PGAA AS AN ANALYZING TOOL FOR GLASS ARCHAEOLOGICAL SAMPLES

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INTRODUCTION: Glass consists of four principal components [1]:
- A former to provide the network of atoms forming the matrix of the glass. This is Silica (SiO_2), which was exploited in the form of siliceous sand by the Romans or crushed quartz in prehistoric and Venetian glassmaking.
- An alkali flux to lower temperature at which the silica melts: sodium-rich plants in ancient and Venetian glass, mineral natron in Greek and Roman glass, ash from wood containing potash (K_2CO_3) in glass of medieval Northern Europe
- A stabilizer to stop the glass dissolving in water and increase corrosion resistance, the most effective being lime (CaO)
- A colorant or opacifier, mainly metallic oxides

The identification of these components gives important information about workshops, technologies and commercial aspects of ancient glass artifacts.

The aim of our study was to investigate the capabilities of Prompt Gamma Activation Analysis (PGAA) methods and external milli-beam Particle Induced X-ray Emission (PIXE) to identify the main chemical elements of historical glasses. Both techniques are non-destructive, i.e. they do not require sampling or any preparation of archaeological objects. We determined the composition of paste and colorants for some fragments of Byzantine bracelets - discovered during the archaeological excavations from 10th-12th Centuries AD Byzantine archaeological sites of Isaccea and Dinogetia, two commercial towns situated in Dobroudja before Danube Delta [2].

METHOD: PGAA was applied at the Budapest Neutron Centre to determine the bulk elemental composition. PGAA is based on the detection of characteristic gamma photons emitted in (n,γ) reactions. The Budapest PGAA facility is described by Szentmiklósi et al. [3]. Figure shows the photo of the instrument. The quantitative analysis is based on the k_0 principle, using own PGAA library [4]. The greatest advantage of PGAA is that it provides average composition for the bulky inner part of the analyzed object. Moreover, it is sensitive for elements, such as H and B that are difficult to analyze with other non-destructive methods. During the PGAA, the glass samples were placed into an external cold neutron beam of 10^8 $cm^{-2} \times s^{-1}$ thermal equivalent intensity without preparation, and irradiated for 1200 to 10000 seconds in order to collect statistically significant counts in the spectra. The cross-section of the external neutron beam varied between 100 mm^2 and 400 mm^2, thus, in most cases the whole object was in the beam. The prompt-gamma spectra were collected by 64k multichannel analyzer and evaluated by Hypermet-PC software. Because of the small-scale activation of Na (the half-life $T_{1/2}$ of ^{23}Na is 14h), some of the samples were kept for 2-3 days cooling.

Photo of the Budapest PGAA facility

Approximate detection limits for the Budapest PGAA

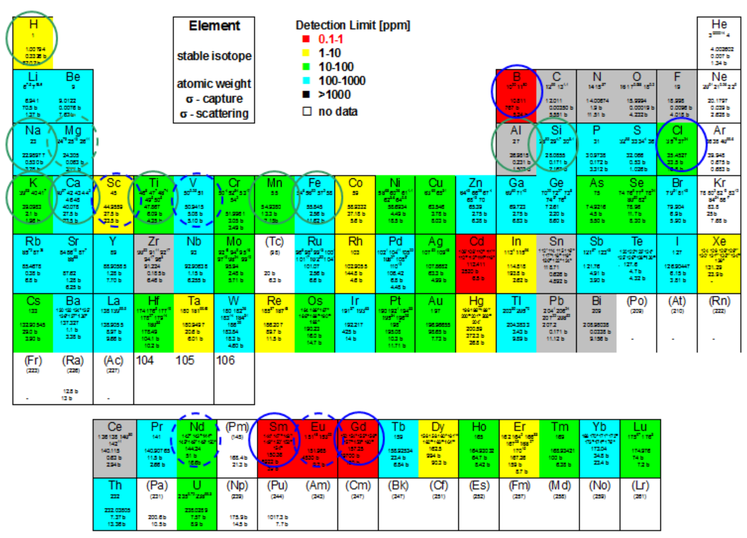
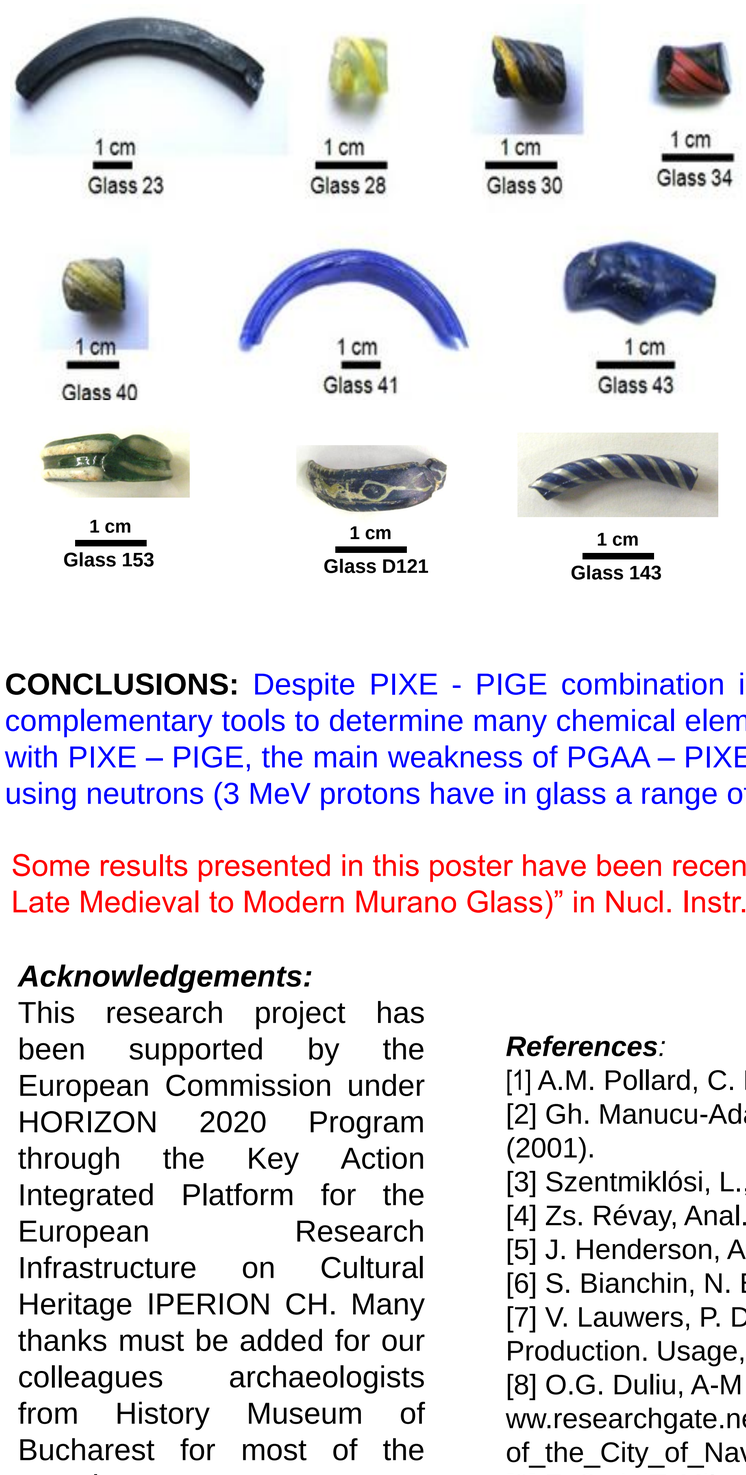


Table: Bulk concentration of selected elements in glasses analysed by PGAA. The concentrations are given in m/m%.

Sample	*H2O*	*B*	*Na2O*	*MgO*	*Al2O3*	*SiO2*	*Cl*	*K2O*	*CaO*	*TiO2*	*Fe2O3*	*MnO*	*CoO*	*CuO*	*Sm*	*Gd*
*Glass 23	0.09	0.07064	17.9	0.10	2.09	65.0	0.737	1.1	7.1	0.076	1.31	3.88	0.024	0.24	1.15E-03	1E-04
*Glass 28	0.17	0.00968	15.2	-	0.55	67.1	0.589	4.7	8.2	0.051	0.28	0.223	-	0.03	-	3E-05
*Glass 30	2.05	0.01119	0.3	-	4.24	66.3	0.054	20.6	0.44	0.134	5.25	-	-	0.08	2.30E-04	-
*Glass 34	0.07	0.10493	17.5	3.90	11.61	53.8	1.050	1.7	6.9	0.666	2.24	0.065	-	0.14	4.22E-04	5E-04
*Glass 40	1.24	0.01334	0.6	-	6.14	65.1	0.075	20.7	3.1	0.201	1.94	0.438	-	0.46	-	7E-05
*Glass 41	0.06	0.00141	14.3	-	0.38	75.8	0.169	2.4	5.9	0.032	0.12	0.018	0.104		1.39E-05	2E-05
*Glass 43	0.13	0.0419	14.3	-	1.85	69.0	0.818	2.3	8.9	-	1.44	0.873	0.095	0.27	7.54E-05	1E-04
**Glass 153	0.38	0.075	14.4	11.1	2.22	60.0	0.73	1.28	6.5	0.134	2.35	0.759	0.01	0.08	1.10E-04	1.20E-04
**Glass 121	0.10	0.051	13.4	2.8	2.08	67.7	0.083	2.47	7.6	0.121	1.51	1.158	0.0434	0.17	7.00E-05	1.30E-04
**Glass 143	0.20	0.148	15.8	-	1.95	69	0.84	1.64	7.7	0.115	1.27	0.940	0.0585	0.18	9.00E-05	13E-0.5
**Glass 71	0.11	0.318	18.8	2.3	10.02	57.5	1.17	1.9	5.2	0.634	1.94	0.105	0.0033	-	4.30E-04	56E-0.5

* samples from Isaccea
** samples from Dinogetia

Photo of the investigated glass samples



RESULTS: We'll illustrate the main results on selected eleven samples – see left Figure and above Table . With PGAA, it was possible to quantify Na, Al, Si, Ti, K, Ca, Fe, Mn, H, B, Cl, Cu, Sm and Gd in almost every glass sample, and S, Mg, Co, Zn, As, Sn Pb, Cd and Au only in specific samples. With PIXE it was possible to quantify Si, P, S, Cl, K. Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, As, Sr, Se, Sn, Sb, Ba, Pb. The concentration values are given in m/m%, the major components are expressed as oxides.

Byzantine bracelets are Soda-lime-silica glass type (strong presence of Calcium and reduced presence of Potassium), excepting samples Glass 30 and Glass 40 which have a high content of Potassium. Aluminum was detected in various proportions in all samples but the presence of Magnesium is relevant only in samples Glass153, Glass 34, Glass 121 and Glass 71 which suggest the use of plant (wood?) ash – possible import from Central Europe. The big differences in Aluminum content suggest different sand sources [5]; this is a common situation in medieval times even for the same site – S. Bianchin found for medieval glass in Florence two sand sources: one with high Al content and significant Ca (calcite) and Fe components and other with high Al content and low levels of other components [6].

The use of natron and of plant ash confirms Byzantine bracelets seem to be manufactured from the mixture of both types of glass as discussed in [7].

Samarium (Gadolinium) traces allow us to issue the hypothesis of a local source of sand for some bracelets and, as consequence, a local workshop, Sm and Gd being components of monazite mineral which accompanies Zirconium black sands at Chituc grind [8]. As concerning medieval samples, they are both Soda-lime-silica glass type, one of them with a relevant Mg, Al, K and Fe content, suggesting two different workshops.

CONCLUSIONS: Despite PIXE - PIGE combination is probably the best one for glass analysis (see [9]), our PGAA - external milli-PIXE methods proved to be adequate complementary tools to determine many chemical elements from glass composition – former (Si), alkali flux (Na, K), stabilizer (Ca, Al and Mg), colorants or opacifiers. Comparing with PIXE – PIGE, the main weakness of PGAA – PIXE is the necessity of two big facilities – particle accelerator and reactor; the advantage is the possibility of real bulk analysis using neutrons (3 MeV protons have in glass a range of approx. 60 – 80 microns, depending on the composition).

Some results presented in this poster have been recently published as "PIXE and PGAA – Complementary Methods for Studies on Ancient Glass Artefacts (From Byzantine, Late Medieval to Modern Murano Glass)" in Nucl. Instr. and Meth. In Phys. Res. B **(2017)** http://dx.doi.org/10.1016/j.nimb.2017.07.017

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