

## Origins of Lead Glaze Technology of the Ceramics of Kazan Kremlin

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### Abstract

*Relevance of the studied problem is conditioned by a possibility to recovery information on the time and place of vessels production that allows to set the directions of trade relations and to establish a level of technologies development and features of vocational schools. The article studies the fragments of glazed ceramic pottery found on the territory of Kazan Kremlin from 1994 to 2001. The main research method of a problem was the method of the emission spectrum analysis. Study of the element glaze composition showed that it is made of the so-called "lead" compounding and has a chemical composition similar to ceramics from the large production centers that existed during various periods: Kadikalesi in Turkey (12th -13th centuries) and in the cities of the Crimea of the 13th -14th centuries. The conducted researches show continuity of production technologies of glazed ceramics of different schools.*

**Keywords:** lead glaze, compounding, source of raw materials, micro impurities.

### 1. Introduction

Samples of glazed ceramic vessels are among the number of expressive findings of the archaeological monuments possessing significant information. Glazed ceramics with different structures was found in the beddings of the Kazan Khanate dated back to the 14<sup>th</sup> -16<sup>th</sup> centuries as a result of archeologists' researches on the territory of Kazan Kremlin in the 1990s (Khalikov, 1989). More than a half of the items are imported ceramics; another part consists of fragments of glazed ware of two types: red ware with blue glaze and white and red ware with green and brown glaze. A preliminary

research of three ceramic fragments was conducted for identification of the most appropriate analytical method (Sitdikov & Khranchenkova, 2015). According to these researches, the emission spectrum analysis that allows defining the main, minor and trace elements as well appeared to be the most informative method.

Studying of the glazed ceramics can give invaluable information about the time and a place of vessels production. It allows setting the directions of trade relations, to establish a level of development of technologies and to define the features of vocational schools. However, more reliable information about vocational schools can be received after conducting a study of the glaze chemical composition. Determination of glaze composition allows us to set both the features of compound and raw materials. Currently, there are a lot of data on element structure of glazed ceramics of different origin (Forster et. al., 2001; Bulgakov, 2005; Koval, 2009). The knowledge of compounding allows looking for the analogues coming from craft provinces of different regions in Europe and Asia. In this regard, the objective of this work was to study the chemical composition of ceramics from the excavations of Kazan Kremlin.

The study of the glaze composition of 33 samples from the excavations of Kazan Kremlin, 9 archaeological samples from the Crimea and 2 samples from Bulgarians is carried out in the presented work. Almost all the fragments are covered with glaze which foundation acts as lead. The content of lead is about 25-66%. In order to identify analogies the authors carried out the comparative analysis. It showed that the similar chemical composition on macro- and trace elements is typical for glaze of archaeological fragments found in the large centers of production of glazed pottery in Turkey and the Crimea. These trade shops existed in earlier time: in the 12<sup>th</sup>-13<sup>th</sup> centuries in the Turkish settlement Kadikalesi in Turkey and in the settlements of the Crimean peninsula of the 13<sup>th</sup>-14<sup>th</sup> centuries.

## 2. Materials and Methods

The mapping of finds through Kazan Kremlin territory allows revealing places of concentration of similar glazed ceramics. 52 samples from the total number come from excavations at the Khansky Yard. Their concentration in this area means that exactly representatives of Khansky' administration was the main consumers of ceramics studied in work.

48 fragments of the total number are connected with the period of the Kazan Khanate. There are 5 fragments from the late period of the Golden Horde. The rest of finds has no stratigraphic referencing or is derived. The ratio of products from the processed beddings most likely assumes their penetration from layers of the Khanate period. Samples of fragments of the studied ceramics are shown in Fig. 1.



**Figure 1.** Fragments of glazed ceramics from the excavations in Kazan Kremlin

The detailed morphological description of the studied samples is given in the work (Sitdikov and Khranchenkova, 2015). Researches showed that 63% of ceramics is made of white ware with green glaze, 16 % of red ware with green glaze, and 14% of red ware with blue glaze, 7% of white and red ware with brown glaze. According to comparison with the analytical data of X-ray fluorescence analysis emission spectroscopy was the most informative analysis (Sitdikov and

Khranchenkova, 2015). This method allows defining simultaneously about 40 elements, as well as major, minor and trace elements. It was necessary to separate 50 mg of the glaze from ceramics for the emission spectrum analysis. This factor is the most negative because it leads to destruction of integrity of a sample. However, taking into account the low cost of the analysis, also from the standpoint of reliability, sensitivity and informative value, this method is rather attractive for the study of archaeological artifacts in that case when inconsiderable selection of a sample is allowed. Accordingly, samples were studied in this research by the method of the emission spectrum analysis for detection of glaze composition features of different groups of ceramic.

*Entity of technique.* The sample of 25 mg is burned from the carbon electrode crater in an alternating current arc to evaporate. Exposition time for easily volatile elements is about 30 seconds at a current of 8A then the part of a diaphragm is blocked and a sample is burned up at a current of 18A. The spectrum obtained with a diffraction spectrograph DFS-458 is recorded on a photo plate PFS-03. A working reticle of the spectrograph No. 3 is 1800 pieces in a mm with the resolution 0,6nm. Photo plates are shown and fixed in standard solutions. The received spectrograms are recorded by the MF-2 spectrophotometer. The studied samples are analyzed by the method of 3 standards. Calculation of concentrations is made by standard computer program. The average of the two determinations is the result of the analysis.

It should be noted that the study did not test the chemical composition of ceramics. It is rather capacity material, the study of which is expected in the future.

### 3. Results and Discussion

The results of analytical researches are given in Table 1. Samples of the Kazan ceramics have codes №KK. These tables show that the pottery was covered (or glazed) by the so-called lead glaze with the content of lead between 25% and 66%. There is a low content of tin practically for all samples. Most samples have the low content of calcium and magnesium - <1%. It means that sand with a minimum calcium component was used for the production of glaze. The aluminium content is rather high and equals 3,95% - 8,54%. It indicates that kaolin, clay or feldspar also were the part of glaze.

The color of glaze is received by traditional methods. The blue color is determined by the addition of 1-3% copper, green color is caused by the presence of 0,26-2% Cu<sup>2+</sup> (Wedepohl et. al., 1995), brown glaze has a high content of iron > 3%.

According to the analysis, the studied glaze can be divided into 8 conditional groups. Each group is characterized by a high content of certain trace elements.

1. high content of nickel (> 300 ppm) and vanadium (> 100ppm)
2. high content of vanadium (> 100ppm)
3. high content of antimony (> 100ppm)
4. high content of vanadium (> 100ppm).
5. high content of antimony and nickel (> 100ppm).
6. high content nickel (> 100 ppm) and low antimony .
7. high content of nickel (> 100 ppm) and bismuth (> 10ppm)
8. high content antimony (> 100 ppm) and bismuth (> 10ppm).

As it was noted above, the authors also conducted research of 9 fragments of the Crimean glazed ceramics. As known there were large centers for production of glazed ceramics in the Crimea in the 13<sup>th</sup> -14<sup>th</sup> centuries. This ceramics was not chosen accidentally as a sample. The color palette of samples of the Crimean peninsula is very close to the Kazan samples of green, brown and yellow. In addition, samples of the Crimean ceramics are found in a large numbers at the excavations of the Bolgar ancient settlement (Tatarstan) in layers of the 13<sup>th</sup> -14<sup>th</sup> centuries. Analytical results for the Crimean samples are given in Table 1. Researches showed that the Crimean glaze contains lead as a composition component, as well as the Kazan ceramic glaze. Analogues of the Crimean ceramics by a chemical composition are available for each of the above-mentioned groups. Thus, identity of structures is observed both for macro - and trace elements. The only difference can be noted for calcium and boron. The content of these elements is higher for the Crimean ceramic than in the Kazan fragments. It demonstrates the sources variety of raw materials of "non lead" components of glaze. The high content of boron in the Crimean ceramics can be explained by the presence of this element in the Crimean sand or clay.

In 2013, the authors had an opportunity to explore the work of sepai from the State Bolgar memorial estate. These attributes of production of glazed ceramics were used as supports during roasting glazed ware, and they are dating by the first half of the 14<sup>th</sup> century. There were glassy sags on the artifacts. Chemical composition of the glassy material has

also been studied and given in the lower part of the Tables 1 and 2. There are also shown the results of the component composition of turquoise glaze of sphere bell (it is thick-walled vessel which has the height of 10-15 centimeter) from the Bolgar ancient city excavation. Lead content in it is similar to the Crimean glaze (43%), however, the tin content is about 3%, and sodium content is about 6%. It indicates that the glaze was prepared according to a recipe that differs from the Crimean by adding soda or ash.

Studying of the obtained analytical data showed that the manufacturing technology of a glazed layer on ceramic vessels from excavations of Kazan Kremlin is similar to the Crimean technology. A very thin layer of white engobe was done before putting glaze on pottery. The composition of engobe from a sample of Kazan Kremlin (#1) and the Crimean glaze (# 2) is given in Tables 1 and 2. White clay with the low content of calcium was used as engobe for Kazan ceramics. White clay was also used for the Crimean ceramics but with a mixture of calcium.

samples		CuO	PbO	SnO <sub>2</sub>	MnO	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	SiO <sub>2</sub>
KK # 137	engobe	0,018	2,37	0,025	0,058	0,36	0,62	0,703	1,519	18,3	1,53	0,51	0,17	75,77
Crimea 8		0,046	2,68	0,0008	0,058	0,61	0,1	3,01	2,18	25,54	1,19	0,71	0,62	64,62
KK # 49	group 1	1,17	33,58	0,0044	0,035	0,36	0,17	0,79	1,28	5,47	0,88	0,1	0,42	55,54
KK # 703		0,42	36,64	0,035	0,027	0,24	0,95	0,97	0,38	6,74	1,28	0,23	0,36	51,47
Crimea 6		0,49	27,96	0,031	0,072	0,42	0,078	4,68	2,29	8,67	1,14	1,55	0,54	51,96
KK #105		0,92	47,25	0,017	0,043	0,47	0,085	0,7	0,76	7,11	0,98	0,69	0,26	40,26
KK #47		0,58	49,86	0,016	0,035	0,38	0,047	0,42	1,05	7,32	0,93	0,17	0,26	38,79
KK #467	group 2	0,72	38,88	0,028	0,025	0,3	0,44	0,42	0,5	6,05	0,64	0,12	0,19	51,25
KK #403		1,01	25,12	0,16	0,075	0,52	0,14	3,68	1,43	7,87	0,98	2,14	0,51	56,22
Crimea 26		0,19	40,85	0,0037	0,055	0,64	0,084	8,19	5,65	8,71	1,19	1,16	0,46	32,46
KK #42		0,21	25,53	0,067	0,035	0,95	0,87	1,74	4,86	8,36	1,33	1,06	0,49	54,37
KK #11A		0,061	25,88	0,11	0,04	0,97	0,25	1,42	1,18	3,78	1,67	1,18	0,46	62,86
KK #266		0,33	42,01	0,057	0,044	0,55	1,68	1,53	4,58	7,94	1,33	0,78	0,46	38,54
KK #137		0,69	49,96	0,052	0,027	0,32	0,16	0,32	0,44	5,68	0,75	0,085	0,11	41,12
KK #43	group 3	0,012	35,96	0,0009	0,13	0,23	0,24	0,26	1,54	5,36	0,94	0,063	0,075	55,11
Crimea 19		0,26	45,04	0,0075	0,046	0,43	0,033	5,12	5,56	4,94	0,99	0,79	0,46	36,39
KK #932		0,008	42,12	0,0041	0,041	0,25	0,42	0,77	4,43	5,29	0,87	0,31	0,36	44,94
KK #311		0,19	51,44	0,013	0,027	0,28	0,36	0,22	0,28	5,54	1,15	0,12	0,086	40,02
KK #1501	group 4	0,38	41,53	0,039	0,033	1,45	1,49	1,61	1,05	8,16	1,02	0,64	0,22	42,23
Crimea 51		0,21	42,38	0,061	0,049	0,87	0,054	4,18	1,15	7,64	1,92	1,29	0,7	39,89
KK #135		0,41	49,89	0,031	0,035	1,27	0,99	1,54	1,07	7,14	0,87	1,16	0,45	35,05
KK #32		0,81	45,12	0,028	0,05	0,39	0,28	0,57	0,4	6,27	1,06	0,26	0,35	44,24
KK #138.5		0,076	66,11	0,006	0,043	0,36	0,21	0,3	0,27	6,89	0,94	0,2	0,16	24,17
KK # 137		0,87	39,64	1,08	0,061	0,3	1,67	2,84	1,41	7,56	0,98	0,95	0,3	42,18
KK #490	group 5	3,05	39,12	5,24	0,052	0,26	1,2	0,68	0,74	3,95	1,23	0,14	0,58	43,56
Crimea 23		0,43	39,94	0,0095	0,02	0,21	0,19	3,27	0,75	5,14	2,02	1,54	0,87	45,49
KK #461		0,04	42,49	0,0076	0,059	0,36	0,08	0,45	3,1	8,54	1,11	0,52	0,23	42,76
KK #58		1,88	29,74	0,065	0,031	0,32	0,39	0,49	0,22	7,37	1,04	0,41	0,37	57,31
KK #354		1,07	55,32	0,043	0,026	0,21	0,18	0,25	0,44	4,92	0,64	0,12	0,16	36,11
KK #261	group 6	0,01	42,11	0,045	0,034	0,35	0,27	0,56	4,57	6,99	0,98	0,69	0,13	43,22
KK #414		0,17	49,86	0,006	0,043	0,37	0,12	0,56	3,57	7,12	0,88	0,37	0,33	36,4
KK #90		0,026	41,38	0,0005	0,031	0,26	0,05	0,29	3,12	6,35	0,83	0,25	0,21	46,89
KK #329	group 7	0,004	32,95	0,0005	0,046	0,28	0,06	0,63	1,27	7,94	1,08	0,78	0,59	54,21
KK #236		1,59	42,23	1,46	0,032	0,37	0,49	0,46	0,82	6,37	0,89	0,23	0,35	44,56
Crimea 38		0,89	46,88	0,0081	0,056	0,45	2,07	4,34	0,59	7,51	2,43	1,68	0,77	33,01
KK #19	group 8	0,26	56,54	0,046	0,036	0,55	3,18	1,92	1,12	7,91	1,01	0,84	0,32	25,98
Crimea 46		0,71	51,24	0,031	0,011	0,14	0,045	0,27	0,38	1,58	1,64	0,17	0,51	42,87
KK #535		0,1	51,92	0,033	0,023	0,3	0,098	0,35	0,43	7,75	0,84	0,15	0,23	37,66
KK #376		0,51	53,48	0,0076	0,053	0,39	0,57	0,82	0,69	8,13	0,88	0,2	0,25	33,51
Crimea 19		2,03	37,75	0,009	0,05	0,32	0,05	3,97	3,79	6,15	1,04	0,59	0,19	45,25
KK #38		0,019	36,32	0,24	0,73	0,27	0,041	0,92	3,29	7,37	0,99	0,1	0,23	49,22
KK #3		0,049	49,27	0,0011	0,027	0,31	0,37	0,61	6,68	4,72	0,66	1,02	0,44	36,75
Sepai #44		1,08	46,19	0,09	0,056	0,7	1,63	3,92	5,01	6,05	0,87	2,04	0,72	31,26
Sepai #59		1,81	58,25	0,062	0,11	0,59	0,25	3,58	4,72	6,54	0,94	2,38	1,15	19,13
sphemko mus		1,69	43,12	2,86	0,041	0,32	0,16	3,32	6,81	2,49	1,35	2,18	0,12	29,33

Table 1. Chemical composition of glaze samples of Kazan Kremlin, the Crimea and Bolgar (major and minor elements, %).

samples		As	B	Ba	Be	Bi	Co	Cr	Ga	Li	Nb	Ni	Sb	Sc	Sr	V	Y	Yb	Zn	Zr
KK # 137	engobe	4	66	350	1,6	0,9	5,5	51	7	35	7	230	8	8	70	82	16	1,5	65	71
Crimea 8		19	320	350	2,5	1,1	11	72	13	28	17	51	7,5	8	80	170	13	2,5	28	94
KK # 49	group 1	90	46	460	1,5	0,7	5	61	12	25	7	380	11	4	80	150	15	1,9	68	89
KK # 703		16	39	280	1,6	1,9	9,5	43	9	31	6	330	28	4	60	110	14	2	66	76
Crimea 6		25	180	310	1,8	1,8	21	65	13	26	7	380	41	5	80	160	10	1,4	25	45
KK #105		16	28	290	1,6	1,7	2,5	71	19	41	11	250	41	11	60	180	21	2,5	69	85
KK #47		5	54	390	1,1	0,8	8	52	14	25	7	290	21	7	50	130	11	1,8	680	140
KK #467	group 2	4	31	260	1,1	0,8	4	92	10	27	8	36	35	8	70	140	9	0,6	870	80
KK #403		20	140	390	1,8	1	10	53	17	26	9,2	89	95	9,1	130	150	19	2,3	410	92

<b>Crimea 26</b>		<b>29</b>	<b>350</b>	<b>490</b>	<b>2,3</b>	<b>1,4</b>	<b>15</b>	<b>79</b>	<b>35</b>	<b>56</b>	<b>14</b>	<b>32</b>	<b>19</b>	<b>21</b>	<b>140</b>	<b>110</b>	<b>19</b>	<b>2,7</b>	<b>73</b>	<b>130</b>	
<b>KK #42</b>		32	65	510	2,8	1,3	8,7	63	18	35	12	26	9,6	16	120	120	21	2,4	53	190	
<b>KK #1гп</b>		34	180	520	2,6	1,6	15	66	23	28	8,2	21	92	13	100	180	14	2,9	90	130	
<b>KK #266</b>		21	61	490	2,5	1,1	11	59	21	25	7,8	32	94	11	210	320	13	2,3	55	87	
<b>KK #137</b>		14	41	210	1,1	3,1	6	28	9	26	8	71	25	6	70	76	14	1,5	69	91	
<b>KK #43</b>		4	26	250	1,7	0,9	3,1	32	9	43	10	60	150	1,2	100	64	11	1,5	42	93	
<b>Crimea 10</b>	group 3	<b>86</b>	<b>280</b>	<b>390</b>	<b>2,1</b>	<b>1,3</b>	<b>35</b>	<b>54</b>	<b>23</b>	<b>43</b>	<b>17</b>	<b>13</b>	<b>280</b>	<b>7</b>	<b>150</b>	<b>61</b>	<b>16</b>	<b>2,8</b>	<b>96</b>	<b>81</b>	
<b>KK #932</b>			16	31	290	1,3	0,9	13	59	8	26	7	86	150	6	60	71	21	2,5	96	78
<b>KK #311</b>			19	46	270	1,4	5,6	4	31	7	23	9	76	350	4	80	43	12	1,5	49	76
<b>KK #1501</b>		110	78	330	2,1	8,7	7,5	71	15	28	8,9	23	1800	12	88	330	9,1	2,1	54	110	
<b>Crimea 51</b>	group 4	<b>14</b>	<b>460</b>	<b>350</b>	<b>2,3</b>	<b>2,4</b>	<b>24</b>	<b>190</b>	<b>36</b>	<b>46</b>	<b>19</b>	<b>88</b>	<b>1070</b>	<b>18</b>	<b>190</b>	<b>200</b>	<b>32</b>	<b>3,6</b>	<b>37</b>	<b>290</b>	
<b>KK #185</b>			24	62	290	2	1,6	6	58	18	26	8,4	75	330	5,4	120	260	11	2,9	51	180
<b>KK #32</b>			39	24	250	1,4	1,4	2,5	34	11	24	8	59	200	2,5	75	150	13	2	67	85
<b>KK #1385</b>			11	15	160	1,1	1,1	2,8	85	7,5	23	6,4	74	260	3,6	90	140	9	1,4	78	79
<b>KK # 137</b>			21	59	380	1,8	6,5	4,5	130	15	31	8	27	110	8	210	110	15	2,1	180	59
<b>KK #480</b>		7	19	140	0,9	2,8	2,5	25	7	26	7	270	280	2	50	61	8	0,8	180	38	
<b>Crimea 22</b>	group 5	<b>400</b>	<b>130</b>	<b>610</b>	<b>3,2</b>	<b>2</b>	<b>10</b>	<b>61</b>	<b>21</b>	<b>72</b>	<b>25</b>	<b>150</b>	<b>790</b>	<b>14</b>	<b>200</b>	<b>73</b>	<b>20</b>	<b>2,3</b>	<b>210</b>	<b>150</b>	
<b>KK #461</b>			14	36	190	1	0,7	7,5	61	13	28	7	120	260	3	60	36	8	1,7	250	90
<b>KK #58</b>			11	48	270	1,1	7,5	5	42	10	25	8	360	190	5	60	51	14	2,1	61	71
<b>KK #354</b>		8	30	140	1,1	2,7	2,2	50	7	25	5	140	120	3	70	110	9,5	1,5	23	77	
<b>KK #261</b>	group 6	13	58	280	1,7	1,2	7	58	13	21	13	430	11	9	50	71	21	2,8	70	190	
<b>KK #414</b>			5	43	280	1,2	0,8	7,5	180	15	27	8	370	36	8	80	73	24	2,3	580	96
<b>KK #90</b>		2	32	200	0,9	1,2	5,8	140	8,4	30	6	170	14	2	53	38	7,4	1,6	34	82	
<b>KK #329</b>	group 7	7	62	340	1,6	4,3	5,5	71	10	29	11	290	10	2	70	48	19	2,9	68	130	
<b>KK #236</b>			47	29	210	1,4	4,2	2,6	38	10	24	9	120	37	4	70	170	11	1,5	55	71
<b>Crimea 38</b>		<b>100</b>	<b>380</b>	<b>570</b>	<b>3</b>	<b>119</b>	<b>12</b>	<b>60</b>	<b>16</b>	<b>45</b>	<b>22</b>	<b>150</b>	<b>60</b>	<b>18</b>	<b>180</b>	<b>120</b>	<b>20</b>	<b>3</b>	<b>64</b>	<b>110</b>	
<b>KK #19</b>		19	61	450	3,2	190	4,8	49	16	38	7,1	28	780	7,4	160	110	8,9	2,1	340	110	
<b>Crimea 46</b>	group 8	<b>120</b>	<b>520</b>	<b>99</b>	<b>1,1</b>	<b>115</b>	<b>8,7</b>	<b>58</b>	<b>27</b>	<b>45</b>	<b>11</b>	<b>21</b>	<b>2900</b>	<b>4,9</b>	<b>81</b>	<b>84</b>	<b>13</b>	<b>1,1</b>	<b>66</b>	<b>38</b>	
<b>KK #535</b>			8	59	310	1,5	5,4	3,5	52	14	38	8	130	130	7	90	82	17	1,8	70	86
<b>KK #376</b>			2	35	260	1,6	5,2	5	32	8	29	8	51	160	7	100	120	14	1,9	37	84
<b>Crimea 19</b>			<b>23</b>	<b>630</b>	<b>430</b>	<b>2,4</b>	<b>39</b>	<b>18</b>	<b>510</b>	<b>16</b>	<b>46</b>	<b>14</b>	<b>280</b>	<b>270</b>	<b>13</b>	<b>96</b>	<b>130</b>	<b>16</b>	<b>2</b>	<b>78</b>	<b>46</b>
<b>KK #38</b>			25	43	570	1,7	2,4	7,5	32	9	27	9	180	130	4	120	25	14	2,3	68	120
<b>KK #3</b>		2	<b>13</b>	<b>130</b>	1	21	6	<b>12</b>	8	<b>32</b>	8	49	130	3	60	<b>21</b>	8	1,8	54	80	
<b>Sepai #44</b>		320	46	650	2,2	3,5	13	45	18	31	6,8	74	1700	12	170	84	12	2,1	84	95	
<b>Sepai #59</b>		390	92	350	2,3	2,1	8,3	48	19	32	8,2	78	2300	7,5	85	110	9,4	2,2	79	91	
<b>spherokonus</b>		0,87	16	2,9	0,99	91	0,82	2,5	1,2	4,2	0,62	3,2	45	0,12	2,9	2,8	0,85	0,85	0,41	0,72	

Table 2. The chemical composition of glaze samples of Kazan Kremlin, the Crimea and Bolgar (trace elements, ppm).

Antimony (one tenth of a percent) and tin (one hundredth of a percent) are the impurities to the lead component in glaze samples of different territorial localization. It may be noted that a similar structure is shown by V.V. Bulgakov for glazed ceramics from Sudak (Bulgakov, 2005).

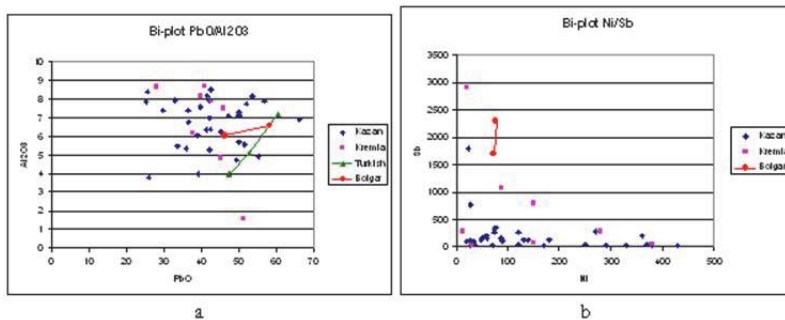
The comparative analysis of the obtained results and of chemical composition of glazed ceramic ware from the large production center of Kadikalesi was carried out for the purpose of identification of origin of technological school. This vocational school has existed in Turkey in the late 17<sup>th</sup> - early 18<sup>th</sup> centuries (Bizantibe, 2013). Turkish researchers relate this production with the traditions of the Byzantium and attribute this type of pottery to the zeuxippus (tseiksipus) type. The study showed that ceramics glaze of Kazan Kremlin is similar to the glaze from Kadikalesi.

According to analytical data, "lead" recipe with a lead content of 40-60% was used in production of Turkish, Crimean and Bolgar glaze and it is corresponding to the samples from Kazan Kremlin. Table 3 shows the content of the main elements in the artifacts glaze from Kadikalesi, also there are results of analysis of the Crimean Funy ceramics and glassy sags from Bolgar ancient settlement sepai for comparison. Copper content exceeds 1% in Bolgar glaze, as in so many of Kazan samples, i.e. this component acts as a dye. It may be noted that the same dye was also used by the Turkish and Crimean medieval ceramists (Table 3).

**Table 3.** Comparison of macro-element composition of lead glaze (Data of Turkey ceramics, Bizantibe, 2013)

lab.No		PbO	SnO	Ti <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	SiO <sub>2</sub>	CuO	MnO
	<b>Turkey</b>	47,42				2,14	1,09	3,97		0,87	0,34	40,32	3,1	0,22
	<b>Turkey</b>	52,65				2,02	3,56	5,12	0,51	0,77	0,33	35,54		
	<b>Turkey</b>	60,3				2,3		7,2		1,1	0,6	28,5		
50	<b>51 Crimea</b>	42,58	0,061	0,87	0,05	4,18	1,15	7,84	1,92	1,29	0,7	38,95	0,11	0,048
44	<b>45 Crimea</b>	49,77	0,11	0,61	0,08	4,35	2,91	7,62	1,95	1,39	0,94	27,52	2,34	0,044
38	<b>39 Crimea</b>	52,15	0,02	0,5	0,05	2,2	0,74	7,85	1,49	1,28	0,59	31,68	1,25	0,04
27	<b>sepai 44</b>	46,19	0,09	0,7	1,63	3,92	5,01	6,05	0,87	2,04	0,72	31,26	1,08	0,056
28	<b>sepai 59</b>	58,25	0,062	0,59	0,25	3,58	4,72	6,54	0,94	2,38	1,15	19,13	1,81	0,11

Figure 2 shows charts of a lead oxides ratio, aluminum, nickel and antimony. Unfortunately, the Turkish samples were analyzed by X-ray fluorescence method that does not give information about impurities, so we had no opportunity to carry out the comparative analysis on all elements. However, the fact of analogy of ceramics glaze composition of Kazan Kremlin, Kadikalesi, the Crimea and Bolgar is obvious.



**Figure 2.** Bi-plot of (a) - PbO:Al<sub>2</sub>O<sub>3</sub>, (b) – Ni:Sb relation

#### 4. Conclusion

The tradition of glazed pottery accounts for several millennia (Gulmini et. al., 2013). The first lead glaze (45-60%) appeared in Europe at the beginning of the first millennium (De Benedetto et. Al., 2004). Researches (Gulmini et. Al., 2013; Maltoni et. Al., 2012) show that in the 10<sup>th</sup> -12<sup>th</sup> centuries glazed ceramics with lead glaze were produced in various regions of the Mediterranean and Europe, in the Middle East (Afghanistan). Samples from Kazan belong to this type of ceramics.

The conducted researches showed that the ceramics glaze compounding from excavations of the Kazan Kremlin is identical to Turkish and Crimean compounding. The glaze was prepared from lead and sand-clay mixtures in various ratios from 2: 1 to 1: 3. According to the analytical data (Gulmini et. al., 2013) glaze of Afghan samples has low content of aluminum. The concentration of this element in Italian samples is 4-7% (Maltoni et. al., 2012) which is similar to Kazan, Turkish, Crimean and Bolgar samples.

According to the researches, the most informative method is the emission spectrum analysis which allows determining both main and minor and trace elements (Sitdikov and Khranchenkova, 2015). The comparison of glaze composition gives interesting analytical data that allows finding sources of raw materials production (Khranchenkova, 2014). Specific groups of antimony, bismuth and nickel in the studied samples are likely determined by the raw source of lead. Based on this, it is possible to assume that the raw sources of lead for the glaze production in Kazan Kremlin and the Crimean peninsula were the same. This assumption can be also carried to the Bolgar samples.

Given the time of samples production, it is possible to notice the following stages. The center of production of glazed ceramics in Turkey is dated by the 12-13 centuries.

Glazed pottery was produced in the Crimea actively in the 13<sup>th</sup> -14<sup>th</sup> centuries. For some reason these complexes of commercial production of glazed pottery ceased to exist. Kazan ceramics is dated by the 13<sup>th</sup> -14<sup>th</sup> centuries. Thus,

possible "migration" of technology of ceramic ware glazing from Turkey to the Crimea, and then in some other centers is observed. Perhaps, this center became the supplier of ceramic ware for the Kazan Khanate. The question of determining the location of this industrial complex is the task of further researches.

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## References

- Bulgakov, V.V. (2005). Glazuri severo-prichernomorskoj polivnoj keramiki XIII-XV vv. Krymskij f-I IA NAN Ukrainy, 359-378.
- Koval', V. Ju. (2009). Himicheskij sostav glazurej srednevekovyh fajansov. *Donskie drevnosti*, 10, 209-237.
- Kokorina, N.A. (1999). Keramika usad'by gonchara is Iski Kazani. *Tatarskaja arheologija* 1-2, 70-71.
- Khramchenkova, R.Kh. (2014) Himicheskij sostav glin kak indikator syr'evogo istochnika. *Povolzhskaja arheologija*, 2 (8), 176-205.
- Bizantibe Craftsmen – Latin Productions (2013). Istanbul. Zero Producksiyon, 87.
- De Benedetto, G.E., Acquafredda, P., Masieri, M., Quarta, G., Sabbatini, L., Zamboni, P.G., Tite, M. & Walton, M. (2004). Investigation on Roman lead glaze from Canosa: results of chemical analyses. *Archaeometry*, 46, 615-624.
- Forster, N., Grave, P., Vickery, N., Kealhofer, R. (2001). Non-destructive analysis using P-XRF: methodology and application to archaeological ceramics. *X-Ray spectrometry* 40, 389-398.
- Gulmini, M., Giannini, R., Lega, A.M., Manna, G., Mirti, P. (2013). Ghaznavid glazed pottery from Bust and Lanshar-i Bazar (Afghanistan). *Archaeometry* 55 (4), 569-587.
- Halikov, A.H.(1989). Arheologicheskie nabljudenija na predbulachnoj chasti posada Kazani XV-XVI vekov. Arheologicheskie otkrytija Urala i Povolzh'ja. Syktyvkar.
- Maltoni, S., Silvestri, A., Maritan, L. & Molin, G. (2012). The Medieval lead-glazed pottery from Nogara (north-east Italy): a multi-methodological study. *Journal of Archaeological Science* 39, 2071-2078. <http://www.sciencedirect.com/science/journal/03054403>
- Sitdikov, A.G., Khramchenkova, R.Kh. (2015). Typology of Glazed Ceramics of the Kazan Khanate and Analysis of Its Element Composition. *Journal of Sustainable Development* 8 (7), 234-244.
- Wedepohl, K.H., Krueger, I. & Hartmann, G. (1995). Medieval lead glass from northwestern Europe. *Journal of Glass Studies* 37, 65-82.