

On tin in the old Russian lead glass

Abstract

Lead glass is widely used in medieval Russia, mainly of pre-Mongolian period X-XIII cen., for manufacturing of artifacts, predominantly bracelets, lead is often accompanied by tin with very low content. Undoubtedly, tin is introduced in glass with lead although it is not the native impurity in lead ores. For lead glass manufacturing the use of slag, essentially litharge with variable tin content from pewter alloying, is proposed. At the same time, the question if slag production could supply the demand of lead glass fabrication still remains unanswered.

Keywords: old Russia, lead glass, analysis, tin presence, cause

Volume 3 Issue 4 - 2018

Egorkov AN

Russian Academy of Sciences, Institute for the History of Material Culture, Russia

Correspondence: Egorkov AN, Russian Academy of Sciences, Institute for the History of Material Culture, Russia, Email yegorkov@mail.ru

Received: December 06, 2017 | **Published:** July 27, 2018

Introduction

In medieval Russia, mainly in pre-Mongolian period X-XIII cen., lead glass was widely used for manufacturing artifacts predominantly bracelets. Centuries of lead glass analyses were carried out in the Laboratory for Archaeological Technology of the Institute for the History of Material Culture, Saint-Petersburg, Russia, showed that lead is often accompanied by tin. Surprisingly, tin, if not deliberately added mainly as opacifier, it was detected in so small contents, where its role is negligible, whereas the imported non-lead glass has not generally small tin content while appreciable concentration of tin is the result of intentional addition. It allows doubting that tin in Old Russian lead glass, although introduced with lead, was added intentionally. What is the cause of this phenomenon? An attempt to explain is done here below.

Method and materials

All the artifacts were analyzed by optical emission spectrograph (OES) with standards from the Corning Museum of Glass (A, B, C, D, JL 3610, JZ 1289) and others, selected by analyst VA Galibin, who worked at the Laboratory for long time and proposed the conditions of analysis.¹ The accuracy of OES is low and this method is often defined as semi-quantitative, but for this investigation it is not so important because the spectrum lines of tin are distinctly visible on photographic plate and detection limit of 0.01 % may be easily achieved. Lead glass artifacts were analyzed by the author from many medieval sites of Russia. Among them are great cities included in the Table 1, where number of analyzed samples and those containing tin are given. The table 1 indicates how often tin is present in Old Russian lead glass. Other analyzed artifacts occur from Dmitrov, Kozelsk, Rostov (Veliky), Vladimir, Tver, Serensk, Beloozero, Torzhok, Vyazma, Ryazan, some sites of Belarus etc. Partly analyses are published by the author.²⁻⁴

Table 1 Number of analyzed samples of lead glass and these containing tin with range 0.01–0.1%

City	All analyzed samples	Samples containing tin
Moscow	62	56
Novgorod	32	30
Pskov	34	30
Smolensk	47	35
Yaroslavl	50	39

Discussion

Introducing tin into glass with lead cannot be native impurity in lead because the primary ores of both metals substantially differ: galena PbS for lead and cassiterite SnO₂ for tin. Lead ores are widely spread whereas the depositions of tin in Europe are, on the contrary, rare. According PT Craddock⁵ tin was mined and melted in Europe from the Bronze Age, and almost certainly tin has been produced in the south west of England, Bohemia and probably in Galicia in North West Spain. Moreover, there are some difficulties for tin melting from cassiterite.⁶ For this reason the early eastern Slavs (VII cen. AD), the predecessors of Russians worked with lead but not with tin. This conclusion is confirmed by Slavic linguistics. Thus the word *olovo* (or similar derivative forms) meaning lead exists in all Slavic languages (as exception in Russian and Ukrainian it means tin) whereas the word meaning tin is unlike. In western Slavic (and Byelorussian) this word is derived from German *Zinn*, whereas in southern languages Bulgarian and Serbian this word is derived from Turkic (as in contemporary Turkish) *kalay*. In addition, the word *olovo* is not only all-Slavic but also Balto-Slavic (Lithuanian *alvas*) and borrowed from Celtic.⁷ It suggests that Slavs, ignoring tin, have used lead during centuries.

Under these circumstances the numerous finds of jewelries manufactured of tin-lead alloy, commonly called pewter, in the early eastern Slavic hoards (ca VII cen. AD) are the subject of wonder. Specifically these hoards were found in Gaponovo⁸ and Kurilovka⁹ (both in Kursk region). Moreover, in Velikie Budki (Sumy region, Ukraine) the number of pewter jewelry in the hoard of VII cen. (stripes, pendants, plaques etc.) exceeded 1200 pieces.¹⁰ In accessibility of tin suggests the import provenance of pewter and leads to conclusion that the trade of eastern Slavs with western world has taken place. There is no almost evidence that Russians, after the early east Slavs, obtained wide access to tin because tin objects in Old Russian time are rare.

Certainly, it is impossible to think that eastern Slavs, and latter Russians, have burned down pewter in order to use resulting oxides in glassmaking. In this case tin content in lead glass would be much higher to act as opacifier and yellow colorant. Another explanation may be taken into account. The ability of lead to be easily oxidized on air when heating is well known. For this reason the slag from pewter production by alloying of both metals is essentially litharge with variable amount of tin, which content being depended on the ratio of components, temperature and time of alloying. The orange litharge is markedly visible on the piece of pewter alloyed by the author as analytical standard on Figure 1. The availability of pewter for Slavs suggests the availability of slag also. Moreover, litharge can

be obtained in the process of melting pewter for filling the casting mould. Undoubtedly, the addition of this slag to litharge, or its use only itself, for lead glass manufacturing could bring in small variable amount of tin to final product.



Figure 1 A piece of pewter alloyed by the author. The orange litharge is markedly visible.

The mode of tin introducing into lead glass is analogous to those proposed by the author for introducing tin into copper colored glass in the Bronze Age.¹¹ The basic primary mineral of copper chalcopyrite CuFeS₂ has other origin then cassiterite SnO₂, while the joint copper-tin mineral stannite Cu₂FeSnS₄, a detrimental admixture to cassiterite, is rare. Thus tin is not commonly native impurity in copper, whereas tin sometimes occurs in glass colored by copper, belonging to the Bronze and Iron Age,^{1,12} and does not play therein any role. The presence of tin in copper colored glass is explained by using bronze for this purpose,¹³ but it is impossible to propose that one burnt down the tin bronze and resulting oxides used for glass coloring. For this purpose just one copper would be sufficient. The revealing of tin in ancient copper colored glass may be explained right by using slag from bronze production in cementation process described by JA Charles.⁶ The slag of copper smelting from chalcopyrite, containing iron that acts like copper as colorant is unsuitable for this purpose.

Conclusion

From technical point of view the problem of small tin presence in Old Russian lead glass may be considered as solved. But there is a problem concerning amount of slag for lead glass production. If manufacturing of glass in the Bronze Age was not widely developed and the amount of slag from bronze production in cementation

process could be sufficient for production of copper colored glass, the situation with use of slag from pewter for lead glass fabrication might be unlike. It is doubtful that amount of thus produced slag could supply the demands of lead glass manufacturing. For this reason the question of tin presence in Old Russian lead glass still remains unanswered and more information from excavations will be desirable.

Acknowledgement

None.

Conflict of interest

Author declares there is no conflict of interest.

References

1. Galibin VA. *The composition of glass as an archaeological source*. Russia: Saint-Petersburg; 2001. 216 p.
2. Korolyova EP, Egorkov AN. Composition of glass artifacts from some medieval sites of Belarus in the context of influence of the Tatar-Mongol invasion on the tradition of early Russian glassmaking. *Stratum plus*. 2016;5:163–174.
3. Egorkov AN, Kildyushevsky VI, Kurbatov AV. Above some traditions of glassmaking in ancient Vladimir (with particular reference to the materials of 2006 year excavations at “Vetchany gorod”). *Transactions of the Institute for the History of Material Culture 2*. Russia: Saint-Petersburg; 2007. p. 257–268.
4. Egorkov AN. Chemical composition of glass objects from the town of Kozelsk. Annexe 2. In: Nigmatullin RA, et al, editors. *Ancient Kozelsk and its neighborhood*. Moscow: 2005; p. 173–175.
5. Craddock PT. Medieval copper alloy production and West African bronze analyses – Part I. *Archaeometry*. 1985;27(1):17–41.
6. Charles JA. The development of the usage of tin and tin-bronze, Some problems. In: Franklin AD et al, editors. *The search for ancient tin*. Washington: Smithsonian Institution Press; 1979. p. 25–38.
7. Holub J. *Stručný slovník etymologický jazyka československého*. Praha: ČGU; 1937.
8. Egorkov AN, Sheglova OA. Composition of tin-lead alloys from early Slavic hoards belonging to the “antiquity of Ants”. *Archaeometry and maintenance of historical and cultural heritage 4*. 2000;56–61.
9. Egorkov AN, Rodinkova VE. The composition of metal in objects from the early medieval Kurilovka hoard. *Brief reports of the Institute of Archaeology*. 2014;168–178.
10. Goryunova VM. A new hoard of Ants from the territory of Middle Dnieper. *Archaeological News 1*. Saint-Petersburg. 1992. p. 126–140.
11. Egorkov AN. On bronze and brass production by cementation in antiquity. *Archaeological News 15*. Saint-Petersburg. 2008. p. 157–162.
12. Brill RH. Chemical analyses of some glasses from Frattesina. *JGS*. 1992;34:11–22.
13. Hartmann G, Kappel I, Grote K, et al. Chemistry and technology of prehistoric glass from Lower Saxony and Hesse. *JAS*. 1997;24:547–559.