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RADIOBIOLOGY, ECOLOGY AND NUCLEAR MEDICINE

Ceramics of Bolgar: the First Results of Usage of Neutron Activation Analysis

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Abstract—The article is devoted to the first attempt to use neutron activation analysis (NAA) to determine the chemical composition of the clay component of the molding mass of archaeological ceramics to identify marker elements characteristic of various medieval ceramic production centers. 15 fragments of medieval vessels from the city of Bolgar, the capital of Volga Bulgaria (now the territory of Tatarstan) were provided for research by the Institute of Archeology of RAS. NAA was carried out by the NAA group of the IREN research facility at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research. Research has shown that all the studied ceramic samples had no significant differences either in the main components or in the traces. Also results were obtained, previously unknown to researchers of medieval ceramics.

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INTRODUCTION

In modern archeology, the study of mass ceramic material is one of the most important directions, allowing with increasing accuracy to date the cultural layers, and hence the artifacts from other materials contained in them, the remnants of buildings and constructions [1]]. However, in addition to chronological measurement, archaeological ceramics carry lot of other important information about its manufacturing technology, cultural impulses, population movements, etc. [2]. The least studied in this series are questions about the places of production of ceramic wares, the number of such places within one city, specific sources of clay raw materials and whether such dishes were made in each city and each large village or distributed from several large production points. Answering these questions without using the methods of the natural sciences is difficult, and sometimes impossible. Therefore, today there is a task to isolate those scientific methods that may be involved in solving these problems.

The authors do not know any other attempts to use the method of neutron activation analysis (NAA) to study the chemical composition of the ceramic paste of medieval vessels in Russian science. Earlier, the methods of emission spectral analysis and mass spectrometry were used to solve this problem [3, 4]; however, these methods were used sporadically for a limited number of samples, so their application did not cause any noticeable scientific resonance. In Europe and the United States, the NAA method was used somewhat more widely [5–8], but it was not widely developed there, probably because of the relatively high cost and the impossibility of re-study the irradiated sample by other physical methods. Although a small sample fragment with a mass of less than one gram is sufficient for NAA, museums that store archaeological collections do not allow to transfer ceramic samples or samples parts for analysis under the current storage procedure and prevent the dissemination of this method. Sometimes NAA is used as an additional source of data on the elemental composition of ceramics, determined by other methods [9].

Nevertheless, the prospects for the use of NAA in archaeological studies are promising because this method is multi-element and has a sensitivity quite often exceeding that of other methods of obtaining information about the chemical composition of ceramic materials [10]. Herewith, this method, as well as other physical methods, has a number of limitations: first of all, physical methods cannot be directly applied to the study of ceramics, which includes a large amount of organic (animal manure), mineral (crushed stone) and organic-mineral (mollusc shell, wood ash) additives. Overwhelmingly, these additives cannot be separated from the clay paste, and an analytical study together with them will lead to an infinite variety of the obtained results. At the same time, ceramics, in which there are no such additives at all or their number is vanishingly small, is quite suitable for research using the NAA method and other physical methods. Among these varieties there is, above all, ceramics made at a high level of development of pottery production: the antique, medieval of the most developed centers of the civilized world, the Western European and Russian from industrial eras (XVI–XX centuries). Ceramics of the Volga Bulgaria of the X–XVth centuries, developed on the basis of late antique pottery traditions introduced from the Northern Black Sea region and Transcaucasia, belong to such varieties. These ceramics was made of clay without additives, well cleaned of impurities, kiln-tempered in perfect bunk horn [11]. The result was high-quality utensils with a smooth surface, standardized in size and design. These features make it a significant difficulty when archeologists attempt to determine the place of manufacture of particular vessels. Even during excavations in large cities of Volga Bulgaria, in which the production of such ceramics is beyond doubt, it remains unclear in which of these cities a particular vessel was made. Thus, the involvement of the NAA method in solving archaeological problems is more than promising.

Studies of mass (kitchen, dining and container) ceramics produced in the city of Bolgar (X–XIV centuries), the capital of Volga Bulgaria (in the X century), and then the Bulgar ulus of the Golden Horde, have been carried out for a long time, using various methods. At the first stage, in the 1950–2000s, the morphology of ceramics was studied and significant success was achieved in this study. [12–14]. Research on the technology of making this ceramic was started in the 1980s and continues to the present day according to the method of historical and cultural approach, which allows restoring the recipes of the molding pastes, the characteristics of vessels firing, and ethnocultural origins of pottery traditions [15, 16]. And only in the most recent years, the study of the Bolgar ceramics began with the involvement of natural science methods – petrography, X-ray fluorescence and emission spectral (AES) analyzes [17–19]. As a result, the accumulation of quantitative data that characterizing the studied ceramics was started.

The complexity of the studied ceramic material is determined by its chronological (more than 5 centuries) and cultural diversity—as part of the dishes used in the Bolgar, T.A. Khlebnikova identified 20 groups of different origin and time of existence [12, 13]. At the same time, the most of the dishes in the Bolgar (from 70 to 95% in different contexts) were made by specialized pottery workshops, distinguished by the high quality of the preparation of the molding material, high-temperature firing in horn, standardized forms and decor. Khlebnikova described this ceramic as "all-Bolgar", i.e., found throughout the entire space of Volga Bulgaria [12, 13].

During the long-term excavations in the Bolgar, dozens of pottery horns were discovered and studied, in which similar ceramics were made. A significant part of the horns was located on the floodplain part, on the bank of the Melenka river, but this territory is now flooded by the waters of the Kuibyshev reservoir, so it cannot be re-studied. There are only a few horns in the upper part of the city, whose products are identical to the ceramics of the settlement. A study of the outputs of pottery clays and their comparison with archaeological ceramics is being conducted, with the main emphasis being placed on comparing the chemical compositions of raw clay and shards of vessels [18, 19]. However, this comparison has not yet provided convincing results. One of the reasons for this is the relatively small database and the inadequacy of the methodology for such comparisons. In particular, it is not clear what chemical elements burn out during high-temperature firing, how much the chemical composition of ceramics differs from the composition of clays due to additions to the molding paste some organic by potters (squeezing of domestic animals' manure and others), water from various sources, as well as cleaning clay raw materials from various organic and inorganic impurities. It is obvious that both the cleaning of clay and any additives change the chemical composition of ceramics in relation to the raw materials.

At the same time, attempts were made to isolate groups of the "all-Bolgar" ceramics that differ in the color of the shard (which is affected by many factors), the degree of firing and the concentration of sand impurities. As a result, they could manage to outline several such groups [20], the differences between which are quite insignificant and can be explained not so much by differences in places of production or chronology, as by random deviations in the selection process of clay raw materials, its preparation and firing of products. Verification of made observations is possible only in the course of natural scientific research. And such studies have already been carried out in relation to the Bolgar ceramics.

Thus, a petrographic analysis made it possible to establish that the products of the Bolgar potters were made from several very similar varieties of natural clay, differing in size of the natural admixture of fine sand, grains of which varied from 0.1 to 0.7 mm. Rare needle shaped pores up to 3 mm long or isometric pores were also noted. However, the vast amount of ceramic was made of well-purified from extraneous impurities paste with low porosity and with the presence of natural impurities fine quartz sand up to 0.45 mm [21].

Petrographic analysis gave an idea of the clay dough recipe, but it could not separate the array of local clays. Kazan researchers tried to solve this problem using a series of emission spectral analyzes of ceramic samples collected in different parts of the Bolgar settlement. To do this, a study was carried out

Fig. 1. Sample b-01 before cleaning.

using 22 samples of ceramics belonging to the considered product group [18, Tables 1–3. № 20, 23, 26–30, 34, 36–38, 41, 42, 47, 51, 54, 56, 58, 61, 68, 75, 81]. However, when processing an array of samples, the author made a methodological error and the ceramics made in specialized pottery workshops was compared with home-made dishes (including stucco wares, i.e., created without the help of a potter's wheel, with specific additives to the dough), that is unacceptable. At the same time, some criteria for distinguishing ceramics were identified (according to the content of a number of trace elements) that require verification. Namely NAA allows us to verify the AES data and establish how reliable the conclusions are. At the same time, significant differences within pottery ceramics of the Bolgar regarding elements such as calcium, aluminum, iron, magnesium, etc., which are far from being traces, did not receive any explanation. Therefore, we can confidently say that the study of the chemical composition of the Bolgar ceramics is still only at the very first stage of material comprehension, and to move to the next stage, there is a lack of reliable data on the chemical composition of the much more representative Bolgar ceramics series, as well as a comparable material, which should include products of Bolgar (made in different traditions), as well as ceramics from other regions, similar to Bolgar in the recipe of molding pastes, color, firing.

EXPERIMENT

At the end of 2017, 15 ceramic samples were transferred to the NAA group of the IREN research facility of the Frank Laboratory of Neutron Physics (FLNP) at the Joined Institute for Nuclear Research (JINR) from the Institute of Archeology of the Russian Academy of Sciences. The elements that needed attention: the main components—Al, Fe, Ca, Pb, Sn, K, Na, Mg, Mn; important traces—Cr, Cu, Ti, Ag, V, Ba, As, Li. In addition, the following traces were of interest—Be, Ga, Ni, Sc, Y, Zn, Zr, Yb. Neutron activation analysis of the samples obtained was carried out by relative and absolute methods [22], as well as X-ray fluorescence analysis.

Receiving Samples

The obtained samples are presented in Figs. 1–15.

Sample Preparation

Before cleaning, the mass of each sample was recorded using an analytical balance Vibra AF 225DRCE. The surface layer of each sample was mechanically removed using an angle grinder with a diamond-coated disk. Before each sample processing, the diamond-coated disk and the angle grinder body were wiped with cotton soaked with alcohol. Next, the samples were washed under a stream of distilled water and cleaned with cotton wool soaked in alcohol.

For the NAA, it was necessary to grind the ceramic samples to a powder. For this purpose, a Fritsch Pulverisette 6 planetary mill was used, equipped with an agate grinding bowl and six balls, also made of agate. The grinding time was chosen—5–8 min, the rotation speed—600 rev/min. The resulting powder was carefully poured for temporary storage in labeled glass vials.

One subsample was prepared from each sample. The mass of each sample was approximately 0.1 g. For subsequent irradiation, each sample was packed in an aluminum capsule.

Standards with a similar mass were packed in the same way as the samples in aluminum capsules. In the experiment, the following standards were used, made at the National Institute of Standards and Technology, USA: 2710A—Montana I Soil, 1633C—Bituminous coal fly ash, 1635A—Trace elements in coal (subbitumimous), 2586—Trace elements in soil containing lead from paint, 2684C—Bituminous coal (nominal mass fraction 3% sulfur), 2431—Titanium base alloy,

Fig. 2. Sample b-02 before cleaning.

Fig. 3. Sample b-03 before cleaning.

Fig. 4. Sample b-04 before cleaning.

Fig. 5. Sample b-05 before cleaning.

Fig. 6. Sample b-06 before cleaning.

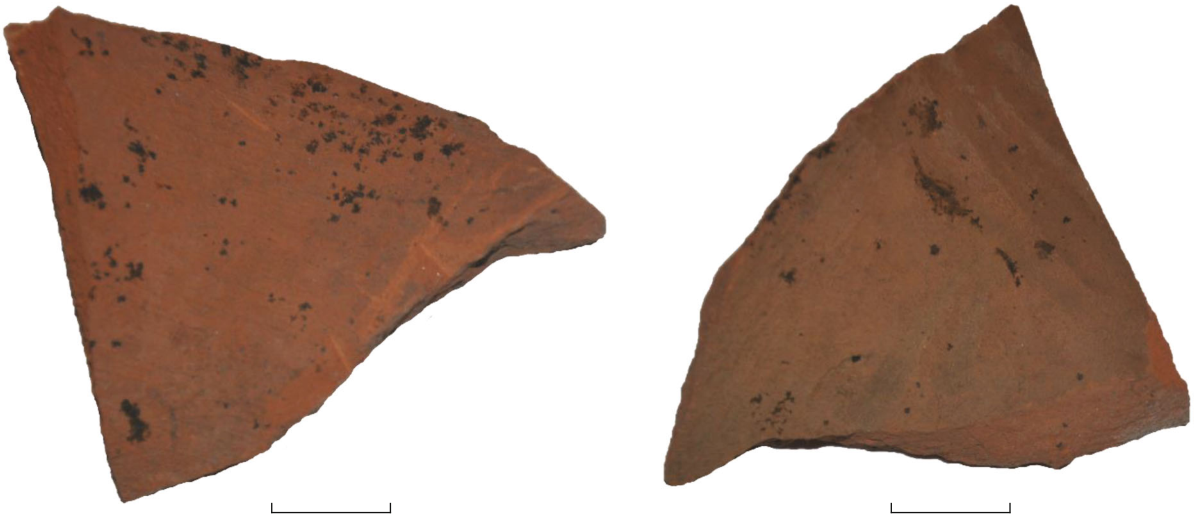

Fig. 7. Sample b-07 before cleaning.

Fig. 8. Sample b-08 before cleaning.

Fig. 9. Sample b-09 before cleaning.

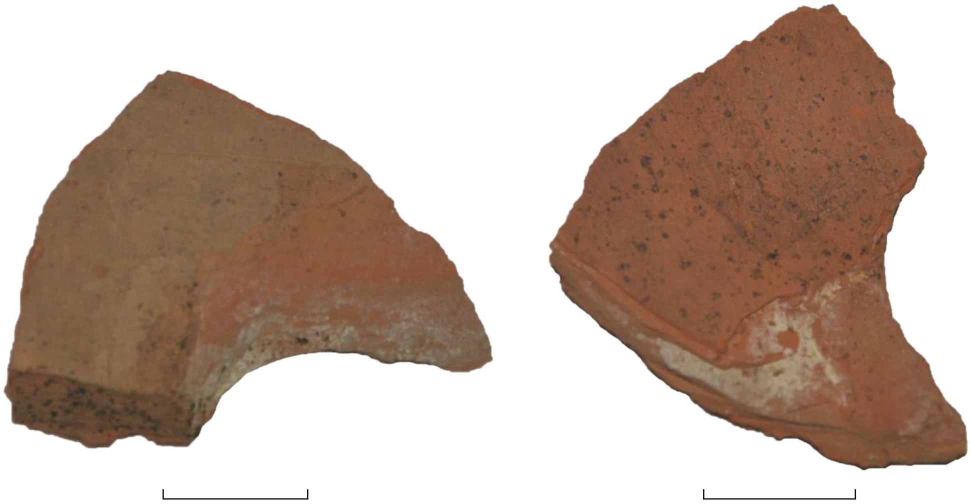

Fig. 10. Sample b-10 before cleaning.

Fig. 11. Sample b-11 before cleaning.

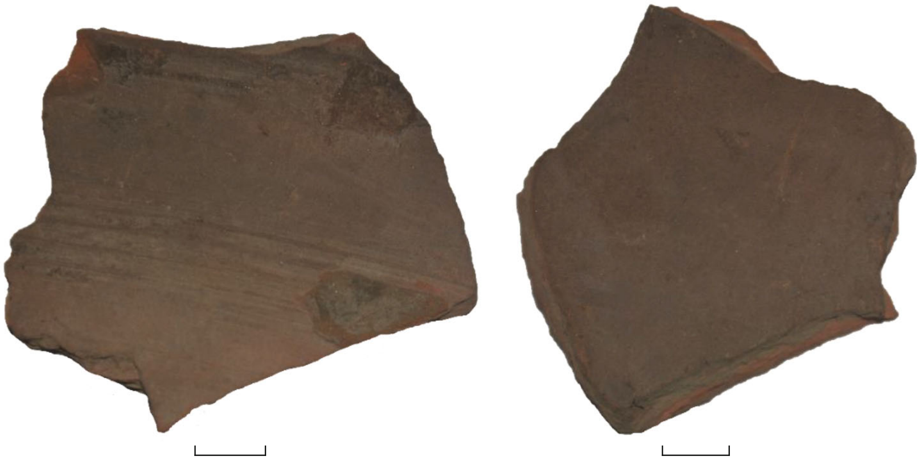

Fig. 12. Sample b-12 before cleaning.

Fig. 13. Sample b-13 before cleaning.

Fig. 14. Sample b-14 before cleaning.

Fig. 15. Sample b-15 before cleaning.

87A—Silicon-aluminum alloy, 2782—Industrial sludge, 50C—Tungsten, chromium, vanadium steel. Standards are needed to calculate the mass fractions of elements in the samples by the relative method of NAA.

In addition to the studied samples and standards, flux monitors were prepared for irradiation – zirconium samples, which were used to calculate thermal and resonance neutron fluxes. We need to know the fluxes to control the flux gradient and to quantify the content of elements by the absolute method of NAA. The masses of zirconium samples were from 0.12 to 0.15 g.

Capsules with samples and standards, as well as flux monitors, were packed with aluminum foil in 9 sets of cylindrical shape. In five sets, zirconium was placed on the first (towards the neutron flux) and the penultimate position, on the last one—zirconium in cadmium protection. The samples under investigation were placed between the zirconium samples, and standards in the middle of the sets. All nine sets were placed in a 3 by 3 matrix and packed in aluminum foil.

Irradiation

A facility for radiation studies at beam no. 3 of the IBR-2 reactor at the FLNP JINR was used to irradiate samples [23, 24]. This facility has unique characteristics. It allows even large objects (180 × 180 mm) to be irradiated with neutrons and gamma quanta just a few tens of millimeters from the reactor core, which makes it possible in a short time to get a sufficiently large neutron fluence on the sample under study ($\sim 10^{18}$ n/cm^2) in wide energy range (25–10 MeV).

Capsules with samples and standards for irradiation was placed out in the head of the facility at a distance of 100 mm from the surface of the water retarder VZ-303 of the IBR-2 reactor. Irradiation was carried out for 2 days at an average reactor power of 1875 kW. Herewith, the thermal neutron flux density Φ_{th} was 7.2×10^{11} n/(cm^2 s), the resonance Φ_{res1}—1.2×10^{11} n/(cm^2 s).

Data Acquiring

Five days after the end of the irradiation, samples and standards were repacked from aluminum capsules into clean plastic containers, and zirconium samples were removed from cadmium protection. Immediately after repacking, the first measurements of the spectra of induced activity were carried out for 1.5 h. The second measurements of the spectra started 22 days after the end of the irradiation. Spectra were measured within 4 hours. An automatic system for measuring the spectra of induced activity, developed and successfully used at FLNP JINR [25, 26], was used for the data acquiring. The spectra were measured with a Canberra GC4018 HPGe detector with a resolution of 2.1 keV for ^{60}Co gamma line with energy of 1332.5 keV.

Spectra Processing

To spectra processing the Canberra Genie-2000 program was used.

Since the end result of the work of the Genie-2000 program is the activities of the isotopes found in the studied samples, the “Concentration” program created at FLNP JINR [27] was used to calculate the mass fractions of the elements.

When processing neutron flux monitors 2 lines of Zr-95: 724.2 keV (intensity 44.2%) and 756.7 keV (intensity 54%) [28] were considered.

XRF

X-ray fluorescence analysis was carried out using a modern portable device Bruker Tracer 5$^{\text{i}}$ with a resolution <140 eV for line of Mn Kα (250 000 pulses/s). Calibration of the instrument was carried out by standard means – using the built-in calibration programs and reference samples from the delivery set. For measurements, grinded samples prepared for NAA were used. Measurements of the grinded samples were carried out using special plastic cuvettes for the study of bulk and liquid samples. An individual cuvette was used to measure each sample. The Prolene film was used as the bottom of the cuvettes.

RESULTS

As a result of the experiment, the mass fractions of 43 elements were determined, 31 with the help of NAA and 23 with XRF. The mass fractions of some elements were determined by both methods, these results were in good agreement. The main components were found: Al, Fe, Ca, Pb, Sn, K, Na, Mg, Mn; important traces: Cr, Cu, Ti, Ag, Ba, As; in addition, the following traces: Ga, Ni, Sc, Y, Zn, Zr, Yb. Additionally, the mass fractions of Si, P, Co, Rb, Sr, Mo, Cd, Sb, Cs, La, Ce, Nd, Sm, Eu, Tb, Lu, Hf, Ta, Hg, Th, U were determined.

The NAA results table shows the uncertainties that take into account the uncertainties in determining the activities of isotopes of samples and standard samples, as well as the passport uncertainties of the mass fractions of elements in standard samples.

Mass fractions of elements in standard samples were in good agreement with the passport values. As part of quality control, the results were verified by the absolute method of the NAA.

ANALYSIS OF THE RESULTS

The main conclusion obtained as a result of these studies is that all the studied ceramic samples, including obviously imported (glazed: nos. 11 and 15), did not have significant differences neither in the main components (silicon, aluminum, iron, magnesium), or in traces. So, at the first stage of research, it is difficult to indicate the signs by which pottery products similar in external appearance could differ. Differences cannot be traced between the dishes made in different eras, which in general should not be surprising, since the same clay was probably used for production. The coincidence of the elemental composition of clays of different geographical origin (from the Bolgar, the Lower Volga region, and the unknown center) is most surprising. However, the singleness of the comparative material allows us to assume that such coincidences are random. To check them, additional studies will be required on a wider series of samples.

Comparison of the analysis results of the molding paste of the Bolgar pottery ceramics carried out by the methods of AES [17] and NAA (our studies) shows that for a number of elements the coincidences were quite complete. Thus, according to the AES data, the fraction of iron in the shards (in terms of Fe_2O_3 oxide) was from 3.7 to 9.0% (with average values in the range of 5–6%), and according to NAA from 3.9 to 6.5%. The fraction of sodium oxide according to AES was from 0.6 to 1.9% (with extreme upward deviations up to 3.3%), according to NAA data, from 0.6 to 1.6%. The fraction of chromium according to AES ranged from 130 to 340 mg/kg, according to NAA—from 161 to 282 mg/kg. The same can be said about the content of nickel traces in the samples (AES—from 41 to 110 mg/kg, NAA—from 48 to 108 mg/kg), zinc (AES—from 31 to 133 mg/kg, NAA—from 76 to 157 mg/kg).

For some elements, the coincidences are not so obvious and the AES data give slightly overestimated

Table 1. Mass fractions of elements found

Sample	Na_2O		MgO	Al_2O		SiO_2		P_2O_5		K_2O		CaO		Sc		TiO	
	NAA		XRF	XRF		XRF		XRF		XRF		XRF		NAA		XRF	
	mg/kg	unc., %	mg/kg	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %
b-01	1.28E+04	2	<3.98E+04	1.10E+O5	4	5.91E+05	1	1.39E+04	6	2.13E+04	2	2.39E+04	1	1.62E+01	2	5.34E+03	6
b-02	1.29E+04	2		1.07E+05	4	6.38E+05	1	2.56E+03	18	1.87E+04	2	1.42E+04	2	1.56E+01	2	5.62E+03	6
b-03	9.92E+03	2	<4.51E+04	1.03E+05	4	5.81E+05	1	4.79E+03	11	2.06E+04	2	1.25E+04	2	1.48E+01	2	5.42E+03	6
b-04	5.84E+03	3		9.85E+04	4	6.56E+05	1	2.26E+04	4	1.87E+04	2	1.70E+04	1	9.72E+00	2	5.11E+03	6
b-05	5.90E+03	3		8.69E+04	5	6.20E+05	1	1.69E+04	5	1.88E+04	2	1.27E+04	2	9.80E+00	2	5.00E+03	6
b-06	1.15E+04	2	< 3.85E+04	9.87E+04	4	5.78E+05	1	7.89E+03	8	2.27E+04	1	1.18E+04	2	1.21E+01	2	5.59E+03	6
b-07	1.28E+04	2	<4.34E+04	1.22E+05	4	5.84E+05	1	2.63E+03	18	2.02E+04	2	1.17E+04	2	1.75E+01	2	6.17E+03	6
b-08	5.74E+03	3		9.64E+04	4	6.21E+05	1	5.78E+03	10	2.24E+04	1	1.10E+04	2	1.07E+01	2	5.78E+03	6
b-09	2.25E+04	2	< 5.29E+04	1.11E+05	4	5.72E+05	1	1.48E+03	29	2.42E+04	1	2.43E+04	1	1.43E+01	2	4.71E+03	7
b-10	1.31E+04	3	< 5.61E+04	1.14E+05	4	5.32E+05	1	9.79E+03	7	2.35E+04	1	5.35E+04	1	1.69E+01	2	5.40E+03	6
b-11	1.44E+04	3	<5.28E+04	1.03E+05	4	5.71E+05	1	2.20E+03	21	2.28E+04	1	2.32E+04	1	1.51E+01	2	5.07E+03	6
b-12	1.17E+04	3	<4.62E+04	1.13E+05	4	5.50E+05	1			1.82E+04	2	1.27E+04	2	1.51E+01	2	6.02E+03	6
b-13	1.62E+04	3	<4.07E+O4	9.94E+04	4	5.80E+05	1			1.66E+04	2	1.08E+04	2	1.84E+01	2	5.64E+03	6
b-14	1.56E+04	3	<3.79E+04	1.08E+05	4	5.73E+05	1			1.85E+04	2	1.18E+04	2	1.95E+01	2	5.73E+03	6
b-15	1.27E+04	3	<3.40E+04	9.96E+04	4	6.18E+05	1	7.76E+03	8	1.95E+04	2	1.18E+04	2	1.34E+01	2	5.58E+03	6

Table 1. (Contd.)

Sample	Cr				MnO		Fe_2O_3				Ni				Co		
	NAA		XRF		XRF		NAA		XRF		NAA		XRF		NAA		XRF
	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg
b-01	2.73E+02	3	< 4.23E+02		1.24E+03	7	7.79E+04	5	5.84E+04	1	7.93E+01	4	7.40E+01	19	2.26E+01	7	<1.56E+02
b-02	2.48E+02	3	< 4.59E+02		1.05E+03	7	7.23E+04	5	5.49E+04	1	8.43E+01	4	8.60E+01	17	2.24E+01	7	<1.83E+02
b-03	2.21E+02	3	1.51E+02	30	6.46E+02	10	7.03E+04	5	5.48E+04	1	8.24E+01	7	8.00E+01	19	2.07E+01	7	
b-04	1.69E+02	3	<3.15E+02		6.47E+02	10	4.60E+04	5	4.16E+04	1	5.41E+01	9	5.80E+01	22	1.22E+01	7	
b-05	1.61E+02	3	< 3.45E+02		2.05E+02	21	4.52E+04	5	3.90E+04	1	4.84E+01	4	6.30E+01	21	1.21E+01	7	
b-06	1.82E+02	3	<3.15E+02		7.73E+02	9	5.32E+04	5	4.26E+04	1	5.11E+01	4	4.70E+01	28	1.74E+01	7	
b-07	2.56E+02	3	< 3.87E+02		1.42E+03	6	8.18E+04	5	6.33E+04	1	9.59E+01	4	8.50E+01	19	2.47E+01	7	<2.70E+02
b-08	1.90E+02	3	< 3.27E+02		2.97E+02	16	5.35E+04	5	4.42E+04	1	6.30E+01	9	6.50E+01	22	1.83E+01	7	
b-09	1.78E+02	3	< 3.39E+02		7.91E+02	8	7.10E+04	5	5.49E+04	1	6.22E+01	4	7.10E+01	21	2.08E+01	7	
b-10	2.16E+02	3	< 4.50E+02		1.34E+03	6	7.95E+04	5	6.16E+04	1	1.14E+02	4	1.32E+02	14	2.61E+01	7	
b-11	1.80E+02	3	< 2.64E+02		8.42E+02	8	7.45E+04	5	5.67E+04	1	6.82E+01	4	8.10E+01	21	2.24E+01	7	<1.74E+02
b-12	2.10E+02	3	< 4.29E+02		1.53E+03	6	7.09E+04	5	6.52E+04	1	9.36E+01	4	1.09E+02	17	2.32E+01	7	
b-13	2.82E+02	3	1.81E+02	26	1.38E+03	6	8.42E+04	5	5.90E+04	1	1.08E+02	7	1.05E+02	16	2.73E+01	7	
b-14	2.71E+02	3	< 4.65E+02		1.28E+03	6	9.11E+04	5	6.46E+04	1	1.03E+02	10	9.20E+01	18	2.84E+01	7	<2.04E+02
b-15	2.36E+02	3	< 4.08E+02		7.01E+02	9	6.42E+04	5	5.26E+04	1	6.97E+01	9	7.40E+01	20	1.85E+01	7	

Table 1. (Contd.)

Sample	Cu		Zn				Ga	As			Rb				Sr			
	XRF		NAA		XRF		XRF	NAA		XRF	NAA	XRF	NAA	XRF	NAA		XRF	
	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	mg/kg	unc., %	mg/kg	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %
b-01	7.50E+01	13	1.57E+02	4	1.35E+02	13	<2.70E+01	8.42E+00	9	<3.90E+01	8.38E+01	16	7.70E+01	8	1.54E+02	9	1.79E+02	5
b-02	4.20E+01	19	9.24E+01	4	7.90E+01	13	<3.30E+01	8.03E+00	9	<1.50E+01	8.01E+01	16	7.40E+01	8	1.32E+02	8	1.47E+02	5
b-03	4.50E+01	18	9.56E+01	4	7.60E+01	9	<3.00E+01	8.26E+00	10	<2.70E+01	7.31E+01	16	6.40E+01	9	1.34E+02	9	1.58E+02	5
b-04	3.30E+01	21	1.04E+02	4	1.06E+02	13		3.77E+00	9	<1.50E+01	6.18E+01	16	5.90E+01	8	2.09E+02	8	2.68E+02	4
b-05	4.00E+01	20	7.59E+01	4	8.00E+01	10	<2.40E+01	5.84E+00	9	<1.80E+01	6.78E+01	16	6.50E+01	9	2.00E+02	8	2.63E+02	4
b-06	4.50E+01	20	1.18E+02	4	1.11E+02	13	<3.00E+01	5.37E+00	9	<2.40E+01	8.44E+01	16	8.70E+01	8	1.25E+02	10	1.66E+02	5
b-07	4.80E+01	19	9.68E+01	4	8.80E+01	12	<3.00E+01	1.23E+01	9	<3.60E+01	8.51E+01	16	8.30E+01	8	1.34E+02	8	1.54E+02	5
b-08	3.70E+01	22	8.85E+01	4	8.30E+01	12		1.04E+01	9	<4.20E+01	7.43E+01	16	7.20E+01	8	1.28E+02	10	1.39E+02	5
b-09	1.31E+02	10	1.01E+02	4	9.10E+01	9	<3.90E+01	7.23E+00	10	<2.70E+01	8.76E+01	16	8.30E+01	8	1.61E+02	9	1.94E+02	5
b-10	5.40E+01	19	1.75E+02	4	1.76E+02	13	<3.30E+01	6.58E+00	9	<2.40E+01	1.00E+02	16	1.01E+02	8	2.66E+02	8	3.02E+02	4
b-11	8.30E+01	13	1.05E+02	4	9.20E+01	12		5.69E+00	9		1.07E+02	16	1.04E+02	8	1.85E+02	9	1.97E+02	5
b-12	4.30E+01	21	8.72E+01	4	9.30E+01	13	<4.20E+01	9.50E+00	9	<3.30E+01	8.02E+01	16	8.50E+01	8	1.24E+02	8	1.46E+02	5
b-13	5.70E+01	18	9.76E+01	4	8.30E+01	12	<4.20E+01	1.04E+01	10	<3.00E+01	8.44E+01	16	7.80E+01	9	1.43E+02	9	1.49E+02	5
b-14	4.80E+01	19	1.07E+02	4	9.00E+01	11	<4.80E+01	1.00E+01	10	<1.80E+01	9.13E+01	16	8.70E+01	8	1.40E+02	9	1.40E+02	6
b-15	4.10E+01	20	9.47E+01	4	8.90E+01	13	<4.50E+01	8.82E+00	9	<2.70E+01	8.07E+01	16	7.90E+01	8	1.76E+02	9	1.95E+02	5

Table 1. (Contd.)

Sample	Y				Zr		Mo		Ag		Cd		SnO		Sb		Cs	
	XRF		NAA		XRF		NAA		NAA		NAA		NAA		NAA		NAA	
	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %
b-01	1.90E+01	21	2.79E+02	3	2.72E+02	4	2.12E+00	5					3.09E+01	5	9.40E-01	4	4.33E+00	3
b-02	2.30E+01	17	3.18E+02	6	2.64E+02	4	1.22E+00	6					2.28E+01	5	9.01E-01	4	4.27E+00	3
b-03	2.10E+01	19	2.87E+02	9	2.39E+02	5	1.27E+00	6					2.04E+01	7	8.84E-01	4	2.90E+00	3
b-04	2.00E+01	20	3.19E+02	6	3.27E+02	3	1.81E+00	5					1.74E+01	7	6.58E-01	4	2.05E+00	3
b-05	2.10E+01	19	3.89E+02	6	3.70E+02	3	1.15E+00	6					1.87E+01	9	9.70E-01	4	2.23E+00	3
b-06	3.00E+01	13	3.97E+02	6	3.72E+02	3	1.27E+00	6	1.69E+00	16	2.30E+00	16	2.22E+01	6	7.50E-01	4	3.79E+00	3
b-07	2.70E+01	15	3.14E+02	7	2.35E+02	4	1.29E+00	6			1.58E+00	16	2.14E+01	6	9.84E-01	4	4.69E+00	3
b-08	2.70E+01	15	4.95E+02	5	4.08E+02	3	1.76E+00	5			1.04E+02	4	1.86E+01	7	7.95E-01	4	3.10E+00	3
b-09	2.60E+01	15	2.23E+02	3	1.74E+02	6	1.20E+00	6					3.15E+01	9	1.08E+00	4	4.52E+00	3
b-10	2.70E+01	19	2.21E+02	11	1.51E+02	6	2.03E+00	5					4.38E+01	6	1.02E+00	4	5.86E+00	3
b-11	< 3.00E+01		2.38E+02	11	1.76E+02	6	1.43E+00	6					2.17E+01	7	1.15E+00	4	5.10E+00	3
b-12	2.90E+01	17	2.68E+02	3	2.40E+02	5	1.57E+00	5			2.43E+00	12	1.74E+01	8	9.46E-01	4	4.43E+00	3
b-13	2.80E+01	14	3.06E+02	3	2.44E+02	5	1.47E+00	6			1.07E+01	11	1.52E+01	12	1.04E+00	4	4.73E+00	3
b-14	2.50E+01	16	3.07E+02	3	2.28E+02	4	1.63E+00	6					1.79E+01	10	1.06E+00	4	5.25E+00	3
b-15	1.90E+01	21	3.56E+02	4	2.77E+02	4	1.32E+00	6			1.45E+01	5	1.54E+01	9	7.40E-01	4	3.16E+00	3

Table 1. (Contd.)

Sample	Ba				La		Ce		Nd		Sm		Eu		Tb		Yb	
	NAA		XRF		NAA		NAA		NAA		NAA		NAA		NAA		NAA	
	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %
b-01	4.78E+02	5	3.10E+02	27	2.57E+01	3	6.24E+01	9	<5.30E+01		4.92E+00	15	9.56E-01	2	5.75E-01	3	2.13E+00	20
b-02	4.61E+02	5	2.64E+02	30	3.24E+01	3	7.36E+01	9	2.66E+01	16	6.69E+00	15	1.31E+00	2	7.93E-01	2	2.70E+00	20
b-03	5.46E+02	6	3.00E+02	26	2.67E+01	3	6.60E+01	9	1.89E+01	18	5.32E+00	15	1.02E+00	2	7.10E-01	4	2.24E+00	20
b-04	6.01E+02	5			2.44E+01	3	5.87E+01	9	<5.80E+01		4.87E+00	15	9.13E-01	3	5.81E-01	2	2.08E+00	20
b-05	4.69E+02	6			2.54E+01	3	5.77E+01	9	2.28E+01	17	5.15E+00	15	9.37E-01	2	6.92E-01	4	2.24E+00	20
b-06	5.34E+02	5	4.07E+02	20	3.30E+01	3	7.86E+01	9	3.08E+01	26	6.54E+00	15	1.21E+00	3	8.27E-01	2	2.81E+00	20
b-07	4.69E+02	5			3.04E+01	3	7.49E+01	9	2.91E+01	16	6.37E+00	15	1.22E+00	2	7.49E-01	2	2.72E+00	20
b-08	6.32E+02	5	3.72E+02	21	3.02E+01	3	7.16E+01	9	2.47E+01	17	6.29E+00	15	1.07E+00	2	7.49E-01	2	2.74E+00	20
b-09	4.36E+02	6	2.81E+02	27	3.55E+01	3	7.87E+01	9	2.58E+01	17	6.32E+00	15	1.24E+00	3	8.38E-01	4	1.95E+00	20
b-10	4.87E+02	5	<6.36E+02		3.31E+01	3	7.64E+01	9	<1.05E+02		6.70E+00	15	1.29E+00	2	8.15E-01	2	2.68E+00	20
b-11	4.74E+02	6	<5.46E+02		3.72E+01	3	8.41E+01	9	3.07E+01	30	6.72E+00	15	1.28E+00	2	7.24E-01	2	2.31E+00	20
b-12	4.23E+02	6			2.87E+01	3	6.60E+01	9	2.74E+01	16	6.35E+00	15	1.18E+00	2	7.93E-01	2	2.35E+00	20
b-13	4.91E+02	6	2.30E+02	30	3.50E+01	3	7.99E+01	9	2.61E+01	18	7.47E+00	15	1.49E+00	2	8.68E-01	2	3.05E+00	20
b-14	4.81E+02	5	<6.36E+02		3.17E+01	3	7.95E+01	9	1.95E+01	20	6.27E+00	15	1.31E+00	2	7.71E-01	2	2.66E+00	20
b-15	4.84E+02	5	2.46E+02	28	2.49E+01	3	5.93E+01	9	<4.50E+01		4.42E+00	15	8.27E-01I	2	6.30E-01	4	1.93E+00	20

Table 1. (Contd.)

Sample	Lu		Hf		Ta		Hg		Pb		Th			U	
	NAA		NAA		NAA		NAA		XRF		NAA		XRF	NAA	
	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	unc., %	mg/kg	mg/kg	unc., %
b-01	3.84E-01	11	1.44E+01	8	7.33E-01	3					8.85E+00	2		1.84E+00	4
b-02	4.65E-01	11	1.49E+01	8	7.84E-01	3			<4.20E+01		9.44E+00	2		1.86E+00	4
b-03	3.90E-01	11	1.36E+01	8	7.29E-01	3			<3.30E+01		8.64E+00	2		1.73E+00	4
b-04	3.65E-01	11	1.47E+01	8	6.65E-01	3					7.50E+00	2		1.53E+00	4
b-05	4.45E-01	11	1.72E+01	8	7.56E-01	3			<3.00E+01		7.88E+00	2		1.65E+00	4
b-06	4.81E-01	11	1.83E+01	8	9.10E-01	3	<4.10E-01		<5.10E+01		1.02E+01	2		2.11E+00	4
b-07	4.49E-01	11	1.41E+01	8	8.15E-01	3					9.68E+00	2		2.00E+00	4
b-08	4.56E-01	13	2.12E+01	8	9.08E-01	3					9.65E+00	2	<2.10E+01	2.04E+00	4
b-09	3.65E-01	11	1.08E+01	8	7.22E-01	3			<4.50E+01		1.06E+01	2	<3.00E+01	2.07E+00	4
b-10	4.44E-01	11	1.00E+01	8	8.29E-01	3			<3.90E+01		1.07E+01	2	O.60E+01	2.39E+00	4
b-11	3.64E-01	11	1.11E+01	8	7.75E-01	3			3.50E+03	2	1.14E+01	2		2.80E+00	4
b-12	4.01E-01	11	1.18E+01	8	7.45E-01	3	5.24E-01	16	<9.90E+01		8.97E+00	2		2.09E+00	4
b-13	5.89E-01	11	1.58E+01	8	8.45E-01	3			<4.80E+01		9.90E+00	2	<3.30E+01	2.24E+00	4
b-14	5.33E-01	11	1.43E+01	8	8.65E-01	3			<4.50E+01		1.06E+01	2	<3.00E+01	2.26E+00	4
b-15	3.45E-01	11	1.53E+01	8	7.17E-01	3			<2.40E+01		8.37E+00	2	<2.40E+01	1.89E+00	4

values for strontium (mostly more than 200 mg/kg, sometimes up to 300 mg/kg), whereas for NAA the amount of strontium ranges from 124 to 209 mg/kg, with a single maximum value of 266 mg/kg (for a sample whose origin has not yet been precisely determined). At the same time, AES values for zirconium appear underestimated (from 150 to 270 mg/kg, with a single value of 300 mg/kg) in relation to the NAA data, showing values from 221 to 495 mg/kg. However, these discrepancies can be explained by different standards used in the analysis.

Thus, it can be stated that the analyzes by the method of AES, carried out in Kazan, are sufficiently accurate and their data can be used in further work on the study of the chemical composition of ceramic pastes.

During the studies of the considered series of samples, as mentioned above, not only NAA was used, but also X-ray fluorescence analysis. It turned out that the data of NAA and XRF are somewhat different. Thus, it was established that the XRF gave underestimated values for iron and barium, although no such discrepancies were noted for many other elements. Clarifying the causes of discrepancies is a separate task, important for further research.

If we go back to the actual results of the research, we should pay attention to those results that can be called unexpected. We are talking about those deviations in the elemental composition of ceramics that require explanation, since, as already noted, in general, the composition of all 15 samples turned out to be very close both in terms of the main components and in trace elements.

(1) Sample no. 10 was distinguished by an unusually high calcium content (5.4% in terms of oxides), while all other samples had a content of this oxide in sizes from 1.1 to 2.4%, which is quite normal for ceramics from highly iron low carbonate clays. However, sample no. 10 was the only one related to products whose outer surface was covered with white engobe. White engobe is a coating made of non-iron (white) clay, and such clays are often carbonized. The core of the shard was analyzed, and not its surface; therefore, 2 versions of the explanation of what happened are permissible:

(a) carbonate compounds penetrated deep into the shard from the engobe coating;

(b) this clay composition is its initial property, and coincidence with the presence of an engobic coating in the vessel is completely random.

To find out which version is the most correct, additional research will be required.

(2) Sample no. 11 was distinguished by an unusually high lead content (0.35% in terms of oxides), while all other samples contained this element 2 orders less. In this case, the explanation for this deviation is unambiguous: this sample was the only one in the series that belonged to a glazed vessel (tuvak), the glaze coating of which consisted of lead glaze (in such glazes, lead is from half to 3/4 of elemental volume). Glaze was applied to vessels in the Middle Ages in the form of a water-based suspension. The infiltration of water into the pores of the vessel walls could facilitate the transfer of particles of glaze into the depth of the shard. Apparently, the infiltration was relatively small, since an extremely small amount of the lead component of the raw glaze got into the shard. Since the initial raw glaze is a suspension, the particles of lead compounds in it have such a size that does not allow them to infiltrate into the bulk layers of the shard to a greater depth, so that the content of the lead component is extremely small. Such an observation was made for the first time and has not yet been described in the literature.

(3) Sample no. 9 was distinguished by a high fraction of copper. Although this proportion was extremely small (0.0131% in the elemental composition), it was nevertheless 2–4 times higher than that of the other samples. The second difference of sample no. 9 was an increased fraction of sodium (2.3% in terms of oxides), while the rest of the analyzed samples showed the content of this oxide in the range of 0.6–1.6%. The deviation seems to be small and it could be taken as accidental, but the fact is that it was exactly the No. 9 sample that belonged to a cup covered with alkaline (sodium) glaze, painted in turquoise color with the help of copper oxide. Such a coincidence does not seem random. Apparently, here, as in the case of glazed tuvak (see above), we can talk about the infiltration of the components of the liquid (raw) glaze into the thickness of the vessel sides at the glazing stage before the second firing of the product (glazed clay vessels were kiln-tempered 2 times: first time unglazed vessel, the second time—after putting the glaze coating to melt and fixing it on the surface). Obviously, a small amount of raw glaze containing sodium infiltrated the shard, but this infiltration did take place. It should be clarified that alkaline glazes usually have a very low degree of fusion of glaze with a shard of vessels made of clay, so the glaze often exfoliates from the surface of such vessels. However, as we can see, even at the same time, at the initial stage of putting the aqueous suspension, the individual components of the glaze composition infiltrated deep into the shard, which was discovered as a result of the carried research. This feature was also not previously recorded by analytical methods.

The first results of the analytical study of the chemical composition of the Bolgar ceramics cannot be called sensational, but they nevertheless made it possible to obtain such data that were not previously known to researchers of medieval ceramics. The accumulation of data, new series of analyzes can significantly promote knowledge of the ancient ceramic industry, providing information that cannot be obtained by other methods.

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