Combined Vibrational Spectroscopic and Elemental Studies of 18th Century Transylvanian Stove Tiles

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Abstract

Three Transylvanian fragments of some 18th century Saxon tiles obtained from excavations in the Central Railway Station Square in Sibiu (Romania) have been studied by Raman microscopy, FTIR, SEM-EDX and XRF techniques. A lead-rich aluminosilicate was found to have been used as enamel/glaze for the tile fragments. An analysis of the band components of the Raman spectra of the enamel of one fragment in the 400–1200 cm$^{-1}$ spectral region indicates that their processing temperature was in the 600–800 °C range, in good agreement with the temperature obtained from FTIR spectra of the other two tile fragments.

1. Introduction

The study of tiles used as components of medieval and ancient stoves has been a subject of recent research [1, 2]. The specific term under which this field is known first appeared in the 17th century when Georg Andreas Böckler published a book that mentioned furnology [3, 4]. Furnology has been strongly developed particularly on the second half of the 20th century, in the context of large restoration projects of medieval towns that involved the documenting and the reconstruction of monuments destroyed during the Second World War. A source of inspiration for this research in Romania was provided by the work of Vámszer [5], who catalogued and analyzed tiled stoves discovered in the territory of medieval Hungary since 1958. Research on these tiles in Romania is well represented in the literature of the last 25 years, especially through the work of Istrate [6], who dedicated a series of studies to this topic which emerged during the 1960s through to the 1980s. Other related studies [7–16] have been reported on the content of lead in glasses.

The appearance of tiled stoves in Transylvania and other regions of Romania is related to the influence of German settlers starting in the second half of the 13th century, but during the 15th -16th centuries the shapes of the stoves and the decorative motifs of the tiles became strongly diversified [17–19]. Standardisation occurred in the 17th century when this kind of stove became a common household item. Several types of tiles are recognised, such as the square-shaped tile, three-sided corner tile and base profile tiles. Serial manufactured products start to dominate the market in the 18th century when terracotta stoves became more common and the production of the stove tiles became strongly influenced by the Haban ceramics production technique.

The objective of the present work is to get knowledge on the composition and firing temperature of this ceramics. Raman microscopy, energy dispersive X-ray spectroscopy (EDX) coupled with scanning electronic microscopy (SEM-EDX), Fourier transform infrared spectroscopy (FTIR) and X-ray fluorescence spectroscopy (XRF) are valuable techniques for this purpose.

2. Materials And Methods
Three pieces of Transylvanian ceramic tiles from the 18th century are studied in this work, Fig. 1(abc). They are representative of the Saxon tile fragments discovered during archaeological excavations carried out at the Central Railway Station Square in Sibiu in a secondary context, whereby their precise original location and archaeological context could not be established. They most likely originated from dwellings located inside the Sibiu city fortifications and reached the area where they were discovered sometime during the 19th century, when urban facilities were established around the current Central Railway Station area. The samples analysed have been discovered during archaeological excavations made in the west and north side of the Railway Station but not in an original position, Fig. 2.

The tile fragments come from different stoves and date from between the early to the second half of the 18th century. The oldest objects discovered in the archaeological excavations comprise the green ceramic tiles with decorations studied in the present work. The Transylvanian tiles have white and green colors. It is believed that these ceramic pieces originated in the Haban ceramics workshop in the late seventeenth or possibly the beginning of the 18th century [19]. The Hutterites (or Habaner in German) were among the most appreciated potters in Europe, they made the well-known Habaner tiles. The Germanspeaking Habaner, Anabaptists, were considered heretical by the Vatican and have been banished from place to place throughout history. They appeared at the beginning of the 16th century in Tyrol, which had an influence on their ceramics.

2.1 Analytical Techniques

Descriptions of the instruments used for Raman microscopy and SEM-EDX studies have been given fully elsewhere [20–22] and only specific experimental details of this work are reported here. X-ray microanalyses of the enamel have been carried out using an EDX spectrometer Rontec Xflash Detector 3001 with the Be window removed and coupled to a Hitachi S-3000N SEM microscope (Everhart–Thornley detector of secondary electrons) with an operating resolution of 3 nm (working distance 4 mm, voltage applied 30 kV and pressure $1.5 \times 10^{-3}$ Pa).

Non-destructive XRF analyses of the green areas of the tile surface and body were performed with a handheld Bruker spectrometer, S1 TITAN series configured with a Silicon diode PIN detector (SiPIN) and Rh target X-ray tube with a maximum voltage of 50 kV.

The study by Raman microscopy was carried out using a Jobin Yvon LabRamIR HR-800 spectrograph coupled with an Olympus BX 41 microscope. The 632.8 nm laser line of a He-Ne laser was used for Raman excitation with a power of 7.71 mW (100 × objective lens) measured at the sample position. An integration time of 20 s and up to 64 accumulations were used to achieve an acceptable S/N ratio. The wavenumber calibration was carried out with 4-acetamidophenol, naphthalene and sulfur standards [23] over the 150–3100 cm$^{-1}$ range. A wavenumber mean deviation of $\Delta \nu_{\text{cal}} - \Delta \nu_{\text{obs}} = -0.96 \pm 0.47$ cm$^{-1}$ ($t_{\text{Student}}$, 95%) was obtained. Spectral smoothing was not applied to the observed spectra. The Origin® software 7.0 from OriginLab Corporation was used to correct the spectral background of fluorescence.
emission radiation, as well as assisting in determining the wavenumber of the peaks and curve fitting to the spectral profiles.

Polished thin cross-sections (thickness ~ 20 µm) of the ceramic fragment a (Fig. 1) were prepared using a polyester resin matrix. The microstratigraphy of the ceramic and the enamel layers was examined in the thin cross-sections with a Leica DM2500 petrographic microscope using polarized light.

FTIR destructive absorption spectroscopy of the stove tile fragments b and c (Fig. 1) was performed using a Jasco 6100 spectrometer in the 4000 to 400 cm\(^{-1}\) spectral range (256 scans) with a spectral resolution of 4 cm\(^{-1}\) and employing the KBr pellet technique.

3. Results And Discussion

3.1 Microstructure

The typical microstratigraphy, Fig. 3ab, of the stove tile corresponding to Fig. 1a shows an external layer of transparent enamel and a layer of green (Fig. 3a) and white (Fig. 3b) pigments superimposed upon the clay substrate of the tile. Raman and EDX spectra of the enamel were obtained by focusing the Raman and SEM microscopes in the enamel layer of the thin cross-sections of the tile, respectively.

3.2 EDX spectra

The EDX spectra obtained from different areas along the enamel layer show a high content of lead, Fig. 4. The Pb M\(^{\alpha 1}\) EDX peak is observed at ~ 2.3 keV and its M\(^{\alpha 2}\) and M\(^{\alpha 3}\) peaks give rise to the spectral shoulder of the M\(^{\alpha 1}\) peak appearing at higher energy. The strong peak of Si and the additional peaks of O, Al, Na and K, suggest the presence of vitreous aluminosilicates in the enamel.

3.4 Elemental XRF analyses

A series of locations of the clay substrate and green surface of the tile fragments has been the object of XRF analyses. Minor differences have been observed in the results. Consequently, the average elemental composition of the clay substrate and decorated surface are presented in Table 1. Only the most significant elements for these samples are collected in the table.
| Clay substrate | Tile surface |
|---------------|-------------|
| Element | % | Element | % |
| Fe | 3.911 | Pb | 32.594 |
| Ca | 2.612 | Ca | 1.446 |
| K | 2.531 | Cu | 1.001 |
| Ba | 0.051 | Fe | 0.560 |
| Co | 0.044 | As | 0.273 |
| Zr | 0.021 | Bi | 0.095 |
| Pb | 0.021 | Sn | 0.011 |
| Sr | 0.019 | Sr | 0.006 |
| Ti | 0.008 | Zr | 0.006 |
| Rb | 0.006 | V | 0.003 |

Table 1
Average XRF data for the clay substrate and decorated surface of the tile fragments.

It is evident that lead, calcium and copper metals dominate in the green decorated surface. However, iron, calcium and potassium are dominant in the clay body of the tiles. These results and those of EDX analyses indicate that lead enamel/glaze have been used in the tiles.

3.5 Raman spectra

The Raman spectra of the vitreous coating (enamel or glaze) of ceramics are very useful to estimate their polymerisation degree and the firing technology applied [24–34]. According to the methods developed for these purposes, the Raman spectra obtained from the enamel of the ceramic fragment a, Fig. 1a, have been the subject of some numerical treatments, Fig. 5. Eight points baseline correction has been applied using the spectral intensities at 163, 252, 365, 568, 702, 798, 1069 and 1192 cm$^{-1}$, Fig. 5b. The Rayleigh line gives rise to an exponential increase of intensity in the 330-0 cm$^{-1}$ region. The polymeric units of the aluminosilicate networks of the enamel can be investigated through the relative intensities of Si–O stretching and bending modes, at ~ 1000 and 500 cm$^{-1}$ respectively [24–30, 32–34]. Therefore, an appropriated spectral region to carry out this type of studies is between 350 and 1200 cm$^{-1}$, Figs. 5c and 5d.

The intensity and wavenumber of the stretching and bending modes of the Si-O bonds in this spectral region depends on the different coordination of SiO$_4$ groups in the enamel. This results in wavenumber shifts and intensity differences of the stretching and bending modes of the Si-O bonds [24–30, 32–34]. Thus, a curve fitting procedure to the spectral profile is highly suitable to associate different SiO$_4$ coordination groups to band components of the spectral profile. The number of components depends on
the silicate coordination number $Q^n$ ($Q^0$, $Q^1$, $Q^2$, $Q^3$ and $Q^4$) between 400 and 1100 cm$^{-1}$ [24, 27, 29, 33]. In addition, no negative component must be accepted in the final fitting. For the band at 976 cm$^{-1}$ deconvolution of the stretching components [26] are considered in the following intervals: $Q^0 \rightarrow 700–850$ cm$^{-1}$, $Q^1 \rightarrow 800–950$ cm$^{-1}$, $Q^2 \rightarrow 900–1050$ cm$^{-1}$ and $Q^3$-$Q^4 \rightarrow 1050–1200$ cm$^{-1}$. The corresponding bending components [25] in the spectral profile around $\sim 500$ cm$^{-1}$ are: $Q^0 \rightarrow 300–370$ cm$^{-1}$, $Q^1 \rightarrow 400$ cm$^{-1}$, $Q^2 \rightarrow 470$ cm$^{-1}$, $Q^3 \rightarrow 400–640$ cm$^{-1}$ and $Q^4 \rightarrow 670$ cm$^{-1}$, Fig. 5d. The full width at half height (FWHH) of the band components of silicate glasses within the 250–1200 cm$^{-1}$ spectral range is usually FWHH $\geq 50$ cm$^{-1}$. Consequently, this limit has been considered as the initial value of the FWHH for the $Q^n$ components to start the curve fitting process. Similarly, Gaussian components are assumed for this process considering that enamel glassy silicates are in an amorphous state [32, 33].

Silica is the main component in the manufacture of the vitreous enamels. Generally, the silica content comprises around 40–60% of the total weight of enamel. The structure of vitreous silica is produced by a three-dimensional combination of tetrahedral SiO$_4$ units. The connectivity of these polymeric units can be investigated from the relative intensities of the components of the Si–O stretching and bending modes at $\sim 1000$ and 500 cm$^{-1}$ respectively [28]. In highly connected structures the spectral feature around a 500 cm$^{-1}$ shows higher intensity than that of the 1000 cm$^{-1}$ region, whereas in weakly connected SiO$_4$ tetrahedrons the opposite is observed [28]. A polymerisation index $I_p$ has been established [26, 33] as the $A_{500}$ / $A_{1000}$ ratio, where $A_{500}$ and $A_{1000}$ are defined as the areas obtained integrating the fitted components in the spectral regions of $\sim 500$ cm$^{-1}$ and $\sim 1000$ cm$^{-1}$ respectively. The vitreous silicates can be classified according to their composition and their polymerisation index $I_p$ [26, 28]. The resulting value of $I_p$ for the enamel of the ceramic fragment a (Fig. 1) is 0.20, which shows that the 500 cm$^{-1}$ band area is significantly lower than the corresponding area near 1000 cm$^{-1}$, i.e. that the $\nu$(SiO) stretching mode prevails over the $\delta$(Si-O) bending mode in spectral intensity. In other words, the enamel silicates are formed with a low polymerisation index [24, 26, 29]. On the other hand, the wavenumber maxima $\nu_{max}$ and $\delta_{max}$ for the stretching and bending Si-O are 957 cm$^{-1}$ and 471 cm$^{-1}$ respectively. The value of $\nu_{max}$ is lower than 1030 cm$^{-1}$, a the reference value found for vitreous enamels formed without modifying agents. The shift of $\nu_{max}$ to 957 cm$^{-1}$ is typical of lead glaze/enamel [33]. A simple intensity analysis of the Raman spectral profile, Fig. 5, shows that the enamel has a low degree of chemical coordination. X-ray microanalyses confirm that Pb is the dominant element after Si. The high content of Pb gives rise to a low polymerisation index. The $\nu_{max}$ value of the enamel when correlated with $I_p$ is similar to those of leadcontaining or luster pottery and glasses classified as family 7 by Colomban [26, 29, 33]. The silicates with similar Si-O stretching frequencies and polymerisation index can hence be assigned to this family of enamels with a low polymerisation index. Enamels of this family contain typically between 20% and 40% percent Pb. These results are corroborated by the X-ray microanalysis of the tile, namely, a glass with a network of aluminosilicates having high Pb content. It is obvious that the introduction of Pb to the mixture leads to a change in the structural dimension of the silica network. A change of Pb content
modifies the local environment of the silicate tetrahedra. The three-dimensional silica network has a tetrahedral coordination for silicon; this can be classified in agreement with the $Q^n$ coordination model, $n$ being the number of oxygen atomic bridges for the SiO$_4$ tetrahedral structure ($n = 0–4$). From the variation of the $Q^n$ distribution, it is possible to describe the silica network polymerisation status and to characterize the role of the Pb atoms. The substitution of Si by Pb does not change the Si-O matrix bonding but affects the ionic partial charge on the oxygen that modifies the Si-O length and polarizability. The ionic exchange of Pb modifies the Raman band wavenumber value to lower values than those expected [33]. This substitution of Si by Pb induces a $Q^n$ coordination degree change. There is also a relationship between the glass polymerisation index and their processing temperature $T_f$. The nature of the replacement cation can modify the value of $T_f$ [26,27,29,33–35]. According to the value of the polymerisation index obtained ($I_p = 0.20$) for the tile fragment a (Fig. 1), the firing temperature of their enamel can be established between 600 and 800 °C.

### 3.6 FTIR spectra

Infrared spectroscopy has been applied to determine the firing temperature of pottery [36–39]. The FTIR spectra of the ceramic fragments b and c have been obtained, Fig. 6, with this purpose. The bands observed at $\sim 3470$ and $\sim 1650$ cm$^{-1}$ are assigned respectively to the O-H stretching and H-O-H bending vibrations of the water molecules included in the fragments. The broad infrared absorption between 1300 and 800 cm$^{-1}$ is dominated by the Si-O stretching bands of the ceramic silicates. The maximum of this strong and broad spectral feature depends on the firing temperature used in the ceramic manufacture [38]. The absorbance maximum of the Si-O stretching region shifts towards higher frequencies and broadens with increasing temperature. This wavenumber maximum can be considered a firing temperature indicator-guide. Their value, 1075 cm$^{-1}$, and the spectral profile observed in the infrared spectra of the ceramic fragments b and c, Fig. 5, indicate that these ceramic fragments were fired at relatively low temperature, not exceeding $\sim 800$ °C [38]. Similar results were obtained from FTIR studies on Transylvanian pottery shards extracted from the same excavation [39]. Considering the results obtained applying different spectroscopic techniques to the three ceramic fragments a, b and c, as well as to pottery shards found in the indicated archaeological site [39], it is concluded that open fires, that reach a maximum temperature of about 800 °C [40], could have been used to process all these pieces. It is well known that lead glazes typically melt at temperatures between 700 and 1000 °C depending on the composition of the glaze [41, 42]. The results indicate that lead alkali glazes, with a high lead content, have been used to coat these fragments. A type of glazes with a content of lead that began to be used in the 10th and 11th centuries in the Western world [42, 43].

### 4. Conclusions

Details on the composition and firing temperature of stove tile fragments of Transylvanian ceramics from the 18th century have been obtained by SEM-EDX, XRF, Raman and FTIR techniques. A lead alkali glaze with high lead content is covering the tile fragments. This produces a low polymerisation index, $I_p = 0.2$, of
the aluminosilicate network coating one of the fragments. Moreover, this value indicates that their enamel belongs to the family 7 established by Colomban [26, 29, 33], and a processing temperature between 600 and 800 °C was used. Similar temperatures were used for the other two fragments, in agreement with the results obtained from FTIR studies on pottery shards extracted from the same archaeological site [39].

Declarations

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Disclosure

I. Bratu and C. Marutoiu are co-first authors

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**Figures**

![Figure 1](image_url)

**Figure 1**

Three 18th Century Transylvanian stove tile fragments a, b and c.
Figure 2

Map of Sibiu. Pale green areas: archaeological excavations in the Main Railway Station.

Figure 3

Microphotographs of the typical microstratigraphy of the ceramic piece a (Fig. 1): (a) green area; (b) white area. An outer layer of enamel covering uneven layers of green (a) and white (b) pigments may be observed. The inner brown layer of clay shaping the tile can be seen in the lower part of the images. The red crosses indicate some of the many points upon which the laser beam was focused to obtain the Raman spectra of the enamel. The microphotographs were obtained with polarized light.
Figure 4

Representative EDX spectrum of the enamel used in the tile fragment a (Fig. 1).
Figure 5

(a) Representative Raman spectrum of the enamel of the tile fragment a (Fig. 1). (b) Baseline treatment of the Raman spectrum. (c) Resulting spectrum after baseline substraction. (d) Band component analysis of the Raman spectrum.
Figure 6

FTIR spectra of the ceramic body of the tile fragments b and c (Fig. 1).