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Golden glazes analysis by PIGE and PIXE techniques

M. Fonseca [a,b,*], H. Luís [a,b], N. Franco [d], M.A. Reis [d], P.C. Chaves [d], A. Taborda [d], J. Cruz [a,b], D. Galaviz [b,c], N. Fernandes [a,b], P. Vieira [a], J.P. Ribeiro [b,c], A.P. Jesus [a,b]

[a] Dept. Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal
[b] Centro de Física Nuclear da Universidade de Lisboa, Lisboa, Portugal
[c] Dept. Física, Faculdade de Ciências, Universidade de Lisboa, Lisboa, Portugal
[d] Instituto Tecnológico Nuclear, Sacavém, Portugal

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ABSTRACT

We present the analysis performed on the chemical composition of two golden glazes available in the market using the PIGE and PIXE techniques at the ITN ion beam laboratory. The analysis of the light elements was performed using the Emitted Radiation Yield Analysis (ERYA) code, a standard-free method for PIGE analysis on thick samples. The results were compared to those obtained on an old glaze. Consistently high concentrations of lead and sodium were found in all analyzed golden glazes. The analysis of the samples pointed to Mo and Co as the specific elements responsible of the gold colour at the desired temperature, and allowed Portuguese ceramists to produce a golden glaze at 997 °C. Optical reflection spectra of the glazes are given, showing that the produced glaze has a spectrum similar to the old glaze. Also, in order to help the ceramists, the unknown compositions of four different types of frits (one of the components of glazes) were analysed.

1. Introduction

There are different ways to classify a glaze: according to its elemental composition, its colour or its opacity. But ceramists usually classify the glazes according to the temperature at which they mature. Following this criterium, glazes are divided into three main groups: low temperature (997–1150 °C), medium temperature (1200–1220 °C) and high temperature (1250–1280 °C). Due to economical advantages, Portuguese ceramists use mainly the lower temperatures glazes. Medium or high temperatures glazes are only used if absolutely necessary. A ceramic glaze contains three necessary components: flux, body and flint. The body used in Portugal is kaolin ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), the flint is usually silica and the kind of flux used will vary depending on the glaze. Besides these components, the glaze may be composed of different oxides, which produce different colours and prevent problems like running, formation of bubbles, crackling or crawling of the glaze. For a low temperature glaze (at 997 °C) the most common fluxes are: borax (where boron is the main element), barium carbonate, calcium carbonate, lead bisilicate, lithium oxide, magnesium carbonate, sodium oxide, potassium oxide and finally zinc oxide. Basic mixtures of body, flint and fluxes, called frits, are commercially available. Ceramists may use several frits and colour producing oxides to obtain the kind of glaze they pretend. Portuguese sellers do not supply the composition of these frits, which can significantly vary regarding their composition. Glazes with lead bisilicate and barium carbonate have to be handled with special care as they are toxic to humans, and should not be applied in glazing surfaces that may come into contact with food. With the IBA techniques it is possible to identify which glazes have Pb and Ba and derive the mass fractions of each element.

Nowadays, there are no golden glazes at low temperatures commercially available (two new, supposed to be, golden glazes show a metallic black colour at those temperatures), with their economic implications for the Portuguese ceramists.

Our work aims at providing the chemical information needed by the ceramists in order to obtain the desired golden glaze around 1000 °C and to quantify Pb and Ba contents due to their toxicity.

In order to determine the composition of currently available "golden" glazes, Glaze B and C, and the previous golden one, Glaze A (see Table 1) samples were analyzed using PIGE [1] and PIXE [2,3] techniques at the ITN ion beam laboratory. For light element analysis, we used a standard-free method for PIGE in thick samples, based on the ERYA – Emitted Radiation Yield Analysis – code, that integrates the nuclear reaction excitation function along the depth of the sample [4]. For PIXE the method used is also a

* Corresponding author. Address: Centro de Física Nuclear da Universidade de Lisboa, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal. Tel.: +351 217904744; fax: +351 217954288.

E-mail addresses: mmfonseca@itn.pt (M. Fonseca), heliofluis@itn.pt (H. Luís), nfranco@itn.pt (N. Franco), mareis@itn.pt (M.A. Reis), cchaves@itn.pt (P.C. Chaves), galaviz@cii.fc.ul.pt (A. Taborda), jdc@fct.unl.pt (J. Cruz), ataborda@itn.pt (D. Galaviz), n.fernandes@itn.pt (N. Fernandes), pmv@fct.unl.pt (P. Vieira), jprib@cii.fc.ul.pt (J.P. Ribeiro), apjesus@cii.fc.ul.pt (A.P. Jesus).

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Table 1
Designation of the analysed glazes.

Old golden glaze	Glaze A
1st Commercially available glaze	Glaze B
2nd Commercially available glaze	Glaze C
Glaze produced with our results	Glaze D

standard-free method based on the DATTPIXE code that takes into account matrix effects, including secondary fluorescence.

Optical reflection spectra were obtained for the different glazes in order to evaluate and compare their colours.

Also, in order to help the ceramists, the unknown compositions of four different types of frits were analysed.

2. Experimental

The samples were pellets of homogeneous fine powders of the glazes and frits provided by Portuguese Ceramists compressed at 10 atm.

The new nuclear reactions beam line, installed at the 3 MV Tandem accelerator of the ITN Ion Beam Laboratory, was used for the PIGE analysis. For the present measurements a proton beam produced by a Duoplasmatron source and accelerated to an energy of 3.960 MeV interacted with the samples prepared for the analysis. The beam current was kept around 10 nA in order to avoid large dead time corrections in the collected gamma spectra (achieved below 4%). Gamma-ray detection was accomplished using a 45% Ge(HP) detector (nominal energy resolution of 2.2 keV at 1173 keV) placed at an angle of 135° with respect to the beam axis. The detector's absolute efficiency was determined using radioactive sources, namely ^{133}Ba and ^{152}Eu, placed at the position of the samples. The results obtained by this method were later confirmed by a PENELOPE simulation [5]. During the actual measurement, more than 10^4 counts were collected for each pertinent gamma-ray line as to assure a statistical uncertainty below 1%.

The PIXE measurements of the three golden glazes were done at the ITN 2.5 MV Van de Graaff – PIXE setup. This setup, described in detail elsewhere [6], makes use of a 150 eV resolution Si(Li) detector kept at an angle of 110° relative to the beam direction. For the present experiment, a Ta collimator (1 mm thickness and 4.7 mm diameter) was placed in front of the Si(Li) detector. Spectra were collected for proton beams of 1.0 MeV energy. Taking into account the characteristics of the material, and the purpose of the analysis, low energy PIXE analysis was decided to be the best choice since this provides results for medium-heavy elements ($11 < Z < 27$) as well for all minor elements present having higher atomic numbers. Once acquired, PIXE spectra were deconvoluted using the AXIL [7] computer code and quantitative data were obtained using the DATTPIXE code [2,3].

An AvaSpec-2048 Standard Fiber Optic Spectrometer from Avantes with an AvaLight-D(H)–S deuterium–halogen light source was employed to obtain the optical reflection spectra of the different glazes.

3. Results and discussion

The spectrum obtained by PIXE corresponding to the Glaze A (see Table 1) is shown in Fig. 1. In Table 2, the mass fractions calculated by PIXE are given for the three different glazes (assuming that the difference for 100% is related to oxygen content). As shown in Table 2, it is the Glaze A (see Table 1) that showed the lowest amount of Pb. The elements Mo and Co were only detected in this glaze (the detections limits for these elements are 150 and 115 ppm, respectively).

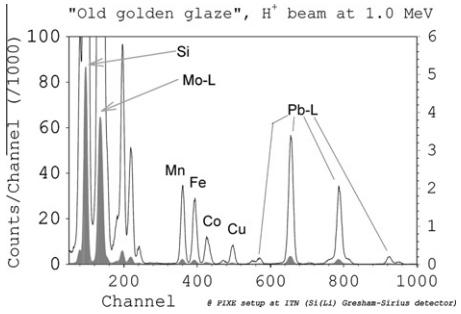

Fig. 1. Energy spectrum of X-radiation produced by the bombardment of the old golden glaze sample by 1.0 MeV protons.

Table 2
PIXE analysis of Glaze A, B and C (the difference for 100% is related to oxygen content). The estimated total uncertainty is 5%.

Element	Glaze A Mass fraction (%)	Glaze B Mass fraction (%)	Glaze C Mass fraction (%)
Al	0.60	1.53	1.61
Si	4.51	6.40	6.10
K	0.29	0.76	0.57
Ca	0.15	2.02	1.00
Ti	1.43×10^{-3}	0.201	2.27×10^{-2}
Cr	1.27×10^{-3}	1.35×10^{-2}	1.56×10^{-2}
Mn	0.36	1.76	1.48
Fe	0.37	0.189	0.21
Co	0.20	–	–
Ni	4.75×10^{-3}	0.51	9.80×10^{-3}
Cu	0.28	0.27	0.22
Mo	0.34	–	–
Pb	18.10	23.70	22.50

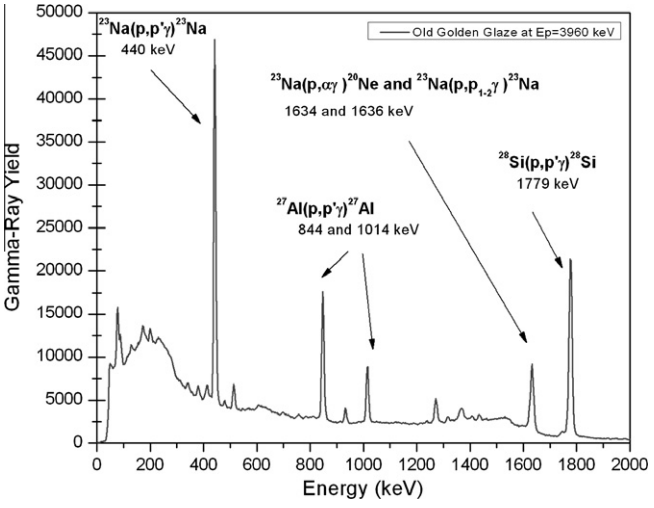

Fig. 2. Energy spectrum of γ-radiation from the Glaze A (old golden glaze). The proton beam energy was 3.960 MeV.

As for the PIGE analysis, Fig. 2 shows a spectrum corresponding to the Glaze A (see Table 1) at 3.960 MeV. Several gamma lines were observed in the presented gamma-energy range, the 440 keV from the ^{23}Na(p,p′γ)^{23}Na nuclear reaction being the most prominent. Gamma-rays from proton-induced reactions on Mg or Ca do not show up in the spectrum, as the concentrations of these elements were below the PIGE's detection limits and have only been seen by PIXE. The elements Li and B were only detected as trace elements below 5 ppm. To quantify the Na present in the three glazes, we used the ERYA – Emitted Radiation Yield Analysis – code, which integrates the excitation function of the

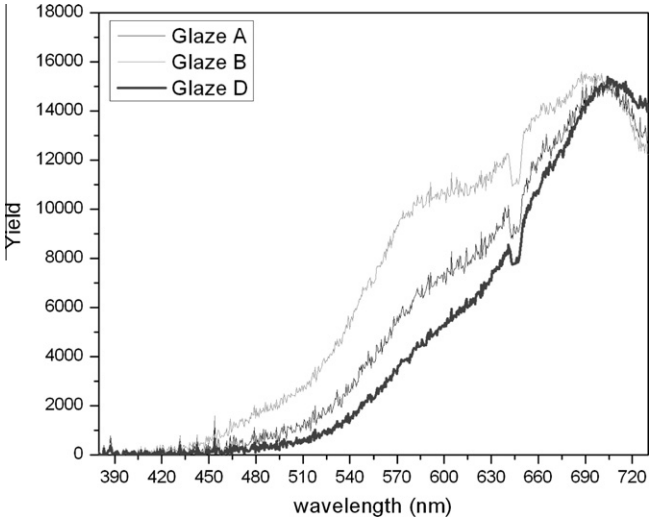

Fig. 3. Optical spectrum of three glazes: Glaze A, B and D (see Table 1).

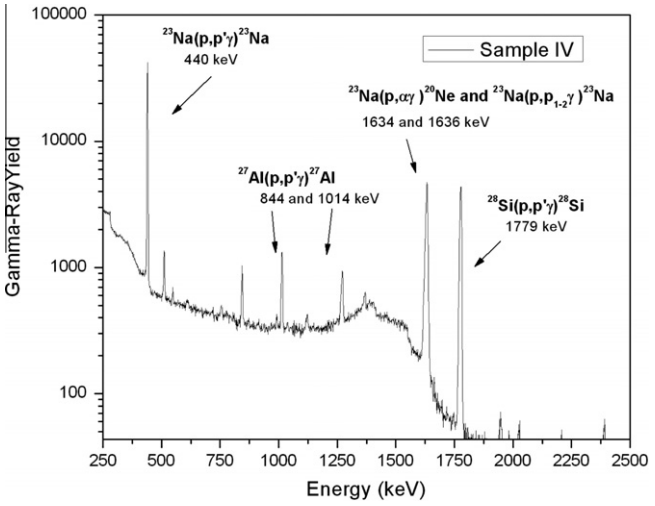

Fig. 4. Energy spectrum of γ-radiation from frit sample IV. The proton beam energy was 3.960 MeV.

$^{23}Na(p,p'\gamma)^{23}Na$ nuclear reaction along the depth of the sample. An input file of the cross section measured in the 1.260–5.199 MeV proton energy range was created. For the energies below 2.4 MeV we used the excitation function previously measured in the Van de Graaff accelerator at ITN [8], and confirmed by new measurements at the 3.0 MV Tandem accelerator [9]. The Caciolli et al. [10] cross section values in the 2.0–5.2 MeV proton energy range were renormalized to our data, since they present a systematic deviation in the energy superposition region [9].

Based on the results shown in Table 2 to established the major matrix, the ERYA code derived the following Na mass fractions: 29.4% for the Glaze A, for the Glaze B 15.5% and finally 23.0% for the Glaze C (see Table 1).

Based on the results from the present PIGE analysis we may conclude that the Glaze A has at least a sodium oxide frit.

The global results showed that all the glazes had lead bisilicate plus sodium oxide frits, although the new ones present higher concentrations of lead compared to the old glaze. The elements Mo and Co were specific of the old golden glaze.

Using the results of this work, namely the Mo and Co concentrations of the old golden glaze, the Portuguese Ceramists were able to produce a golden glaze at the desired temperature conditions.

Table 3
PIXE and PIGE analysis of four different types of frits (the difference for 100% is related to oxygen content). All the results are from PIXE analysis with the exception of the element Na. The estimated total uncertainty is 5%.

Element	Sample I Mass fraction (%)	Sample II Mass fraction (%)	Sample III Mass fraction (%)	Sample IV Mass fraction (%)
Na	3.2	18.2	7.5	6.2
Mg	1.47	–	–	0.275
Al	8.3	5.97	7.9	8.5
Si	24.4	30.1	37.6	37.8
K	0.99	8.51	3.83	0.98
S	–	–	–	–
Cl	–	0.42	0.07	–
Ca	4.05	1.05	2.57	4.87
Ti	0.026	0.046	0.062	0.041
Fe	0.084	0.084	0.125	0.123
Ni	0.010	–	–	–
Zn	19.9	0.041	1.32	0.78
Zr	–	0.072	0.22	5.9
Sr	–	–	–	–
Ba	0.064	0.057	0.85	0.091
Hf	–	–	–	0.176
Pb	19.5	0.37	1.43	2.46

Optical reflection spectra are given in Fig. 3 for Glaze D, Glaze A and Glaze B (see Table 1), showing that indeed the Glaze B has several optical components in the blue and green wavelength range contributing to its metallic silver aspect. The Glaze D, produced with the results given by our analysis, has a spectrum similar to the Glaze A, centred in the yellow wavelength range, but with slight higher red content and less blue and green contents, which contribute to a golden colour closer to gold than the old one.

In order to assist the ceramists in their choice of frits, several commercially available frits were also analysed by PIXE and PIGE (see Fig. 4). Table 3 presents the analytical results, indicating a major composition based on silica and kaolin, presenting also added metal (Pb, Zn) compounds (sample 1), and sodium, potassium and calcium compounds. None of these frits has boron or lithium or barium in its major composition. The information about lead and barium content is particularly relevant due to their toxicity.

The IBA techniques proved to be highly suitable to help Portuguese ceramists in the understanding of the composition of different glazes, as well as helping lowering the costs associated to the process of obtaining a golden glaze. Given the success of this analysis, further work should be devoted to analyze all the different glazes and frits available in the market.

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