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Experimental Study of Technological Changes in Ceramics' Industry

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***Abstract**:*

The relevance of the given problem is caused by the lack of research methodologies and the identification of ceramic raw materials sources used to produce unglazed ceramics of medieval Bulgaria.

The article aims to identify changes in the mineralogical and chemical composition of unglazed pottery in the process of its manufacture.

The leading method to the study of this problem is a multidisciplinary approach using experimental technology and the physical and chemical analytics.

Because of extensive research in the field, changes in the petrographic and elemental composition are made. These changes are due to the use of various organic impurities of mineral and organic origin. Article materials are the first observations of the mineralogical and chemical transformations occurred in the process of ceramic production.

Keywords: *Organization Anomie, Derivatives, Derivative Mishandling, Anomic Behavior.*

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1. Introduction

The study of unglazed ceramics of one of the largest medieval cities of Volga Bulgaria, Bulgarian settlement, revealed 18 major groups of ceramic products, which were produced on the territory of the city (Khlebnikova, 1984). These groups are peculiar to its own methods and means of production, which revealed morphological features and the technical and technological features. The study of the chemical and mineralogical compositions showed their significant difference in each group. In this regard, question arises about the clay used in the production of ceramic products. Artisans used the same raw material source and the differences in the composition are due to technological additives in ceramic dough or since each craft town of Bolgar school had its own particular source of clay. As an illustration, we can give an example comparing the chemical composition of the major groups of pottery Bulgarian settlement with the composition of clay samples taken in the monument district (Hramchenkova, 2014). The objective of this study was to identify patterns of change in the chemical and mineralogical composition depending on ceramic manufacturing methods based on experimental data and multi-disciplinary approach.

The chemical composition of the ceramic was determined by emissive spectral analysis, the identification of the mineralogical composition was performed by petrographic method. Part of the samples was examined by x-ray. An interdisciplinary approach with the use of natural-scientific methods to the study of archaeological artifacts is quite relevant in modern archaeological materials science (Braekmans *et al*., 2011; Hall and Minaev, 2002; Fernandez-Ruiz and Garcia-Heras, 2007; Costa *et al*., 2004; Griffits, 1999; Ammerman *et al*., 2008; Gliozzo and Memmi Turbanti, 2004; Kreiter *et al*., 2007; Scarpelli *et al*., 2010; De Francesco *et al*., 2011; Wever *et al*., 2012).

The solution of the problem was carried out on three issues: 1) the identification of the influence of different types of impurities on the ceramics composition; 2) fixing the difference of the chemical and mineralogical composition of ceramics with one kind of impurities in different states and concentrations; 3) determination of the possibility of comparing the experimental compositions of samples of ceramics and original clay to identify the exact source of raw material locations.

2. Materials and Methods

1.1 Methods

The studies were conducted on the experimental samples. Methodical principles of this study are based on the historical-cultural approach of Bobrinsky (1978, 1999) and Tsetlin (2012), in combination with natural science researches, including physical and chemical analysis and technological experiments. The preparatory phase includes several steps associated with the selection and production of raw materials, the preparation of the molding material. All feedstock was selected near the Volga Bulgarian settlement with terrace about 30 m in height (Sitdikov and Huzin, 2007).

1.2 Obtaining experimental samples

Brown clay was taken as the starting raw material of plastic. It was selected near the Bulgarian settlement. Basic additions used in the manufacture of Volga Bulgaria ceramics were taken as initial non-plastic raw materials. That is grog, sand, manure of cattle, Crushed shell (Vasilieva, 1988; 1993). All the impurities are divided into three classes: organic, mineral, organo-mineral.

Mineral contaminants include sand and grog. Fine river sand (grain size 1 mm) near the Bulgarian settlement was taken for sand impurity. Ceramics I of general Bolgarian group of XII-XIVth centuries was taken for the preparation of fireclay. It was split in a cast-iron mortar to the dimension of no more than 5 mm.

Organic impurities are presented with cattle manure in several states - dry, wet, squeeze from manure (organic solution). Fresh and dry manure has the same territorial binding to the neighborhoods of Bulgarian settlement as the original clay. Squeeze was obtained from the same fresh manure by spinning through several layers of cheesecloth manually. Dry manure was manually grind.

Organic impurities are impurities of mixed state and the origin - shells of river clams. Shell clams on the river shore of Kuibyshev reservoir were taken for the preparation of these impurities. Shells are used in two conditions: without preliminary heat treatment and pre-heat treatment. Raw shell without clam was crushed in a mortar. “Roasted” shell also without clam was obtained by burning at the stake for about 20 minutes then granulated in a cast-iron mortar.

Preparation of the molding compositions was carried out based on pure, unmixed traditions involved in the formulation of the original plastic raw material (clay) and only one kind of impurity. All these types of the original non-plastic raw materials were mixed with wet clay wet in different concentrations. The main concentration of the impurities, found in archaeological unglazed ceramics medieval town of Bolgar, were used, in the ratio of impurity and clay – 1:1, 1:2, 1:3, 1:7 (Vasilieva, 1988).

Briquettes measuring approximately 10*1*1 cm were molded from obtained molding compositions. As a result, groups of samples with different types of impurities at various concentrations were prepared. Samples of the pure clay without adding impurities are also prepared. As a result, 27 kinds of test specimens were produced.

To impart strength, all samples were dried to a solid state. After that they were roasted. Oxidation firing was carried out in laboratory conditions (muffle furnace) in a slow increase in temperature and exposure time in the oven for an hour at a temperature 820-850ºC (Vasilieva and Salugina, 2013; Avgustinik, 1975). After firing, the samples acquired a red hue without layers in chips. On the surface of the sample with an admixture of shells after firing appeared glassy smudges, then these samples cracked and crumbled. It is obvious that the production of the samples with a shell, a technology that was used by Bulgarian potters for the manufacture of ceramic tableware with this impurity has not been reproduced.

1.3 Analytical studies

Experimental samples were examined by various analytical methods. Determination of macro- and microelement composition was carried out by emission spectral analysis with a diffraction spectrograph DFS-458. To identify the mineral composition of the samples, their structure and texture were produced thin sections of the samples. Petrographic studies of thin sections were performed on a polarizing microscope "AxioImeger.A2". An important feature of the test samples is their great petrographic similarity, which causes difficulties in separating them into groups. Because of the interpretation of analytical data, the dynamics of changes in the chemical and mineralogical composition of the different samples groups was obtained (Table 1).

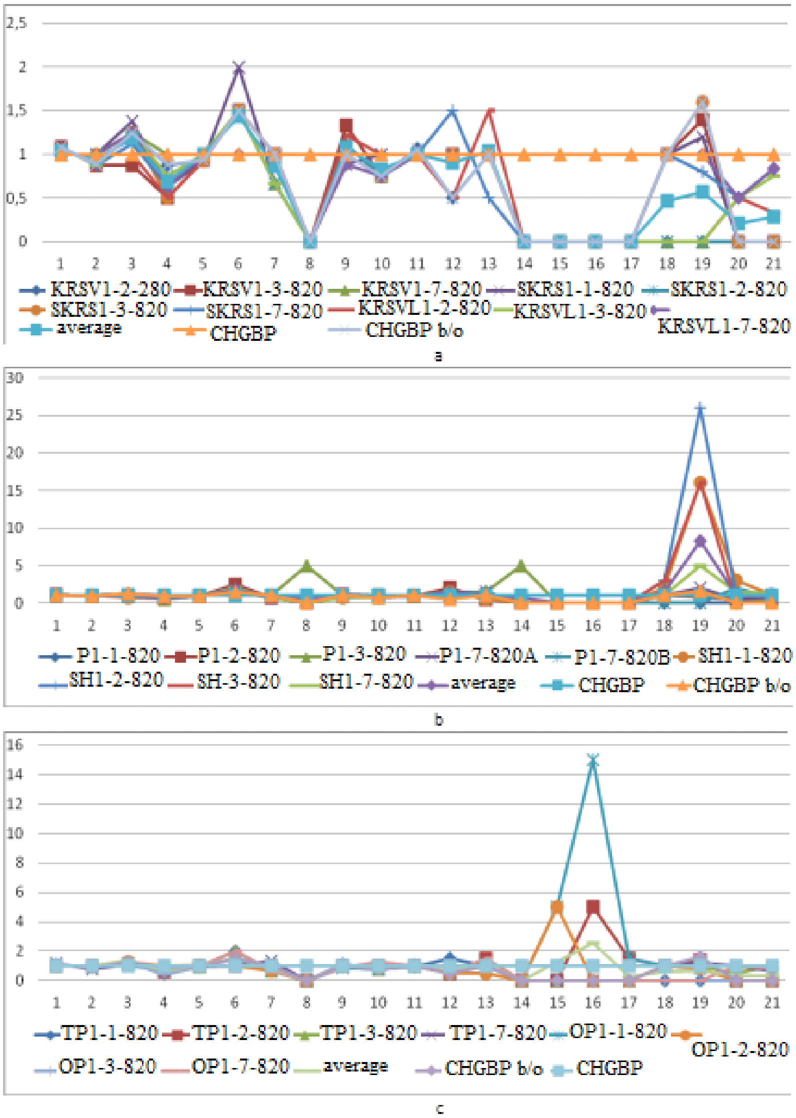
Table 1: *Main categories and Petrographic Characteristics.*

Code in the graphic	Petrographic characteristics	Code in the graphic	Petrographic characteristics
1	The amount of optically amorphous substance	12	Number of feldspar of sand dimensions
2	The amount of detrital material	13	The number of fragments of siliceous rocks of sand dimensions
3	The amount of silt material from total detrital material	14	The number of fragments of crystalline rocks of sand dimensions
4	The average size of silt grains	15	The amount of other minerals of sand dimensions
5	Number of quartz of silt dimension	16	Number of grussy material
6	Number of feldspars of silt dimension	17	The average size of grussy grains
7	The number of siliceous rocks fragments of silt dimension	18	The number of "fireclay"
8	The number of crystalline rocks fragments of silt dimension	19	The average grain size of „fireclay"
9	Number of sandy material	20	Number of lumpy clay aggregates
10	The average size of sand grains	21	The average grain size of lumpy clay aggregates

3. Results

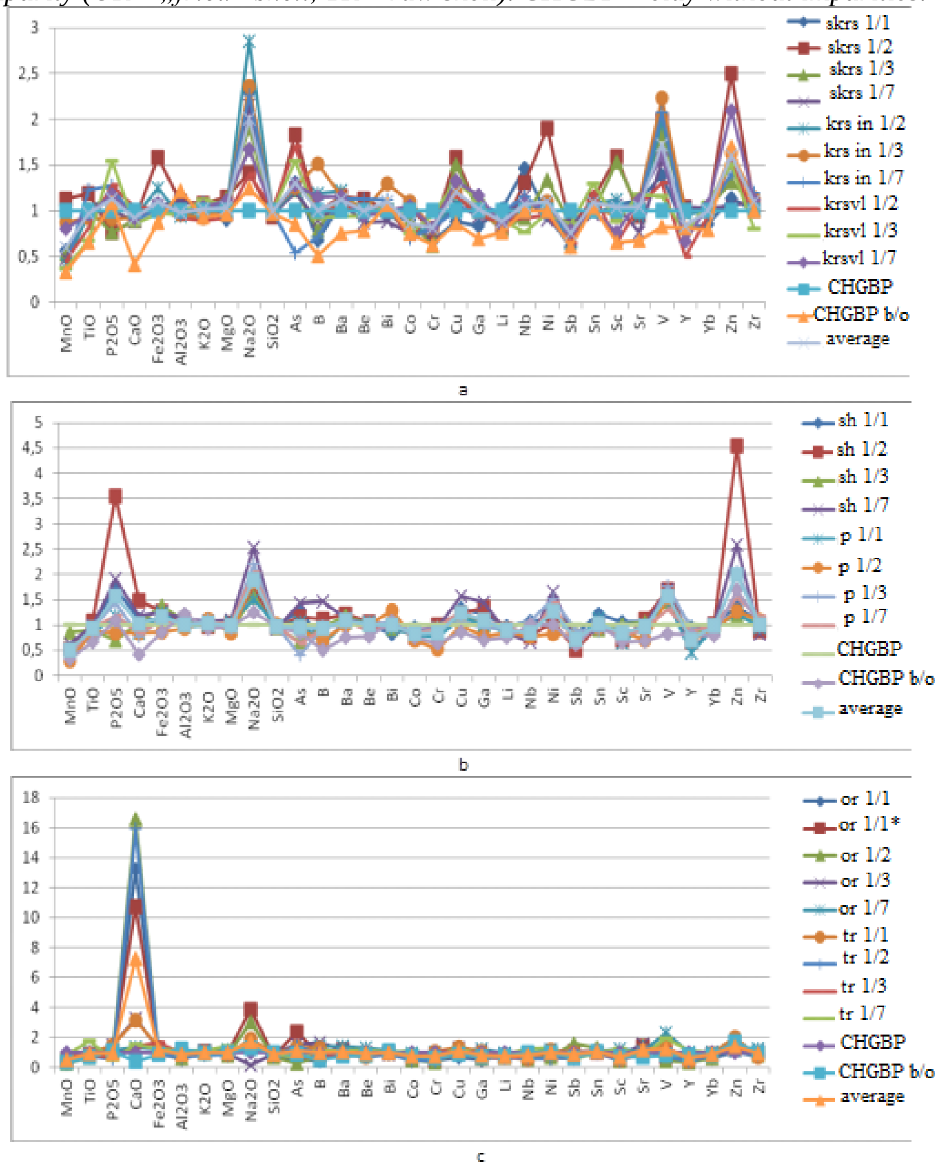
As it was already mentioned, the change patterns were studied for both groups of ceramic samples with different kinds of impurities, and for experimental samples with different concentrations of impurities. The results are shown in the graphs. All samples have similar mineralogical characteristics associated with a single source of raw materials - the number of optically-amorphous material, the amount of silt components are the same. The dynamics of the other characteristics associated with the use of a impurity: detrital component in the samples with a shell, in a fireclay fireclay samples, grussy component in sand samples. The greatest changes occurred in the mineral and organic impurities samples (Figure 1).

***Figure 1**: Diagram of changing mineral composition according to the petrographic analysis: a – organic impurities (KRSVL – wet manure KRSV – manure overflow, SKRS – dry manure), b – mineral impurities (P – sand, W – fireclay), c – organic impurities (OP – "fried" shell, TR – raw shell). CHGBP – clay without impurities.*



The chemical composition revealed a more complex picture. Samples with organic impurities differ with the highest content of sodium oxide. The mineral impurities samples are characterized by high zinc content and phosphorus oxide. Samples with shell differentiate with high calcium oxide. All samples are characterized by low manganese oxide content in comparison with those of pure clay (Figure 2).

Figure 2: *The dynamics of the chemical composition according to the spectral analysis: a – organic impurities (KRSVL – wet manure KRSV – manure overflow, SKRS – dry manure), b – mineral impurities (P – sand, W – fireclay), c – organic-impurity (OR – „fried" shell, TR – raw shell). CHGBP – clay without impurities.*



4. Discussion

There are about 20 groups in the unglazed ceramics of Volga Bulgaria. They are various in a variety of origins, appearance and technology. The issue of technological traditions was and still is the most relevant in the study of the Bulgarian pottery which is based on the historical-cultural approach.

In recent years, studies of technological features of Volga Bulgaria unglazed ceramics continued in the framework of a multidisciplinary approach with the help of analytical methods (Bakhmatova 2012; Bakhmatova *et al*. 2014; Khramchenkova and Sitdikov, 2014). Conducted analyzes have identified potential in multi-disciplinary approach in identification of the different sources of raw pottery in medieval Bulgaria of XII-XIVth centuries (Hramchenkova, 2014).

The proposed experiment is unique and is the first step in a large program dedicated to study the dynamics of the mineralogical and chemical compositions of unglazed ceramics in Bulgarian settlement. It illustrates the dynamics of ceramic compositions roasted in an oxidizing environment at a temperature of 820-850°C. This experiment focused on the dynamics of the experimental samples of compositions made with different kinds of impurities.

A comparison of the compositions of samples with impurities and without the impurities allowed us to make some observations concerning the ceramics matching mechanism and the raw clay. Comparative analysis of petrographic characteristics of samples of pure clay before firing and after firing revealed slight changes in the composition. The situation with and without lumpy clay aggregates are rather contradictory. Petrographic characteristics of the group with the addition of sand and manure are identical. Only samples with a dash of grog, “fried” shell, “raw” shell differ from the others.

Most of the values of the elements of the chemical composition of clay without firing are less than the original sample values with firing. But many items which values are not changed were revealed - titanium oxide, potassium oxide, magnesium oxide, silicon, bismuth, niobium, nickel, tin and zirconium.

In macro-element part the behavior of all the elements in samples with different kinds of contaminants does not change except for naturally increasing calcium. An exception is the manganese oxide - the value of the sample without firing is considerably less than in the sample with firing and practically equal to the values in all groups of samples with impurities.

According to micro-element composition the following picture may be observed: only zinc and vanadium have active dynamics, bismuth and tin have stability values. The values of all other microelements are changed within the passive dynamics.

5. Conclusions

Thus, the experimental studies of ceramic composition change due to the addition of impurities and calcination showed that the comparison of both chemical and mineralogical composition of the system, “ceramic-source” is possible only in ascertaining at least two conditions - kind of added impurities, temperature and roasting environment. That is, we must be aware of the technological features of the ceramics manufacture.

At this stage, the results were obtained for compositions change only in the addition of impurities in pure form, without combining them with each other, and firing in an oxidizing atmosphere at a temperature of 820-850°C. When working with a real archaeological ceramics situation is complicated by the presence of many technological factors, which is not always possible to determine.

In further experimental studies, the experimental samples will be studied, obtained by firing at other temperatures. The mineralogical and chemical composition of impurities will also be determined. This fact is extremely important to work with mineral and organic impurities.

The conducted experimental studies in this field have identified promising areas of research. To compile the most complete picture of the transformations that occur in the clay on the way to the finished ceramic products, studies of the effect on the composition of unglazed ceramics are needed, such technological factors as the environment and the firing time, the mixed molding compositions recipes, etc.

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