 ± 0.01
S	Kalar-Barlut	Parthian	Bronze	81.54 ± 2.10	16.98 ± 2.04	<LOD	0.18 ± 0.01	<LOD	1.11 ± 0.04	<LOD	<LOD	0.01 ± 0.01	0.21 ± 0.02
W	Germian	Sasanian	Silver	2.34 ± 0.68	<LOD	<LOD	0.08 ± 0.01	96.75 ± 0.66	0.75 ± 0.02	0.05 ± 0.02	<LOD	0.01 ± 0.01	0.02 ± 0.01
Y	Khanaqin	Sasanian	Silver	0.17 ± 0.01	<LOD	0.01 ± 0.01	0.09 ± 0.04	98.65 ± 0.17	1 ± 0.18	0.05 ± 0.05	<LOD	0.01 ± 0.01	0.01 ± 0.01

Glass samples

The qualitative and quantitative analyses of the glass samples were carried out using μ -XRF. The parameters used for the point measurements of the samples are listed in Table 5.

A point measurement per sample was carried out. The element contents determined through μ -XRF over a fundamental parameter model are listed in Table 6.

Table 5. Parameters used for the point measurement of the glass samples.

Parameter	Setting used
Tube current	320 μ A
Tube voltage	40 kV
Spot size	50 μ m
Measuring time	150 sec
Atmosphere	vacuum

In addition, the respective oxide contents for Na, Mg, K, Si and Ca was quantified by the device software given in Table 7. They are mainly soda ash glasses (Si, Na, Ca > 1%. MgO, K₂O>1%).

Due to the low Mg and K contents (<1% MgO, <1% K₂O), sample J could be soda-lime glass (see Figure 5).

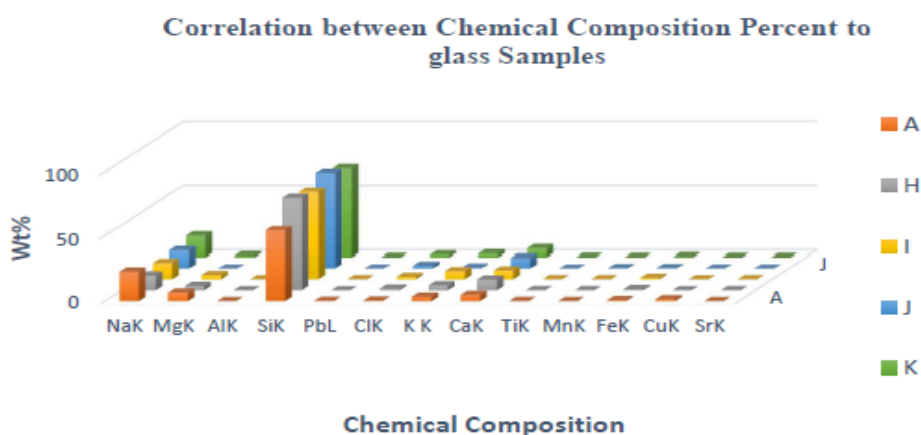


Figure 5. Correlation between element percent and glass sample.

The blue color in sample A could indicate the presence of Cu. Other possible colored elements such as Co could not be detected. The bright blue-green color results from the contained Fe, as does the yellow-brown color of sample K. Depending on the oxidation stage and coordination, different colors are formed in the glass due to Fe.

The X-ray lines used for the quantification are indicated next to the element symbols. All element

contents are given in % by weight. All data were standardized by the software to 100%. The < LOD elements were not quantifiable.

Table 6. μ -XRF analyses of metal objects for 13 quantifiable elements (one-point measurement each).

ID	Origin	Dating	Color	NaK	MgK	AlK	SiK	PbL	ClK	K K	CaK	TiK	MnK	FeK	CuK	SrK
A	Sarqala	Parthian	Blue	22.77	6.59	<LOD	54.47	0.25	0.37	3.38	4.89	0.08	0.04	0.73	1.44	0.05
H	Khanaqin (Bakhtiary)	Sasanian	light blue-green	11.19	3.3	<LOD	71.22	0.01	1.21	3.79	8.16	0.07	0.07	0.86	0.02	0.09
I	Sarqala	Parthian	light blue-green	12.85	3.16	<LOD	67.67	0.03	1.84	6.29	6.9	0.1	0.05	1.04	0.01	0.06
J	Sarqala	Parthian	light blue-green	13.75	<LOD	<LOD	73.91	0.07	2.31	0.83	8.04	0.06	0.44	0.47	0.04	0.08
K	Sarqala	Parthian	yellow-brown	16.65	1.4	<LOD	69.42	<LOD	1.93	2.83	6.93	0.07	0.06	0.62	0.02	0.06

Table 7. μ -XRF analyses of metal objects for Na, Mg, Si, K and Ca given as oxides (one-point measurement).

ID	Origin	dating	color	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO
A	Sarqala	Parthian	Blue	23.51	6.77	62	1.56	2.52
H	Khanaqin (Bakhtiary)	Sasanian	light blue-green	14.75	5.05	74.56	1.41	3.34
I	Sarqala	Parthian	light blue-green	13.12	3.32	76.25	2.69	3.23
J	Sarqala	Parthian	light blue-green	13.82	<LOD	80.8	0.33	3.63
K	Sarqala	Parthian	yellow-brown	16.99	1.42	76.07	1.16	3.18

All oxide contents are indicated as % by weight. The < LOD elements were not quantifiable.

Ceramic samples

The qualitative and quantitative analyses of the ceramic samples were carried out utilizing portable X-ray fluorescence analysis (p-XRF).

Due to the already visually recognizable inhomogeneity of the samples, a larger sample range could be analyzed (8 mm spot). A measurement per sample was carried out with a measuring mode for ores (ores plus), which gives the contents of Si, Al, Mg, K, Ca, Ti, and Fe directly as oxides through the software. A total of 27 elements were measured, 6 of which (Cl, Co, As, Mo, W, Bi) were not quantifiable (<LOD) (see Figure 6).

All other oxide and element content are listed in Tables 8 and 9.

At first sight, it is noticeable that the determined total content of the sample partial exceeds 100%. The results measurements of p-XRF provide more qualitative results and allow rough classification and differentiation of the samples. However, the data is obviously not quantitatively accurate enough.

The analysis using p-XRF was also carried out on non-embedded samples, because of which surface curvatures and the porosity of the samples were adversely affected.

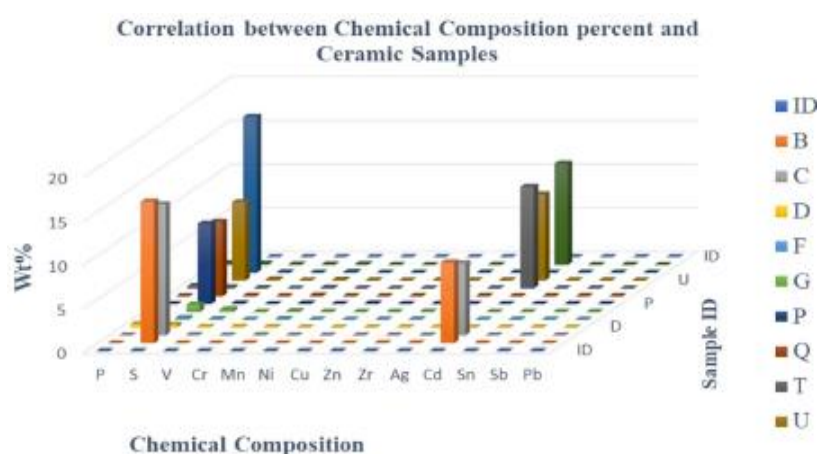


Figure 6. Correlation between element percent and ceramic samples.

Table 8. The p-XRF analyses of ceramic objects for Si, Al, Mg, K, Ca, Ti and Fe indicated as oxides.

ID	Origin	Object	Dating	SiO ₂	Al ₂ O ₃	MgO	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
B	Sherawand	Vassal Pottery	Sasanian	22	8	<LOD	<LOD	27	<LOD	2
C	Sarqala	Coffin	Parthian	36	13	8	1	23	<LOD	6
D	Qala Tapa	Vassal Pottery	Sasanian	82	23	8	3	26	1	6
E	Kifri	Vassal Pottery	Parthian Sasanian	38	11	11	1	50	<LOD	5
F	Pebaz	Vassal Pottery	Sasanian	88	35	10	2	18	1	8
G	Barlut	Coffin	Parthian	90	28	10	2	18	1	8
P	Sarqala	Coffin	Parthisch	64	22	9	1	29	1	6
Q	Khanaqin	Vassal Pottery	Sasanian	44	17	<LOD	1	33	<LOD	4
T	Kifri	Vassal Pottery	Parthisch-Sasanidisch	75	32	14	3	25	1	6
U	Barlut	Coffin	Parthisch	54	18	<LOD	2	25	1	5
V	Qurato	Coffin	Sasanian	32	14	<LOD	<LOD	33	<LOD	4
X	Sarqala	Vassal Pottery	Parthisch	91	28	9	1	16	1	7

All oxide contents are given in %. The elements <LOD were not quantifiable

Table 9. p-XRF analyses of ceramic objects for 14 elements.

ID	Origin	P	S	V	Cr	Mn	Ni	Cu	Zn	Zr	Ag	Cd	Sn	Sb	Pb
B	Sassanian	0.00	16.18	0.00	0.00	0.02	0.00	0.00	0.00	0.02	0.02	9.20	0.01	0.01	0.00
C	Parthian	0.00	14.96	0.05	0.00	0.05	0.01	0.00	0.01	0.02	0.02	8.20	0.01	0.01	0.00
D	Sasanian	0.37	0.31	0.08	0.08	0.07	0.01	0.00	0.01	0.04	0.02	0.00	0.01	0.01	0.00
E	Parthian & Sasanian	0.17	0.96	0.05	0.00	0.06	0.00	0.00	0.01	0.03	0.02	0.00	0.01	0.01	0.00
F	Sasanian	0.14	0.17	0.05	0.00	0.07	0.01	0.00	0.01	0.02	0.02	0.00	0.01	0.01	0.00
G	Parthian	0.00	0.82	0.28	0.00	0.09	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
P	Parthian	0.00	9.19	0.06	0.00	0.07	0.01	0.07	0.01	0.02	0.01	0.00	0.00	0.01	0.01
Q	Sassanian	0.00	8.50	0.04	0.00	0.07	0.00	0.00	0.01	0.02	0.02	0.00	0.01	0.01	0.00
T	Parthian	0.26	0.12	0.04	0.00	0.08	0.01	0.00	0.01	0.02	0.02	11.60	0.01	0.02	0.00
U	Parthian	0.00	8.95	0.11	0.00	0.07	0.01	0.00	0.01	0.02	0.02	9.84	0.01	0.01	0.00
V	Sassanian	0.00	17.81	0.04	0.00	0.08	0.00	0.00	0.01	0.02	0.02	0.00	0.01	0.01	0.00
X	Parthian	0.18	0.13	0.05	0.05	0.07	0.01	0.00	0.01	0.02	0.03	11.57	0.01	0.02	0.00

All element contents are given in %. The <LOD elements were not quantifiable.

CONCLUSIONS

In this work, Samples of glass, Metals and Ceramic are collected during the excavations in Garmian were analyzed using two different analytical techniques. Metallic materials in the Parthian period were mostly made of bronze and iron, but in the Sassanid period, they were mostly made of silver or copper alloys. We need to quantify the isotopes of lead present in the composition of these materials, especially metal samples, which are examined using μ -XRF, to know the provenance of the artworks discovered during an excavation in different areas of the Garmian region. The glass samples are mostly soda-ash glasses. Sample J could be soda-lime glass due to the low Mg and K contents.

In the ceramic samples, it can be seen that the percentage of cadmium in the samples (B. Sherawand, C. Sarqala, T. Kiffri, U. Kiffri, X. Sargala) (9.20, 8.20, 11.60, 9.84 and 11.57) is above the normal rang (21.67-55.00 $\mu\text{g/g}$) [15] (see Figure 6, Table 9). It would be better to investigate the element cadmium in the trench where the artefacts were excavated

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