RESEARCH ARTICLE

X-ray spectrometry applied for characterization of bricks of Brazilian historical sites

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This paper presents the results of X-ray fluorescence (XRF) analysis of bricks sampled from historical places in Pernambuco, a state in the northeastern region of Brazil. In this study, twenty bricks found in historical sites were analyzed. Two bricks made in the 17th century, presumably used as ballast in ships coming from Holland, five locally manufactured bricks: one from 18th century, three from 19th century, and one from 20th century, and thirteen bricks collected from a recent Archeological investigation of Alto da Sé, in the town of Olinda. Qualitative determination of the chemical elements present in the samples was undertaken using a self-assembled portable XRF system based on a compact X-ray tube and a thermoelectrically cooled Si-PIN photodiode system, both commercially available. X-ray diffraction analysis was also carried out to assess the crystalline mineral phases present in the bricks. The results showed that quartz (SiO_2) is the major mineral content in all bricks. Although less expressive in the XRD patterns, mineral phases of illite, kaolinite, anorthite, and rutile are also identified. The trace element distribution patterns of the bricks, determined by the XRF technique, is dominated by Fe and, in decreasing order, by K, Ti, Ca, Mn, Zr, Rb, Sr, Cr, and Y with slight differences among them. Analyses of the chemical compositional features of the bricks, evaluated by principal component analysis of the XRF datasets, allowed the samples to be grouped into five clusters with similar chemical composition. These cluster groups were able to identify both age and manufacturing sites. Dutch bricks prepared with different geological clays compositions were defined.

1 | INTRODUCTION

X-ray fluorescence (XRF) and X-ray diffraction (XRD), both well-established analytical techniques, have been playing an essential role in the fields of archeology and ancient art allowing historians and archeologists to address issues of where, when, or by whom historical objects were made.[1–4] The use of XRF and XRD techniques for investigating the chemical and mineralogical composition of bricks has been reported in several articles available in the literature.[5–7] The most common use of this technique has been to determine the characteristics of bricks in the framework of research on historical buildings to elucidate hypotheses on construction phases, potential trade interactions between communities, and conservation purposes. In this work, XRF and XRD techniques are applied to investigate the chemical and mineralogical composition of bricks sampled from historical sites located in Pernambuco, a state in the northeastern region of Brazil.

The sites Brum Fort, Santo Antonio Convent, and Chamber House and Jail were chosen by its relevance to the Brazilian construction history during the Portuguese colonization (1500–1822) and Dutch dominance (1630–1,654) periods. The Brum Fort was constructed in Recife city by the Dutch with bricks assumed to be brought as ballast in the hull of the vessels coming from Holland. This hypothesis is based on the inexistence of local brick factories until the 18th century. The use of bricks for masonry and paving streets started during the Dutch dominance. The Santo Antonio Convent was built in the 18th century by the Portuguese, as well as the Chamber House and Jail, both sites in Iguarassu city. According to historians, there were three Chamber Houses and Jail. The first was built between 1,560 and 1,564 with stone masonry, shortly after the arrival of the Portuguese in Brazil, but it was destroyed during the Dutch invasion in 1632. A second was constructed in another location in the early 18th century, which due to lack of maintenance, was demolished at the beginning of the 19th century. In 1876, the third Chamber House and Jail was built, and in the 1950s, it underwent a large-scale renovation.[8,9]

This work aims to evaluate the application of XRF and XRD techniques to characterize bricks from Brazilian historical sites, trying to identify the period of their production. The use of these techniques can impact the studies of archeological sites and can be useful to support the activities of the Metrology and Archeological Heritage group of the Federal University of Pernambuco (UFPE).

2 | MATERIALS AND METHODS

For this study 20 bricks found in historical sites in the State of Pernambuco were analyzed. Two bricks (B-1 and B-2) are from the 17th century and were sampled from Brum Fort located in the city Recife. Five bricks were collected in the city Igarassu, being one (B-3) from Santo Antonio Convent built in the 18th century, B-4 to B-6 were taken from the Chamber House and Jail, dated to the 19th century, while B-7 was also sampled from the same building after its large-scale renovation in the 20th century. Thirteen bricks (B-8 to B-20) were collected taken from a recent Archeological investigation of Alto da Sé, in the town of Olinda, UNESCO world heritage site, located close to Recife. The bricks were quite different regarding color, dimension, and finishing conditions showing that some of them were obtained by better manufacturing techniques. The main features of the bricks evaluated in this study, their collection sites, and the probable Century of manufacture are described in Table 1.

TABLE 1 Main features of the bricks with its collection sites and the probable manufacture centuries

Sample	Collection site and manufacture century	Main characteristics of the bricks
B-1	Brum Fort, Recife city, 17th century	Red color, good cooking aspect, and surface slightly uneven. Dimension (cm): 8 × 3.5 × 17.
B-2	Brum Fort, Recife City, 17th century	Yellow color, good cooking aspect, and surface slightly uneven. Dimension (cm): 7.8 × 4 × 14.5.
B-3	Santo Antonio Convent, Iguarassu city, 18th century	Brown color, good cooking aspect, and uniform appearance. Careful treatment of the paste and the clay used in its production. Dimension (cm): 18.7 × 6.5 × 37.
B-4 to B-6	Chamber house and jail, Iguarassu city, 19th century	Light beige color, past with stones and voids. Irregular shapes and surfaces. It appears to be produced by hand. Average dimension (cm): 17 × 7 × 33.
B-7	Chamber house and jail, Iguarassu city, 20th century	Red color, fine paste, and sharp corners. Industrial machines likely obtain it. Dimension (cm): 10 × 6.5 × 24.
B-8 to B-20	Bricks from Olinda city	Red colors, irregular shapes and surfaces. Different dimensions. The lowest dimension is 3 × 13 cm and the highest is 10 × 25 × 46 cm

Note: Dimensions are given by width × thickness × length.

All samples were cleaned with water and then lightly brushed to take out fungi and lichens added to their surfaces. A small piece of each brick was crushed in an agate mortar and sieved with a 150–200 mesh size fraction.

To establish the mineral phases, first XRD patterns were collected using a Shimadzu XRD-600 diffractometer (40 kV; 20 mA), with Cu Kα radiation, covering the range of 2° to 65°/2θ and scanning speed of 2°/min. The mineral phases were identified by computerized searching of

powder XRD patterns from the International Centre for Diffraction Data PDF-2 database.

The qualitative determination of the chemical elements present in the samples was undertaken using a self-assembled energy dispersive XRF system. It consists of a portable air-cooled X-ray tube Magnum, MOXTEK (40 kV; 100 μA; W anode) and a thermoelectric cooled Si-PIN diode spectrometer XR-100CR, AMPTEK (Be window of 12.5 μm, 300 μm thickness, 13.5 mm^2 active area, the energy resolution of 204 eV at 5.9 keV),
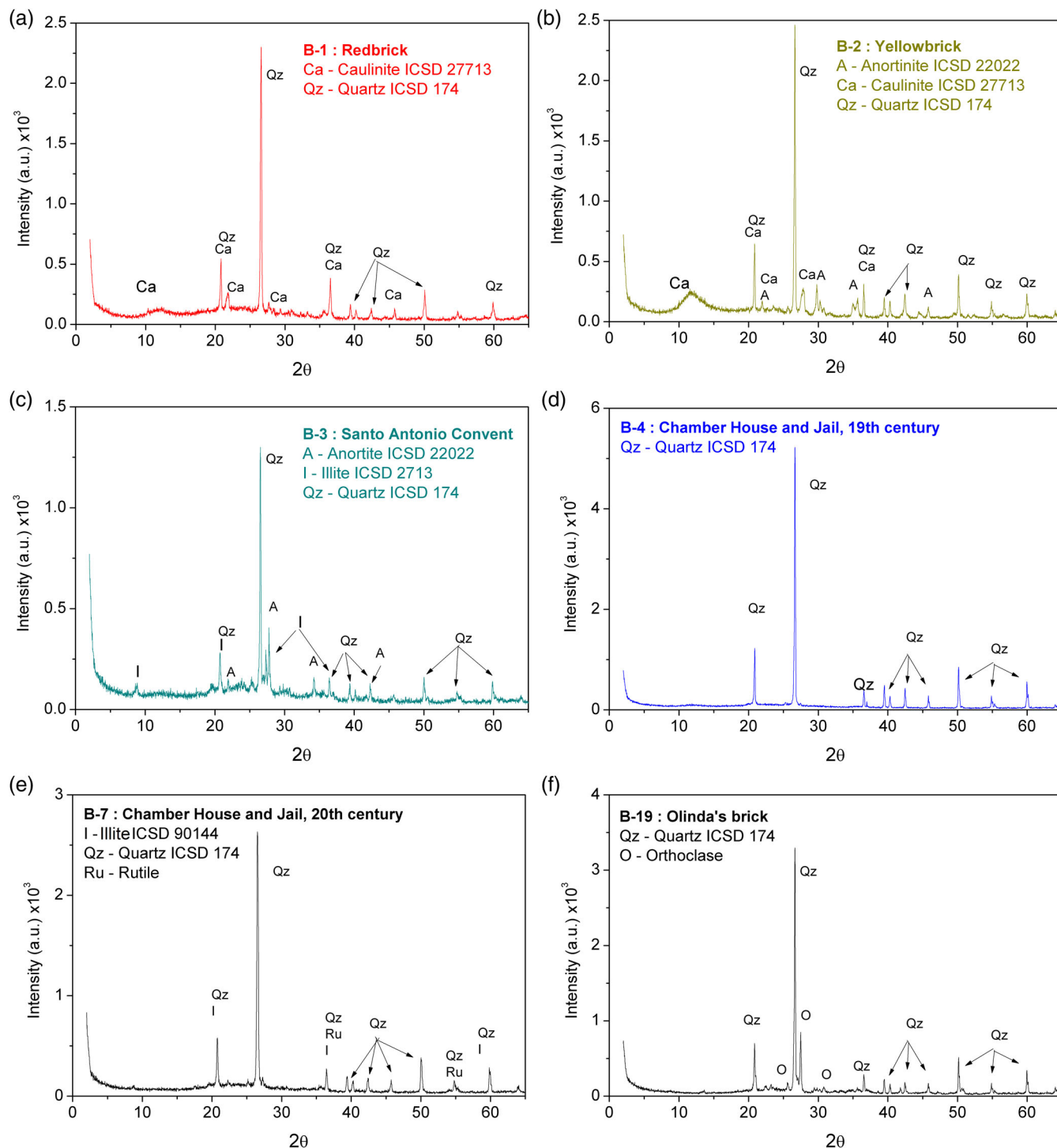
FIGURE 1 XRD patterns of powder samples taken from the bricks evaluated. (a) redbrick B-1, (b) yellowbrick B-2, (c) Santo Antonio convent brick B-3, (d) Chamber house and jail-19th century B-4, (e) Chamber house and jail-20th century B-7, and (f) Olinda's brick B-19. The reference standards of the Inorganic Crystal Structure Database (ICSD) used to identify the mineral phase is also indicated. a, anorthite; I, illite; ka, kaolinite; qz, quartz; r, rutile [Colour figure can be viewed at wileyonlinelibrary.com]

within a metal box. Aluminum conical collimators were used at the exit of the X-ray tube (0.16 mm) and in the Be window of the diode (0.44 mm) to mitigate the contribution of the scattered radiation and characteristic X-rays from the materials in the experimental setup. To achieve better energy resolution with maximum detection efficiency, several studies on different geometries and sample positioning were performed. The best results were found with the sample placed at the crossing-point of the beam's incidence direction and the detector's axis at an angle of 60° with 2.0 cm of sample-diode (SD) distance. The calibration of the whole system was performed through the XRF spectra of reference metal blades (Cd, Cu, Pb, Fe, Sn, and Zn) by setting 30 kV/10 μA to the X-ray tube and 240 s of excitation time. After the pulse amplification, the signals from the diode were sent to a multichannel analyzer AMPTEK MCA8000, directly coupled to a portable computer, for digital pulse processing with real-time data acquisition. The acquired spectra were analyzed using the AXIL (Analysis of X-ray spectra by Iterative Least-squares fitting) software package in QXAS (Qualitative X-Ray Analysis System) developed by the International Atomic Energy Agency (IAEA).[10] The calibration curve of this XRF system is quite linear ($R^2 = 0.9998$) with a threshold energy of 2.0 keV due to the photon absorption in the air layer, and the Be window of the spectrometer. Therefore, characteristics X-rays with energy less than 2.0 keV, mainly those from light elements, cannot be detected by this system. Otherwise stated, all XRF spectra herein presented were recorded under the aforementioned experimental conditions.

Four XRF spectra were measured at different points on the inside of each brick to evaluate its elemental composition. The average value of these photopeak areas of the selected elements was used for data analysis.

Principal component analysis (PCA) was applied to all sets of XRF data on trace chemical components of the bricks to evaluate the similarities and differences between the samples. Initially, a pre-processing procedure was applied to the data, consisting of normalization and baseline correction. PCA calculations were carried out with the "Unscrambler" software package, version 9.2, from Camo Analytics. The PCA was applied using the counts of each channel obtained for the entire fluorescence spectrum, that is, using 2048 channels as variables, resulting in an n versus $p = 40 \times 2048$ data matrix. To assess the influence of trace elements, the same PCA was performed considering only the fluorescence spectrum information corresponding to the energy range between 13 keV and 18 keV, whether using 313 channels as variables, resulting in a matrix of 28×313. This analysis was performed only for the bricks from Recife and

Igarassu, because we want to evaluate their differences since they are from different centuries.

3 | RESULTS AND DISCUSSION

Figure 1A-E shows the XRD pattern of the bricks B-1, B-2, B-3, B-4, and B-7 from Recife and Igarassu, and Figure 1F shows, as example, the XRD pattern of one of the samples of Olinda bricks. The mineral phases were

TABLE 2 Qualitative mineralogical composition of the bricks identified by XRD technique

Bricks	Qualitative mineralogical composition of the bricks
B-1	Quartz (SiO_2); kaolinite ($[Al_4 (Si_4O_{10})(OH)_8]$)
B-2	Quartz (SiO_2); kaolinite($[Al_4(Si_4O_{10})(OH)_8]$); anorthite ($[CaAl_2Si_2O_8]$)
B-3	Quartz (SiO_2); anorthite ($[CaAl_2Si_2O_8]$); illite[a] $[K_xAl_2(Si_xAl_x)O_{10}(OH)_2]$
B-4	Quartz (SiO_2)
B-5	Quartz (SiO_2)
B-6	Quartz (SiO_2)
B-7	Quartz (SiO_2); illite[a] $[K_xAl_2(Si_xAl_x)O_{10}(OH)_2]$; rutile $[TiO_2]$
B-8 to B-12	Quartz (SiO_2); mulite ($Al_6Si_2O_{13}$)
B-13 to B-16	Quartz (SiO_2); metakaolinite ($Al_4(Si_4O_{10})(OH)_8$)
B-17 to B20	Quartz (SiO_2); orthoclase ($K(AlSi_3O_8)$)

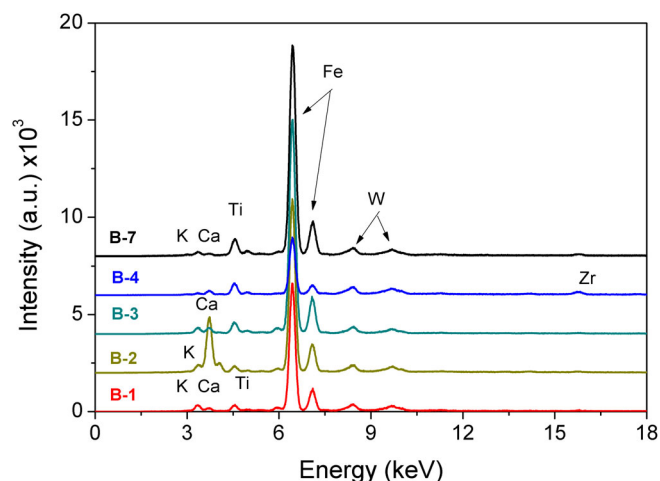[a]Illite has variable chemical composition due to impurities in its crystalline structure.

FIGURE 2 X-ray fluorescence spectra of the bricks from Recife and Igarassu, with exception of those of B-5 and B-6, due to its great similarity to the spectrum obtained with the sample B-4 [Colour figure can be viewed at wileyonlinelibrary.com]

identified in the respective diffractograms based on the reference standards of the Inorganic Crystal Structure Database (ICSD). The XRD patterns depicted in Figure 1 evidence that quartz (SiO_2) is the major mineral content of all bricks. Although less expressive in the diffractograms, mineral phases of the alumino-silicate (illite) ($K_xAl_2[Al_ySi_zO_{10}](OH)_2$) in samples B-7 and B-3; kaolinite ($Al_2Si_2O_5(OH)_4$) in samples B-1 and B-2; anorthite ($CaAl_2Si_2O_8$) in samples B-2 and B-3; and rutile (TiO_2) in sample B-7 are also identified. Exceptions are samples B-4, B-5, and B-6 whose diffractograms reveal quartz as the only mineral phase present in their compositions. The presence of kaolinite in the bricks B-1 and B-2, according to Teixeira et al,[11] is related to the

materials added to achieve good plasticity in the production of the bricks. The qualitative mineralogical composition of the bricks is shown in Table 2.

The data on the XRF spectra of the bricks B-1 to B-7 are displayed in Figure 2, where the major chemical components (Si, O, Al, and, H), previously obtained by XRD analysis, are not detected due to the 2.0 keV threshold energy imposed by the experimental setup. Consequently, only the radiation from the trace chemical elements is shown in the XRF spectra, except the characteristic L lines from the W anode of the X-ray tube. The chemical content of the bricks is dominated by Fe and, in decreasing order, by K, Ti, Ca, Mn, Zr, Rb, Sr, Cr, and Y with slight differences among them.

FIGURE 3 Histogram of the relative abundance of the trace elements of each sample of the bricks from Recife and Igarassu [Colour figure can be viewed at wileyonlinelibrary.com]
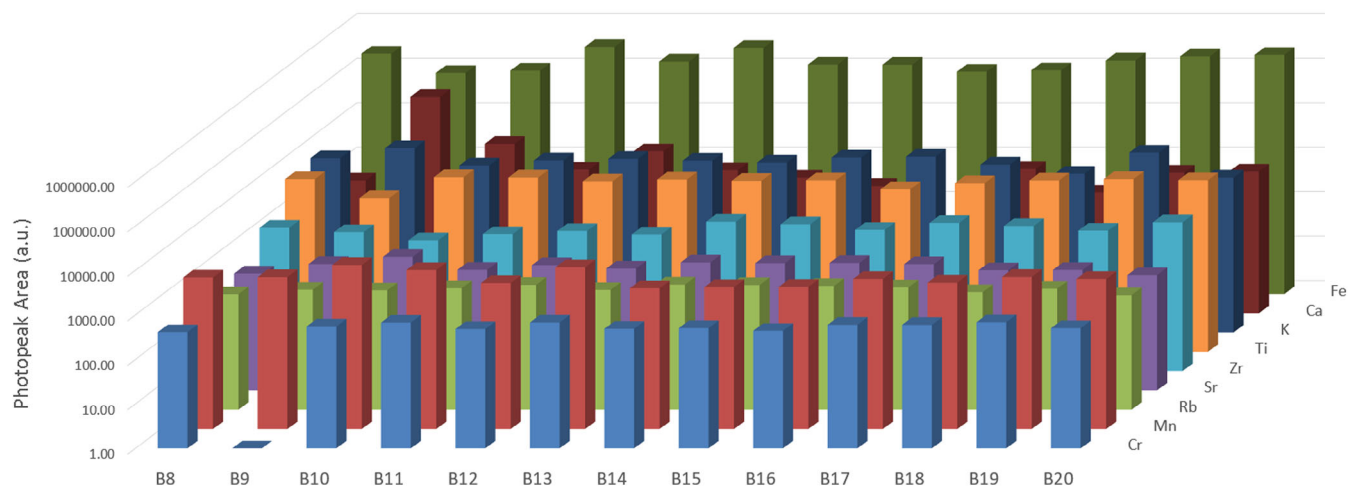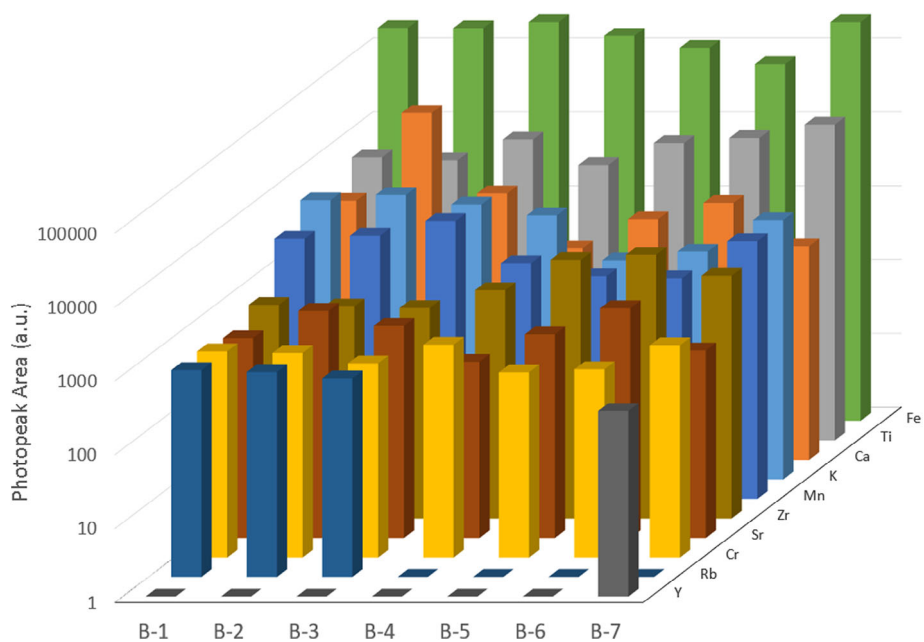

FIGURE 4 Histogram of the relative abundance of the trace elements of each sample of the bricks from Olinda [Colour figure can be viewed at wileyonlinelibrary.com]

Figure 3 shows the relative abundance of the elements found in the XRF analysis of each brick sample from Recife and Igarassu and Figure 4 shows the results found for the bricks from Olinda. The parameter used is the photopeak area of each element, whose values are the average of the four XRF measurements performed with each brick. This figure reveals that all bricks B-1 to B-7 contain the highest relative concentration of Fe in the amorphous phase since any iron oxide/hydroxide crystals were not detected in the XRD patterns. Furthermore, the Ca content in bricks B-2 and B-3 is in accordance with the anorthite crystal phase identified in its XRD spectra. The trace element composition of the bricks B-1 and B-2 taken from the Brum Fort, namely by Fe,

Rb, Sr, and Zr, is quite similar to those found by Sopko and Mcevoy[4] with bricks of 17th and 18th centuries sampled from several Dutch colonial sites along the eastern seaboard of North America.

The data of Figure 4 show that chemical elements found in the bricks from Olinda are practically the same as those detected in the bricks of Igarassu and Recife. The difference lies in the complete absence of yttrium and the presence of rubidium in all the bricks. The bricks B-14 and B-16 have a higher iron content compared to the others bricks, even more than bricks from the Igarassu and Recife. It is also observed that, unlike the previous group, most of these bricks have a lower amount of calcium than potassium.
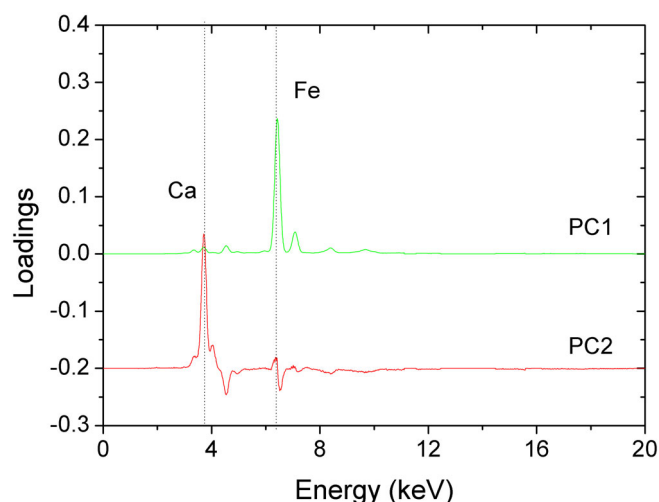

FIGURE 5 Loadings plot for the principal component analysis to the fluorescence spectrum using entire fluorescence spectrum [Colour figure can be viewed at wileyonlinelibrary.com]
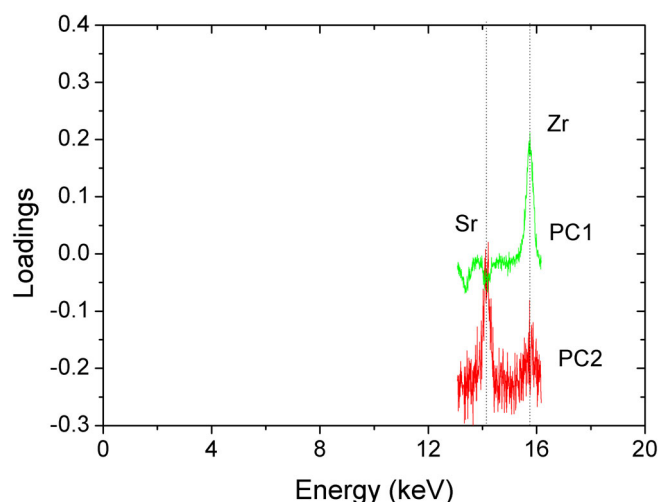

FIGURE 7 Loadings plot for the principal component analysis to the fluorescence spectrum of the bricks from Recife and Olinda using fluorescence spectrum in the region from 13 to 17 keV [Colour figure can be viewed at wileyonlinelibrary.com]
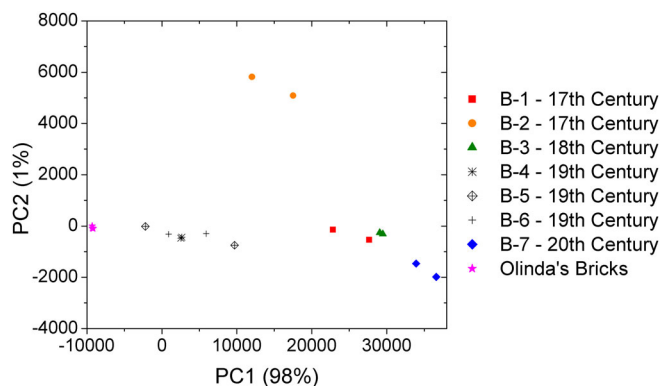

FIGURE 6 Principal component 1 (PC1) versus Principal component 2 (PC2) plot resulted from a PCA applied to the XRF spectra. Distinct colors and symbols represent the 20 bricks samples evaluated [Colour figure can be viewed at wileyonlinelibrary.com]
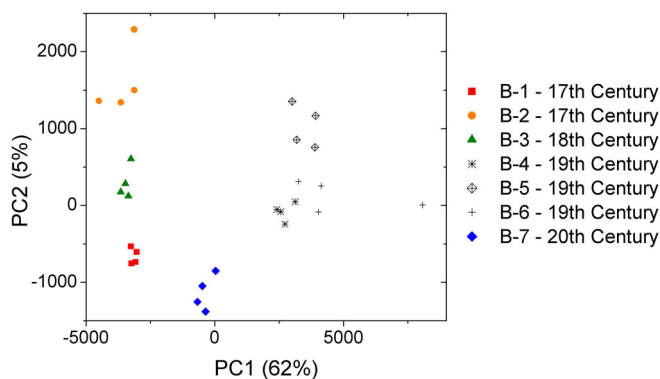

FIGURE 8 Scatter plot of Sr (PC2) versus Zr (PC1) resulting from PCA applied to the XRF spectra from 13 to 17 keV of the bricks from Recife and Olinda a PCA. Distinct colors and symbols represent the seven bricks samples evaluated [Colour figure can be viewed at wileyonlinelibrary.com]

To investigate the chemical compositional variability based on the trace elements in the bricks, Principal Components Analysis (PCA) was applied to the XRF dataset. Figure 5 shows the loading plot for the PCA. The first principal component (PC1), dominated by the Fe peak, and accounts for 98% of the total variance. The PC2 largest loadings refer to Ca (positive values) with 1% of the total variance. Figure 6 shows the Principal component 1 (PC1) versus Principal component 2 (PC2) plot resulted from a PCA applied to the XRF spectra. Distinct colors and symbols represent the 20 bricks samples evaluated. It is possible to observe that the bricks are sorted into six clusters according to the centuries they were produced. The bricks B-1 together with those of the Santo Antônio Convent (B-3) and Casa da Câmara and Cadeia (20th century) (B-7) are on the positive axis of CP1, indicating a higher presence of iron, compared to the bricks from Olinda..

As the maximum variability of the trace elements stems from the higher Fe concentration, another PCA was performed for the bricks from Recife and Igarassu, using only the XRF data within the energy range of 13–17 keV, corresponding to the characteristic X-ray from Rb, Sr, and Zr. The first two principal components account for 67% of the total variance in this dataset, revealing that the data selection lost some information. PC1 (62%) is dominated by Zr, whereas PC2 (5%) is assigned to Sr (Figure 7), both with positive loadings. Figure 8 shows the score plot of Sr (PC2) versus Zr (PC1), and evidence that the bricks are sorted into five clusters according to the centuries they were produced. Exceptions are those (B-1; B-2) dated to the 17th century, which despite having a similar amount of Zr, are separated by the difference between their Sr content. As these trace elements are mostly related to the clay used to produce the brick, it can be inferred that samples B-1 and B-2 were produced at a different geological site. Regarding the bricks of the 19th century (B-4 to B-6), the results show great similarities in its lighter element composition characterized by the highest amounts of Zr and intermediate content of Sr. On the other hand, brick B-7, taken from the same building of the samples B-4 to B-6 after its large-scale renovation during the 20th century, is in a distinct cluster indicating a different clay material used in its ceramic mass.

4 | CONCLUSION

XRF and XRD analytical techniques are applied in this work to investigate the chemical and mineralogical composition of 20 bricks, dated between the 17th and 20th centuries, sampled from Brazilian historical sites. A portable XRF spectrometer was developed based on a small X-ray tube and a thermoelectrically cooled silicon PIN diode. The spectrometric response of this system shows that it is suitable for XRF applications, although not being able to detect photons from light chemical elements ($Z \leq 15$). For this reason, only the trace composition of the bricks (Fe, K, Ti, Ca, Mn, Zr, Rb, Sr, Cr, and Y) is assessed through the XRF spectra. Analyses of the chemical compositional features of the bricks, by use of a statistical treatment of the XRF datasets, allowed the samples to be grouped into five clusters with similar chemical composition under its probable production centuries. Exceptions are the samples B-1 and B-2, assumedly of Dutch origin, with a marked different geological clay composition.

Despite the limited number of samples, the results confirm the presumed origin of the bricks, namely either the former use of ballast bricks on the ships coming from Holland or the use of locally made bricks. Furthermore, the spectrometric results showed that the XRF system and the application of multivariate statistical analysis to XRF data are useful tools to support research conducted in the field of Archeological Heritage, allowing identify some characteristics of bricks from historical places.

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