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Chemical studies of ancient glasses in Poland (with particular reference to the Roman Period)

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The homogeneity of Roman glass composition (invariably soda-glass) requires the use of the most effective methods of analysis and comparison of results. The article discusses certain analytical methods, among them the recent use of spark source mass spectrometry. The results of analysis by this method are presented in Table 1, compared with the quantitative results of spectral analysis and flame photometry analysis. It would be most useful to adopt a two-stage research strategy (semi-quantitative analysis, followed by quantitative analysis). Summing-up recent comparative methods of glass analysis, two different methodological trends can be detected. The first is concerned with the somewhat mechanical sorting of data (mathematical-statistical — see Fig. 1), the second interpretative (the chemico-technological — see Fig. 2). This second approach, used also in Poland, has recently gained more adherents.

KEY WORDS: glass, chemical composition, Roman Period, analytical methods

INTRODUCTION

One of most difficult problems in studies of Roman glass is determining the origin of artefacts, due to the similarity in glassware from different Roman provinces. Technological examinations give us the chance to explain some problems of provenience of objects.

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In comparison to other periods during which different recipes were applied (sodium, potassium, leaden, *etc.*), the Roman period is characterized by the use of only one recipe — sodium. We meet many difficulties when we try to identify the origin of vessels, the majority of which were made by using a specific type of sodium recipe with soda of mineral origin (the chemical composition of beads was more differentiated — see Stawiarska 1984). Therefore, applying the most efficient methods of analysis and its comparison is very important.

ANALYTICAL TECHNIQUES

In the last twenty years world laboratories have applied many and various techniques to studies of glass remains. Techniques used included the classical methods of wet chemical analysis, gravimetry, flame photometry, atomic absorption spectrometry, calorimetry, electrolysis, polarography, combustion analysis, emission spectroscopy, auger electron spectroscopy, neutron activation analysis (NAA), X-ray fluorescence analysis (XRF) and others (Brill 1969; Frank 1982: 50—62).

In Poland research on ancient glasses has been done primarily by the Institute of History of Material Culture, now the Institute of Archaeology and Ethnology (IAE), Polish Academy of Sciences. This Institute joined the Corning Museum of Glass in New York in its work aimed at unification of patterns and methods of analysis of glass remains (see Brill 1972). The patterns for glass analysis finally prepared by the IAE do not diverge from world standards and have been applied extensively since 1969 at the Central Laboratory of this Institute in Warsaw.

The analytical technique employed in the Central Laboratory include quantitative spectral analysis of 23 glass constituents. This is made on a quartz spectrograph (IPS—28), with the use of graphite electrodes (spectra were registered on plates ORWO WU—2 and WU—3). Sodium and potassium contents were determined by flame photometry. Loss on ignition was determined by gravimetric analysis. Silica was calculated as the difference to 100%. The content of each constituent was expressed in weight percentage (Pawłowska 1976; Pawłowska and Łachnik 1965).

NAA and XRF are the non-destructive methods of analysis most frequently applied in world laboratories. These methods were used to examine glass ornaments (36 objects) found in Poland and dated to late Bronze Age — Middle La Tène Periods. The analyses were carried out at the Nuclear Physics Institute of the former Czechoslovak Academy of Sciences. The analyses took into account 44 elements and in 17 cases the results were given in per cent of weight, the others in ppm.

The investigators' evaluation of accuracy is:

> "Unfortunately the quantities of major components of glass cannot be identified precisly by the method applied. Usually only the content of sodium, calcium and aluminium can be considered as reliable" (Frána and Maštalka 1990:40; see also Frána Maštalka and Venclova 1987).

It is undoubtedly profitable to widen the list of elements by a number of "trace-trace" elements.

According to R.H. Brill (1969:48)

> "most recent findings indicate that the long hoped-for useful patterns of trace element concentration, for example the rare earths, may be emerging".

Very interesting research by means of NAA through the use of lithium drifted germanium diode counters was presented by E.V. Sayre (1965:220). In his opinion in future studies in determination of raw materials used in manufacturing of ancient glass, europium and cerium concentrations should now provide criteria for judging the probablity of use of various substances in the formulation of these glasses.

Recently studies of ancient glasses as to the concentration of "trace-trace" elements, by the method of spark source mass spectrography (SSMS), have been initiated in Poland. This method is employed by the Research and Development Centre of Vacuum Electronics in Warsaw. A JOEL JMS 01—BM 2 mass spectrograph of Mattauch—Herzog geometry was used. The isotopic spectrum was exposed on Ilford photographic plates. After plate developing the blackening of the isotopic lines was measured on the peak height. Dependent on the material purity 30 to 50 elements were determined with the detection limit of 0.1 ppm for heavy elements and of 0.01 ppm for light elements (Samborowski 1988).

The analyses of the same glasses from Alexandria which had been previously analyzed in IAE PAN in Warsaw were done (Table 1). The method SSAS (as in the case of the NAA and XRF methods used in Czechoslovakia) is less accurate in the results of analyses with regard to elements concentrated more (higher) than 1%. Therefore, the major elements must be examined by using other methods, among them the methods used in IAE.

Table 1. Results of analysis of glasses from Alexandria

	SaFP		SSMS	
	a	b	a	b
SiO_2	~65%	~63%	69.2%	67.5%
Na_2O	19.6%	16.8%	···	···
K_2O	1.0%	0.85%	0.38%	0.33%
CaO	7.8%	6.9%	5.6%	3.9%
MgO	0.88%	1.3%	0.42%	0.84%
Al_2O_3	2.5%	2.5%	1.9%	2.6%
Fe_2O_3	1.4%	2.1%	0.84%	3.3%
MnO	0.14%	1.6%	0.28%	0.09%
Sb_2O_3	—	—	13.0	30.0
PbO	~0.25%	~0.01%	0.29%	0.038%
CoO	—	—	Co_3O_4 6.8	22.0
CuO	0.057%	0.021%	0.077%	0.022%
BaO	0.008%	0,1%	0.023%	0.14%
TiO_2	0.20%	0.38%	0.18%	0.41%
SnO_2	~0.05%	~0.001%	140.0	36.0
B_2O_3	0.042%	0.14%	0.038%	0.088%
SrO	tr.	tr.	0.09%	0.04%
V_2O_5	—	—	43.0	120.0
Cr_2O_5	~0.005%	~0.01%	82.0	140.0
NiO	~0.001%	~0.001%	13.0	25.0
ZnO	~0.5%	~0.5%	54.0	28.0
ZrO_2	tr.	tr.	0.016%	0.044%
Ag_2O	~0.0005%	0.0005%	1.3	1.0
As_2O_3	—	—	65.0	19.0

	SaFP		SSMS	
	a	b	a	b
UO_3	···	···	2.2	2.1
ThO_2	···	···	16.0	19.0
Bi_2O_3	···	···	1.6	—
HfO_2	···	···	3.5	17.0
Eu_2O_3	···	···	0.8	0.3
Er_2O_3	···	···	—	2.4
Ho_2O_3	···	···	—	0.7
Dy_2O_3	···	···	—	3.5
Tb_2O_3	···	···	—	1.0
Sm_2O_3	···	···	2.8	2.2
Nd_2O_3	···	···	11.0	22.0
Pr_2O_3	···	···	2.6	4.4
CeO_2	···	···	39.0	45.0
La_2O_3	···	···	11.0	15.0
Cs_2O	···	···	0.2	0.1
J	···	···	—	0.5
CdO	···	···	2.9	—
MoO_3	···	···	—	10.0
Nb_2O_3	···	···	5.6	9.5
Y_2O_3	···	···	11.0	12.0
Br	···	···	—	4.4
Sa_2O_3	···	···	4.4	8.1
Cl	···	···	0.48%	0.6%
S	···	···	0.11%	0.17%
P_2O_5	···	···	0.32%	0.08%
F	···	···	28.0	46.0
BeO	···	···	2.5	1.4
LiO	···	···	—	7.2

SaFP — Spectral analysis and Flame Photometry
SSMS — Spark Source Mass Spectrometry
a — blue glass
b — green glass
without % — components in ppm
— — not detected
··· — not determined
tr. — traces

METHODS OF COMPARISON OF THE RESULTS OF ANALYSIS

Methods of comparison of chemical composition of ancient glasses applied in Poland have been described many times. They consist generally of a correlation of chemical types of glass, proportion of certain components reflecting technology recipes (RN), alkali and calcium-magnesium raw materials and various components of sand.

In the case of glasses examined by the method NAA and XRF approximate values obtained as a result of analysis allow speculation about the types and relations:

> "speculations on glass type according to content ratios of Na:K, Ca:Mg, (Na+K):(Ca+Mg), *etc.* can be only approximate (for element ratios see Shchapova 1973, 1977; Dekówna 1980a; Stawiarska 1984). Therefore we had to choose a rather different standpoint by evaluating the similarity of the samples discussed and their relationships. With regard to the contents of all elements, we have tried to divide them into several groups..." (Frána and Maštalka 1990:48).

Statistical methods were applied to classification and among them the so called algorithm cluster was the main one used. Its base is a modified arithmetic average and it has been used for determination of improbability measure of individual samples. Further statistical steps (normalization, conversion, single cluster) gave a classification presented in a dendrogram (Fig. 1).

N. Venclová (1990) tried to compare the results of two different interpretational methods – one statistical (Frána and Maštalka 1990) and another, chemical-technological (Shchapova 1990) used for classification of prehistoric glasses from Poland. It may be observed that division of samples into groups displays an overall similarity to the assessment of first and second method (Venclová 1990: table 1), but this similarity is too general.

Many scientists, among them M.J. Baxter (1992) from the Institute of Mathematics, Statistics and Operational Research Technical University in Nottingham have recently criticized the usefulness of statistical methods for studies of ancient glasses (especially cluster algorithm). He writes (Baxter 1992:267) referring to Atchison's earlier studies that

> "the problem is that statistical analyses can be dominated by small subsets of minor or trace elements and can give rise to results that have little substantive meaning and/or ignore much of the information in the data".

Many of the minor or trace elements are "accidental" inclusions that enter with the main ingredients. The results using the correlation rather than covariance matrix are most satisfactory.

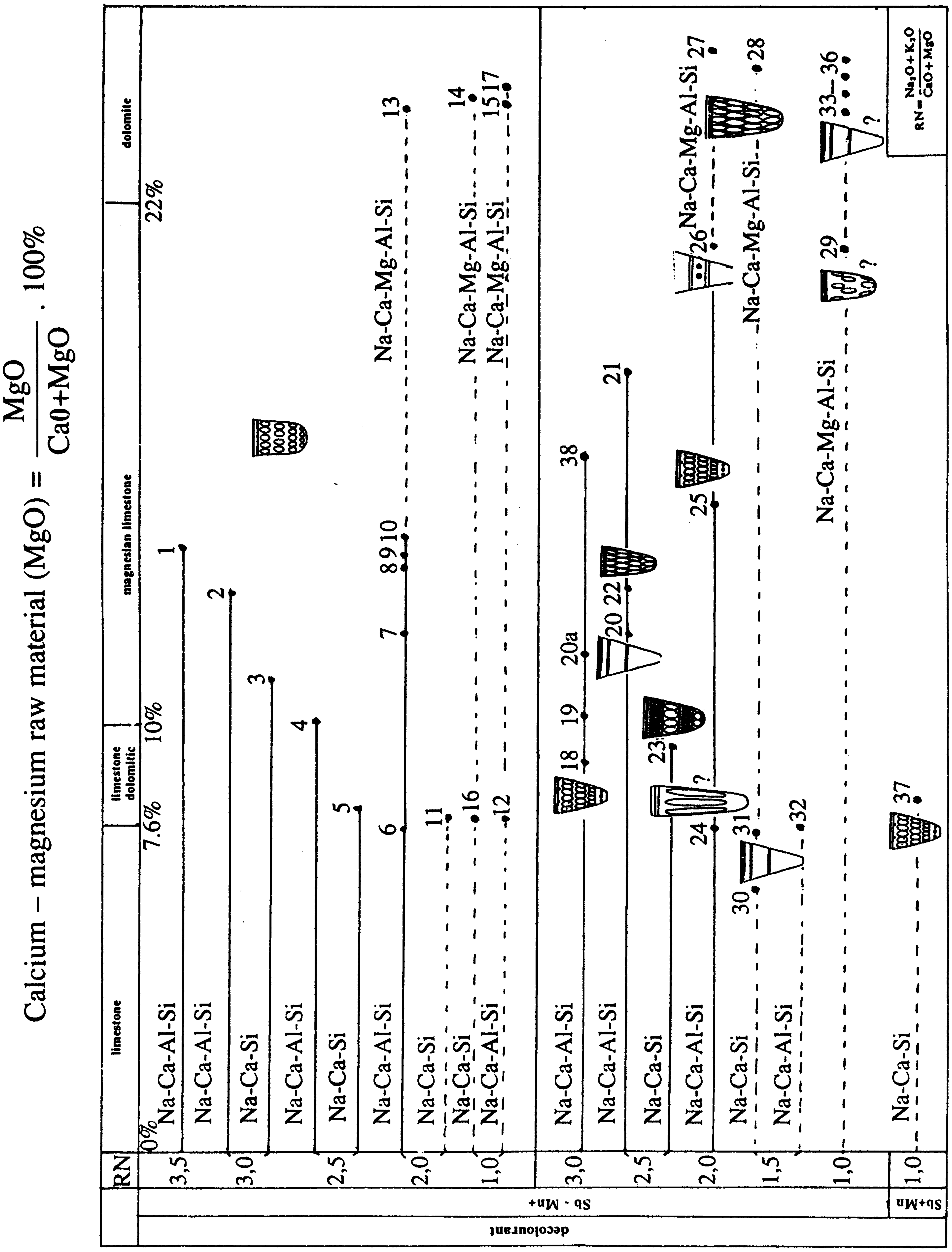

Fig. 1. Dendrogram of the prehistoric glasses from Poland (according to Frána and Maštalka 1990, fig. 2)

Many variations of comparison of different components and their sums have been recently introduced by the leading researchers of glass technology: J. Henderson (1988; 1989), R.H. Brill and others (see Velde and Sennequier 1985). In his new work Brill (1992) introduced various correlations, *i.e.*, MgO/K_2O; Na_2O/CaO; K_2O/Na_2O; Fe_2O_3/Al_2O_3 and $(CaO+MgO):(Na_2O+K_2O)$ ratios. These methods are comparable to those used by Polish researchers mentioned above (see also Dekówna 1980b, 1990; Stolpiak 1988).

The statistic-mathematical methods are often used for comparison of chemical composition of archaeological artefacts. Their principle lies in the to some extent mechanical classification of data. In contrast, the methods applied in Poland for comparison of glass analyses may be described as chemical-technological. They come from that current of investigation in which researchers try to interpret (not only to classify) a glass composition from the point of view of recipes and raw materials used for manufacture (Turner 1956a, 1956b; Caley 1962; Smith 1963; Sayre 1963; Bezborodov 1969 and many others). This approach seems recently to have acquired more and more adherents.

CONCLUSIONS

The number of the results of physico-chemical analyses of Roman glass objects, including those coming from concrete workshops, has been growing in recent years. The number of the results totals 800. More that one-fifth of these analyses has been made by the Central Laboratory of IAE, including glass objects from Roman workshops, as well as many other specimens from Poland and East-Central Barbaricum.

It should be clearly stated that as the number of data increases, the picture becomes more blurred rather that elucidated. Inasmuch as the differences for the Early Roman period are greater between the particular glassmaking centres of the Roman Empire, in the Late Roman Period one can observe unification of recipes and a tendency to use less pure raw materials (*cf.* Stawiarska 1988:216–18).

In the latter period, some centres still tended to use pure calcium-magnesium raw materials and definite decolouring agents.

It should be said that comparisons ought to be made between the results of the analyses of glass objects belonging to the same or similar formal type. To illustrate chemical and typological-formal correlation the author of this paper has used a visual graph (Fig. 2). The value of the methods used is demonstrated to some extent by the fact of the grouping of glass objects of one type on one axis (*e.g.*, E 230 glass objects from the territory of Poland; see Fig. 2:6–10).

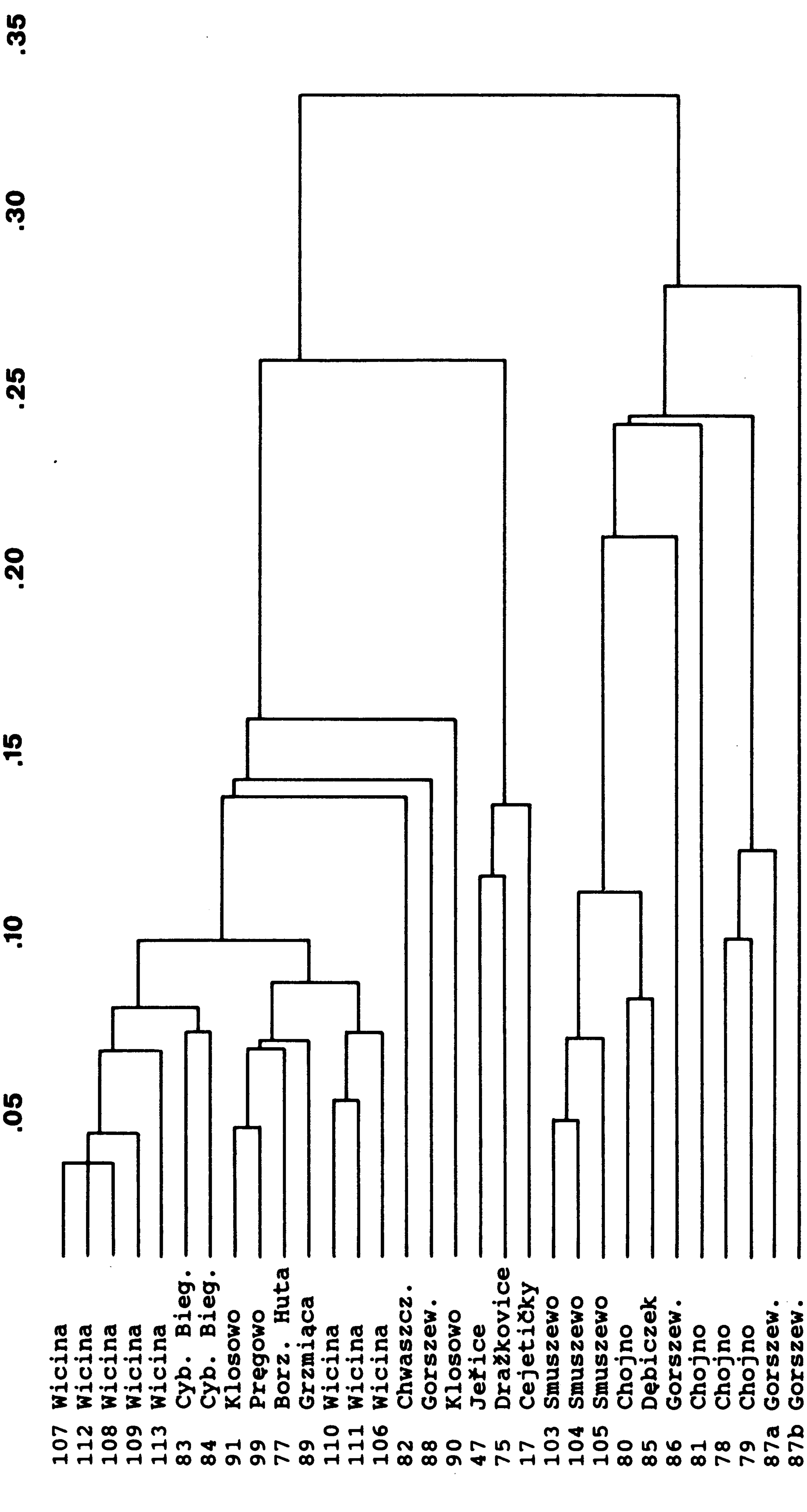

Fig. 2. Beakers of Kowalki (E230), E231—E237 and Sintana de Mureş types.

POSTULATES

We may define here some research postulates:

1. Ancient glass objects may be still analyzed using the methods of the IAE Laboratory but other methods should also be used to investigate other trace elements, including the rare earth elements. It should be added that it seems necessary to introduce patterns for some elements of the minor/trace group, such as PbO, which – as investigations show – in some cases may occur in higher concentrations.
2. We should also try – in order to grasp the limit of error – to investigate the same samples in other laboratories (*e.g.*, in the Academy of Mining and Metallurgy) by Neutron Activation Analysis.
3. To compare the results of the analyses, correlation methods should be developed rather than the statistical ones.
4. In the future, attempts should be made to compare the results of the analyses of the same glass objects by various interpretation methods. A basic source should be provided by the collection of the analyses of ancient objects with strictly determined typology and chronology.

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