

Analysis by raman spectroscopy and XRF of glass beads from excavations in the harbor area of rio de janeiro, Brazil



I.M.N. Ribeiro^a, R.P. Freitas^{a,*}, C. Calza^b, A.L.C. Oliveira^a, V.S. Felix^{a,b}, D.S. Ferreira^a, R.T. Batista^d, E.A.S. Gonçalves^a, M.O. Pereira^e, P.C.L. Brito^c, T.A. Lima^c, A.R. Pimenta^a, M.J. Anjos^{b,d}, R.T. Lopes^b

^a Laboratório de Instrumentação e Simulação Computacional (LISCOMP-IFRJ/CPAR), Rua Sebastião Lacerda s/n, Paracambi, RJ, 26600-000, Brazil

^b Laboratório de Instrumentação Nuclear (LIN-UFRJ), Ilha do Fundão, RJ, 21941-972, Brazil

^c Museu Nacional (MN-UFRJ) Quinta da Boa vista, São Cristóvão, RJ, 20940-040, Brazil

^d Instituto de Física Universidade do Estado do Rio de Janeiro (IF-UERJ), Rua São Francisco Xavier, RJ, 20559-900, Brazil

^e Centro Federal de Educação Tecnológica Celso Suckow da Fonseca – Uned-NG, 26041-271, Nova Iguaçu, Brazil

ARTICLE INFO

Article history:

Received 10 February 2016

Received in revised form 22 September 2016

Accepted 23 September 2016

Available online 23 September 2016

Keywords:

Glass beads

Raman spectroscopy

XRF

ABSTRACT

In this paper, nine beads from excavations in the Valongo Wharf, located in the harbor area of Rio de Janeiro, Brazil that were utilized as ornaments by Africans and Afrodescendants during the 19th century were analyzed by Raman and X-Ray Fluorescence (XRF) spectroscopy. All samples in the analysis showed Raman spectra with two bands of maximum intensity around 1000 and 500 cm⁻¹ related to the maximum stretching (ν_{\max}) and bending mode (δ), respectively, of the tetrahedral network of the SiO₄ present in the glass matrix. However, there is variation in the intensity and position of the bands that are directly associated with the burning process and the raw material utilized in the manufacture of the beads. Based on the polymerization index ($I_p = A_{500}/A_{1000}$), it is possible to relate these two parameters. By establishing a correlation among the I_p and the ν_{\max} band, the beads were classified into groups. The results reveal that the beads' base paste exhibits differences, allowing their classification into groups according to the manufacturing process. Based on the combination of the elemental characterization and Raman spectroscopy results, it was also possible to conclude that European and Asian countries are the possible origins of the beads.

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1. Introduction

The study and characterization of objects of historic value have intensified in recent years. Using these analyses, it is possible to obtain information on the chemical composition, manufacture technology, historic period and conservation state of these artifacts [1,3]. In recent years, Raman spectroscopy has become one of the most efficient techniques in the investigation of artifacts of historic and cultural value. Its increasing use in studies concerning cultural heritage is directly related to several advantages of this technique such as high sensitivity. In addition, the technological innovations that took place in the last decade allowed the creation of portable Raman systems, making *in situ* evaluations possible [2].

While Raman spectroscopy is widely used in pigment analysis of works of art, this technique can also be used to analyze other

types of historical artifacts, for instance, vitreous ones, since it is sensitive to both amorphous and non-amorphous materials [3,4].

To explore the potential of Raman spectroscopy for the analysis of vitreous artifacts, in this study, Raman spectroscopy was used to characterize nine glass beads found in recent excavations performed in the harbor area of Rio de Janeiro, Brazil. The elemental composition of the samples was also characterized through X-Ray Fluorescence (XRF). The results obtained, aside from allowing the discussion of the beads' manufacturing process, also enabled the evaluation of the probable time and place of their manufacture.

2. Experimental

2.1. Samples

The samples studied in this paper were found in the harbor area of Rio de Janeiro, Brazil in a region known as the Valongo Wharf that was the gateway to over a million African slaves during the

* Corresponding author.

E-mail address: renato.freitas@ifrj.edu.br (R.P. Freitas).

beginning of the 19th century. In the mid-nineteenth century, the emperor of Brazil, D. Pedro II built a new berth in the area, landfilling the Valongo Wharf, in order to receive his future wife, the empress Tereza Cristina.

Recent excavations performed in the region of the former Valongo Wharf revealed the presence of several artifacts related to the African world. Glass beads that were used as ornaments by the African slaves are noteworthy because of their amount and variety.

The connection between these artifacts and the African world is demonstrated through the nineteenth-century iconography left especially by the painters Debret and Rugendas, who in their work portraying slavery in Brazil, demonstrated an extensive use of such beads as ornament by the slaves. Reports in the literature, such those of DeCorso et al., [6] and Prinsloo et al., [5], also endorse the relationship of these artifacts to the African people and their descendants, following the analysis of glass beads excavated in the African continent that show great similarities in their morphologic appearance to the beads analyzed in this paper.

The nine beads with different colors and shapes analyzed in this study are shown in Fig. 1. Following the timeline of the Valongo Wharf, the dating of such artifacts predates the beginning of the 19th century, the period of time for which there are no reports on glass manufacturing in Brazil. Therefore, the probable origins of

the beads are European and Asian countries that pioneered glass production [5–8].

2.2. Methods

Measurements were performed using a Horiba Jobin Yvon's Raman spectrometer, model LabRam HR Evution. The samples were excited through a 514 nm laser source adjusted to a power of 10 mW, focusing on the samples through 50× objective lenses. The Raman spectra were collected in the range from 1400 to 100 cm^{-1} , using a grid of 600 l/mm and acquisition time of 2 s with 10 accumulations.

For removing the contributions from fluorescence in the Raman spectra, present in the samples of old glasses, four segments linear baseline (~ 700 –100, ~ 800 –700, ~ 1300 –800 and >1300 cm^{-1}) were subtracted. This methodology was employed with success in the works of the Prinsloo et al., [5] and Colomban et al., [10] for the analysis of vitreous artifacts.

XRF measurements were performed using the equipment model TRACER IV from Bruker, which carries an Rh-anode X-ray tube. The spectra were collected for 240 s with the tube operating at the current and voltage of 10 μA and 40 kV, respectively.

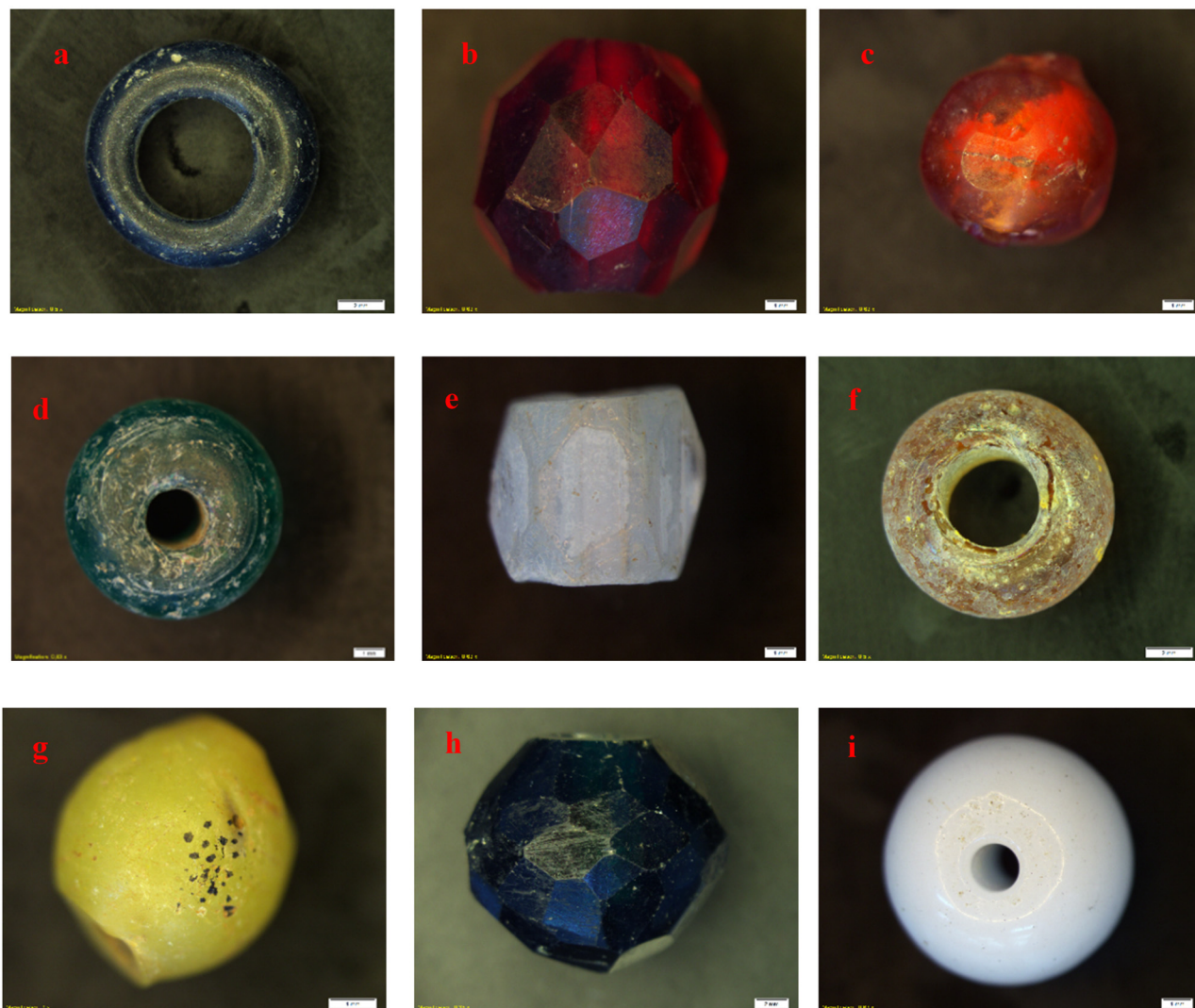


Fig. 1. Images of the analyzed beads.

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