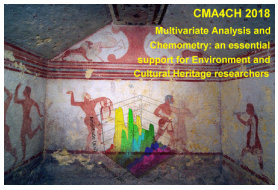

Chemometric Expertise of a Data Set of Bulgarian Medieval Glasses

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Abstract

The results obtained for the chemical composition of a data set of 25 medieval glass fragments (21 of them excavated on the territory of present Bulgaria) were subjected to cluster analysis and principal components analysis (PCA) in order to discover appropriate linkage between the glass fragments and between the chemical parameters characterizing them. The investigated artefacts are classified into several patterns depending on their chemical composition and are related to the origin of glasses, the specific characteristics of the raw materials used for their production and/or the glassmaking technology.

Introduction

Archaeological excavations in villages and necropolises have proven that glass has been used on Bulgarian territories since the end of the sixth century BC. During the Middle Ages intense development of material culture and, in particular, of production and trade of glassware in Bulgaria was observed. Together with the import of glass, a number of Bulgarian glass workshops have been discovered so far [1] and the glass production flourished in medieval Bulgarian towns during the ninth to the tenth centuries and later [2]. Along with the well characterised glass artefacts there are numerous uninvestigated finds of more or less unknown archaeological context.

The great variety of glass artefacts with respect to their location and chemical composition often requires a specific approach for elucidation of glassmaking technology and origin. Chemometric data classification, modelling and interpretation seems to be the most reliable assessment procedure. Subject of the present work is the chemometric expertise of a data set of Bulgarian medieval glasses, most of them excavated on the territory of present Bulgaria. The results obtained can give information on the technology for their production, the raw materials used and the origin of glass, as well as on the trade and cultural relationship in the past.

Materials & Methods

The present study deals with the application of multivariate statistical treatment to a data set of 25 medieval glass fragments, previously subjected to chemical analysis and described in detail in [1-4]. The results obtained for glass composition were treated by hierarchical cluster analysis (z-transformation of the raw data, Ward's method of linkage and squared Euclidean distance as similarity measure [5] and PCA (z-transformed data, Varimax rotation mode) in order to discover appropriate linkage between the glass fragments and between the chemical parameters characterizing them.

Results

The input data set subject to multivariate statistical treatment has dimensions [25x7] (25 glass fragments treated for 7 chemical parameters - SiO_2, Na_2O, K_2O, MgO, CaO, Al_2O_3 and Fe_2O_3). The similarity grouping of the artefacts is most probably due to their origin, the raw materials used for their production and glassmaking technology. All glasses in the present study contain more than 1% K_2O and the ratio Na_2O:K_2O is less than 13 which suggest that plant ash is added to the melt as alkali

source. The presence of Al_2O_3 in the concentration range of more than 1.5% assumes the use also of clay–kaolin sands as raw material. Fig. 1 presents the hierarchic dendrogram for clustering of the 7 variables from the data set [25×7] and three clusters (denoted as K1, K2 and K3, respectively) are formed as follows: K1 (Fe_2O_3, MgO, CaO); K2 (Al_2O_3, Na_2O, K_2O) and K3 (SiO_2). This data structure is additionally verified by the PCA, where three latent factors appear to be responsible for the structure (Table 1). The first principal component (PC1) shows significant correlation between Na_2O and Al_2O_3 which is also observed from the cluster analysis as well as negative correlation with SiO_2 (in the cluster analysis this parameter has independent significance, which is confirmed by the PCA). This latent factor explains 31.5% from the total variance and could be defined as "main component" factor because it includes the influence of the main components in the raw materials (e.g. coastal and/or clay–kaolin sands). The second principal component PC2 (explained variation 28.7%) shows the correlation of CaO, MgO and Fe_2O_3, which is probably due to the fact that magnesium-containing carbonates (as dolomite) were also used as raw material by the glassmaking. It could be connected with the stabilizing effect of the alkali-earth oxides hence the increase of melting temperature and corrosion resistance of glass ("glass stability" factor). PC3 points to the influence of the amount of K_2O in the raw materials (explained variation 17.2%) and is connected with the use of plant ash as a flux in medieval glass production ("plant ash" factor). It follows from the results shown in Table 1 that three main sources form the composition of the examined fragments, two of them being related to the major components in the mineral raw materials (PC1 and PC2), and the third one (PC3) – mainly to the plant ash which has been added intentionally as a flux to the batch.

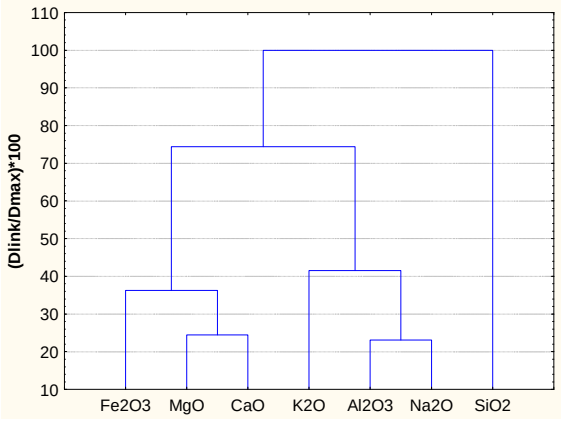

Fig. 1. Hierarchic dendrogram for clustering of 7 variables

Factor loads for the data matrix [25×7]			
Variables	**PC1**	**PC2**	**PC3**
SiO_2	**0.78**	-0.49	-0.18
Na_2O	**-0.88**	-0.13	-0.05
K_2O	-0.17	0.04	**0.94**
CaO	-0.39	**0.79**	-0.24
MgO	0.015	**0.79**	0.23
Al_2O_3	**-0.79**	0.12	0.39
Fe_2O_3	0.016	**0.68**	0.01
Explained variance	**31.5%**	**28.7%**	**17.2%**

Table 1. Principal components (PC) analysis - Factor loads for the data matrix [25×7]

Conclusions

The present study has indicated that the medieval glass fragments in consideration could be classified into several patterns depending on their chemical composition. The separation is obviously related to the origin of glasses, the raw materials used for their production and/or specificity of the glassmaking technology. The analytical data provide evidence that local craftsmen were well acquainted with the knowledge of glassmaking, but the precise nature of the raw materials is unknown.

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