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Multivariate Statistical Interpretation of a Data Set of Bulgarian Ancient and Early-Christian Glasses

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Abstract

The present study deals with the application of cluster analysis as a chemometric method to an ancient glass data set of 91 ancient and early-Christian glass fragments from Bulgaria. They have been analysed for different chemical components; the analytical data were treated by hierarchical clustering analysis in order to obtain appropriate linkage between glass artefacts and between the chemical parameters characterizing them. The clustering using different variables has indicated that the grouping of the chemical characteristics is probably related to the specific composition of the raw materials.

Introduction

Archaeological investigations have proven that glass was known and used on Bulgarian territories as early as the sixth to the seventh century BC. Later, during the Roman times, Bulgaria became part of the Roman provinces Moesia, Thracia and Macedonia. Together with intensive importation from Egypt, Byzantium, and the Near East local glassmaking was developed in the period from the first to the fifth century AD. Antique glass-workshops have been discovered by excavations at the ancient cities Odessos, Oescus and Nove so far. The great variety of glass artefacts with respect to their location and chemical composition often requires a specific approach for expert assessment of glassmaking technology and origin. Chemometric data classification, modelling and interpretation seem to be the most reliable assessment procedure. Subject of the present work was the chemometric assessment of a data set of ancient and early-Christian glasses, most of them excavated on the territory of present Bulgaria. The results obtained can give information on the glassmaking technology, the raw materials used, the recipe norm, the colouring elements, and the origin of glass, as well as on the trade and cultural relationship in the past.

Materials & Methods

The data set includes elemental composition of 91 glass artefacts. 18 of them are analysed by means of ETV-ICP-OES (ICP-spectrometer model SPECTRO ARCOS - SPECTRO A. I. GmbH &Co. KG, Kleve, Germany and ETV 4050 A, Spectral Systems, Fürstenfeldbruck, Germany) by Detcheva et al (unpublished data), the others are reported in literature [1-4]. The excavating sites on Bulgarian territories are ancient cities (Odessos, Apollonia Pontica, Oeskus and Nicopolis ad Nestum), antique Roman villas (Armira and Bela Voda), castles (Trimamium, Kaliakra and Sitan Kale), early-Christian basilicas (Bansko and Batak) and a Tracian necropolis (Karagonsko). A set of Thessaloniki glasses [1] was also investigated, as well as several glass-types typical for the antique period [4]. All investigated artefacts in the present study are characterized by 20 chemical variables (SiO_2, Na_2O, K_2O, MgO, CaO, Al_2O_3, Fe_2O_3, Mn, Cu, Co, Pb, Sb, Cr, Ti, Ba, Sr, Zn, S, Zr and Br). The raw data were coded by z- transformation. The clustering procedure uses the Ward's method of linkage and the Sneath's criterion for cluster significance. Squared Euclidean distance was used as a similarity measure applying the STATISTICA 7.0 software [5].

Results & Conclusions

Figure 1 presents the hierarchical dendrogram for clustering of the 91 glass samples from the data set. As can be seen, five clusters (denoted as K1, K2, K3, K4 and K5, respectively) are formed at the significance level of 33.3 % Dmax. All Thessaloniki glasses form a separate cluster K1 characterized by high content of SiO_2, Cu, Pb and S and low content of Na_2O, CaO, MgO, Al_2O_3, Mn, Sb, Ti, Ba and Sr. Hence, the hypothesis for common origin with the investigated Bulgarian glasses is not confirmed. On the other hand, all glasses from Sitan Kale and Nicopolis ad Nestum form a separate cluster K4 characterized by high content of Na_2O, CaO, Sr and lower content of SiO_2, Co, Cr, S with respect to the other groups, which indicates probable common origin of these artefacts. The rest of the glasses are distributed within the other three clusters. The largest one K3 (39 glasses) is characterized by high content of Ba and low content of K_2O, Zn and Zr. Cluster K2 (14 glasses) is characterized by high content of Sb, Cr and Co and low content of Fe_2O_3 and Pb and cluster K5 (24 glasses) is characterized by high content of K_2O, MgO, Al_2O_3, Fe_2O_3, Mn, Zn, Ti and Zr and low content of Cu.

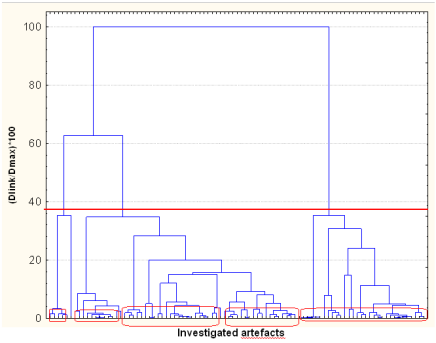

Fig. 1. Hierarchical dendrogram for clustering 91 samples (clusters marked by red right angled shape from left to right K1, K2, K3, K4, K5)

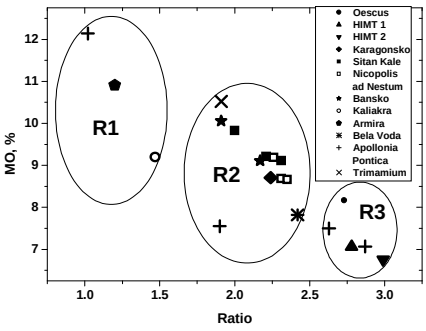

Figure 2. $[M_2O]$: [MO] ratio vs. MO in ancient glasses where: $[M_2O]=[Na_2O+K_2O]$ and [MO]=[CaO+MgO]

Important characteristic in the study of archaeological glasses is the recipe for their production. Using the approach of Shtapova [6] the glasses with ratio alkali oxides/alkaline earth oxides around 1.5 were produced according to the so-called Near-East recipe norm (**R1**), those with a ratio around 2.0– 2.5, according to the Roman-province recipe norm (**R2**), and those with ratio around 3 - to the Roman-capital recipe norm (**R3**). Applying this approach it was proven that most of the glasses in the present study were made by following the Roman-province recipe norm (Figure 2). This confirms the strong influence of the Roman Empire traditions on glassmaking technology in ancient Bulgaria.

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