A closer look at the ancient bricks of historical monuments: Essential step for the conservation of pottery

| Tomas Petrėnas, | In this work, the ancient bricks of the monastery of San Filippo (Italy) were analyzed and characterized using elemental analysis. X-ray diffraction (XRD) analysis and infrare | | | | |
|-----------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--|--|--|
| Jonas Kiuberis, | spectroscopy (FTIR). These methods are indispensable tools in order to investigate some | | | | |
| Olga Opuchovič, | special features of ancient pottery, identifying their chemical and phase composition and structure. From the obtained results it was concluded that such characterization of ancien | | | | |
| Stasys Tautkus, | pottery is an essential step for the conservation of pottery. Possible theoretical approaches for the conservation of investigated bricks were evaluated. | | | | |
| Aivaras Kareiva* | Key words: ancient pottery, characterization, chemical analysis, XRD, FTIR | | | | |
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INTRODUCTION

Lithuania

The physical-chemical characterization of pottery used in ancient times provides historical and technological information as regards their manufacture [1–8]. Moreover, the knowledge of chemical and mineralogical compositions is mandatory in the characterization studies of pottery. A careful characterization of ancient pottery is a very important task not only for archaeologists but for materials scientists and people working in the field of conservation chemistry as well [9–15]. Important historical objects suffer very serious damages as a result of the destructive effects of environment. The desire to conserve the ancient cultural values necessitates the development of effective treatments methods, which can only be possible after determination of the chemical composition of the conservation object [16–18].

Recently, a sol-gel conservation method based on the formation of protective coatings from Y-Al-O acetate-glycolate gels on the surface of pottery has been developed [19]. The influence of Y–Al–O acetate-glycolate protective coatings on the surface conditions of ancient pottery excavated in the Lithuanian archaeological complexes Benaičiai (West Lithuania) and Turlojiškės (South Lithuania) has been investigated by SEM, TEM and AFM measurements. These investigations clearly showed that the main morphological features of the surface of the ancient pottery sample from Benaičiai during conservation and deconservation procedures remained without changes. However, the surface of the ancient pottery sample from Turlojiškės has changed significantly during the conservation procedure. The XRD measurements revealed that the main crystalline component of the Turlojiškės ceramic sample was calcite [20]. Therefore, the surface of pottery containing calcite is destroyed during the sol-gel processing by the reaction between calcite and acetic acid:

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$$CaCO_{3} + 2CH_{3}COOH \rightarrow$$

$$\rightarrow (CH_{3}COO)_{2}Ca + CO_{2} + H_{2}O.$$
(1)

These results, once again, confirm that the conservation process can be greatly influenced by chemical reactions appearing due to the specific chemical compositions in the object of conservation.

The unsuccessful development of sol-gel technique for the conservation of any sample of ancient ceramic initiated the idea to prepare a novel non-destructive method to the conservation of pottery. The aim of the study [21] was to develop a novel polymeric method for the fabrication of coatings for the protection of degradation of pottery. The ceramic specimens were dip-coated in the aqueous (distilled water) 2% solution of polyvinylalcohol (PVA). The main advantages of the proposed method of preparation of protective coatings for pottery were expected to be simplicity and a totally non-destructive aspect. However, the polymeric coating only partially protected migration of Al, Ca, Mg and Fe ions from pottery to solution and did not influence the migration of Li, Na, K, Sr, Cr and Zn ions. Thus, the proposed polymeric conservation method did not protect fully the migration of cations in the pH range from 3 to 11.

It is clear that the preparation of low cost and environmentally benign technological procedures for the conservation of ancient pottery is still a big problem. Besides, to avoid possible destructive effects, a careful characterization of ancient pottery samples should be conducted before conservation. In the present study, attention has been focused on the characterization of pottery samples obtained from different parts of the monastery of San Filippo (Italy) using elemental analysis, X-ray diffraction (XRD) analysis and infrared spectroscopy (FTIR). Previously it was demonstrated that some bricks of the monastery of San Filippo were manufactured by calcareous clay while other ones made of limeless clay, i. e. raw clay were excavated from different sources [22]. The main aim of this study is to explore the potentialities of the above mentioned methods of analysis in assessing the chemical and mineralogical composition of ancient pottery and to determine the possible ways of conservation of historical buildings.

EXPERIMENTAL

Six samples of historical ancient pottery from different locations of the archaeological complex of San Filippo have been selected. The sample area of Specimen No. 1 was near the gate, inside the courtyard, at the bottom. The sampling area of Sample No. 2 was near the gate, outside, at the bottom. The sampling area of Specimen No. 3 was near the gate, inside the courtyard, at the top. The sampling area of Specimen No. 4 was near the gate, outside, at the top. The sampling area of Sample No. 5 was inside the courtyard, ruin. The sampling area of Specimen No. 6 was inside the courtyard, different splinters of ruin. For the analytical characterization of ceramics the samples were carefully grinded in an agate mortar and passed through the sieve with pores of 45 µm.

For the analytical procedures 36% HCl (Lachema), 65% HNO₃ (Lachema), 98% H₂SO₄ (Roth), 85% H₃PO₄ (Lachema), KBr (Merck), $(NH_4)_6 Mo_7 O_{24} \cdot 4H_2 O$ (Russia), CuCl₂ (Aldrich), SiO₂ (Aldrich), Ti (Nilaco), Na₂CO₃ (Aldrich), NaOH (Merck), H₂BO₂ (Aldrich), EDTA (C₁₀H₁₆N₂O₈) (Merck), 1-(2-pyridilazo)-2-naftol $(C_{15}H_{11}N_{2}O)Cu(CH_{2}COO)_{2} \cdot H_{2}O$ (Russia), ascorbic acid (C₄H₆O₆) (Merck) and 36% H₂O₇ (Aldrich), all of them analytical grade, were used. For the preparation of different solutions the initial salts were dissolved in double distilled water. For the determination of potassium, sodium, magnesium, calcium, manganese and iron by the flame atomic absorption spectrometry (FAAS) method [23] the standard solutions were prepared from CH₂COOK, CH₂COONa, $Mg(CH_3CO_2)_2$, $Ca(CH_3COO)_2 \cdot H_2O$, $Mn(CH_3CO_2)_2 \cdot 4H_2O$ and $FeCl_2 \cdot 4H_2O$ (Aldrich), respectively. For the determination of titanium and silicon the photometric methods [24, 25] were used. The amount of aluminium in the pottery samples was determined using the titrimetric analysis method [26].

The pottery samples were characterized by the powder X-ray diffraction analysis (XRD) performed with a D8 Advance (Bruker AXS) powder diffractometer equipped with a conventional X-ray tube (CuK $\alpha_{1,2}$ radiation) using a Ni filter/monochromator. The XRD patterns were measured in the range of 10 to 60° 2 θ . The infrared (FTIR) spectra were recorded on a Perkin Elmer Spectrum BX FTIR spectrometer. The samples were powdered in an agate mortar and mixed (~1.0%) with dried KBr and pressed into pellets. The elemental composition of all pottery samples were determined by FAAS (flame atomic absorption spectroscopy) using a Hitachi 170-50 spectrometer. The instrumental parameters were adjusted according to the manufacturer's recommendations. The following conditions for metal determination by the FAAS method were used: (i) absorption line (766.5 nm K, 589 nm Na, 285.2 nm Mg, 422.7 nm Ca, 279 nm Mn and 248.3 nm Fe); (ii) flame (acetylene-oxygen K, Na, Mn and Fe and propane-butane-oxygen Mg and Ca). For spectrophotometric analysis a KFK-3 spectrophotometer was used. The analyses were performed using 10 mm cells at $\lambda = 410$ nm (Ti) and $\lambda = 597$ nm (Si).

RESULTS AND DISCUSSION

For the determination of the amount of main and trace elements in the ancient bricks of the monastery of San Filippo FAAS (K, Na, Mg, Ca, Mn, Fe), spectrophotometric (Ti, Si) and titrimetric (Al) analysis methods were applied. The obtained results were calculated to oxides and are summarized in Table 1. It is necessary to note that the R. S. D. values obtained for the determination of elements in the ceramics (5.7–11.4%) indicated a high degree of homogeneity, which could be expected for ceramic samples. Moreover, the values obtained are not unusual for such types of analysis and can be considered as suitable for routine analysis. Interestingly,

| | Amount of oxide, mass% | | | | | | |
|--------------------------------|------------------------|-------|-------|-------|-------|-------|--|
| Element | Sample | | | | | | |
| | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 | No. 6 | |
| Na ₂ O | 0.08 | 0.02 | 0.16 | 0.03 | 0.03 | 0.06 | |
| MgO | 6.1 | 1.1 | 0.5 | 0.8 | 1.2 | 0.2 | |
| K ₂ O | 0.6 | 0.7 | 0.6 | 0.6 | 2.4 | 0.5 | |
| CaO | 2.3 | 0.2 | 0.1 | 0.3 | 0.1 | 10.3 | |
| MnO ₂ | 0.02 | 0.03 | 0.08 | 0.04 | 0.06 | 0.07 | |
| Fe ₂ O ₃ | 6.2 | 4.1 | 4.3 | 5.3 | 5.7 | 6.0 | |
| TiO ₂ | 2.0 | 1.1 | 0.9 | 0.9 | 0.9 | 1.1 | |
| SiO ₂ | 53.1 | 58.4 | 53.0 | 55.8 | 55.2 | 51.9 | |
| AI_2O_3 | 19.2 | 20.5 | 17.6 | 21.6 | 19.6 | 20.3 | |

Table 1. Results obtained for the determination of the amount of elements (calculated to oxides) in the ancient bricks from the monastery of San Filippo



Fig. 1. FTIR spectrum of Sample No. 1 of historical ancient pottery



Fig. 2. FTIR spectrum of Sample No. 2 of historical ancient pottery

when broader sampling and ICP-AES (inductively coupled plasma atomic emission spectrometry) methods were used for the elemental analysis [22], the obtained results allowed grouping the bricks into three groups by considering the CaO content. However, our results do not offer such a possibility. All six samples could be attributed to the samples containing a low CaO content (0.1-2.3%). Nevertheless, the determined amount of CaO as well as MgO in Samples No. 1 and No. 6 is slightly higher in comparison with others. The amount of the main oxide silica varies between 51.9% and 58.4%. The concentrations of aluminium (17.6–21.6% Al₂O₃) and iron (4.1-6.2% Fe₂O₃) cover sufficiently narrow ranges. Thus, elemental analysis data show quite similar chemical composition of all six investigated samples.

The FTIR spectra of the corresponding ceramic samples are presented in Figs. 1-6. As seen in Fig. 1, the FTIR spectrum of Sample No. 1 contains a broad band located at 3 600-3 350 cm⁻¹ (centred at 3 443 cm⁻¹) as well as the band centred at 1 636 cm⁻¹. These two bands correspond to the v(O-H) stretching vibration of H₂O adsorbed on the surface of pottery and the bending H-O-H vibration (δ) of water due to the exposure of the powders to atmosphere, respectively [27]. The broad absorption band located at ~1066 cm⁻¹ could be attributed to the stretching vibrations of Si-O possibly in the quartz phase [28]. The FTIR spectrum of Sample No. 2 (Fig. 2) contains the same bands centred at 3 440 cm⁻¹ and 1 627 cm⁻¹ which correspond to O-H vibrations and a broad band centred at ~1083 cm⁻¹ which corresponds to Si-O vibrations. Additionally, the observed several intense bands in the range of 900-600 cm⁻¹ $(804, 798, 701 \text{ cm}^{-1})$ are characteristic of the

metal-oxygen vibrations (M-O) in the ceramic sample [28]. The FTIR spectrum presented in Fig. 3 is very similar to the previous one. However, one additional not very intensive absorption peak is visible at 1381 cm⁻¹. This absorption is characteristic of stretching vibrations (v_{λ}) of carbonate ion (probably from calcite phase) [28]. According to the FTIR analysis results (see Fig. 4), we could conclude that the main chemical composition of pottery Sample No. 4 may be almost the same as that of Sample No. 3, since their FTIR spectra are also almost identical. On the other hand, the FTIR spectrum of ceramic Specimen No. 5 (Fig. 5) does not contain any peaks attributable to the C-O vibrations in the carbonate ion. The observed bands at 3 440, 1 627, 1 083 and 794 cm⁻¹ let us to predict that the chemical composition of this sample is very close to that of No. 2. Fig. 6 shows the FTIR spectrum of the Specimen from the ancient bricks No. 6. The main difference of this FTIR spectrum in comparison with others is that it contains very intensive absorption peaks of ionic carbonate. The corresponding characteristic bands of stretching vibrations of CO_3^{2-} are seen at 1460 cm⁻¹ and 1385 cm⁻¹. The observed splitting of the carbonate peak v, in the FTIR spectrum may indicate the presence of two phases, such as calcite and aragonite in the ceramics.

The XRD pattern of pottery Sample No. 1 is shown in Fig. 7. It can be seen that the main crystalline phases are quartz SiO₂ (PDF [46–1045]), sodium aluminium trisilicate NaAl₃Si₃O₁₁ (PDF [46-740]), potassium aluminium trisilicate K₅Al₅Si₃O₁₆ (PDF [32-731]) and other potassium aluminium trisilicate crystalline phase KAl₃Si₃O₁₁ (PDF [46-741]). These XRD results are in a good agreement with the FTIR spectroscopic analysis data. The XRD pattern of pottery Sample No. 2 (Fig. 8) implies that the major compound present in this sample is quartz as well. Other determined crystalline phases are sodium aluminium trisilicate NaAl₂Si₂O₁₁ and kilchoanite $Ca_6(SiO_4)(Si_3O_{10})$ (PDF [29–370]). According to the determined crystalline phases in Samples No. 1 and



Fig. 3. FTIR spectrum of Sample No. 3 of historical ancient pottery



Fig. 4. FTIR spectrum of Sample No. 4 of historical ancient pottery



Fig. 5. FTIR spectrum of Sample No. 5 of historical ancient pottery



Fig. 6. FTIR spectrum of Sample No. 6 of historical ancient pottery



Fig. 7. XRD pattern of Sample No. 1 of historical ancient pottery. The main crystalline phases: (o) – quartz, $Si0_{2'}$ (+) – sodium aluminium trisilicate, $NaAl_3Si_30_{11'}$ (#) – potassium aluminium trisilicate, $K_3Al_5Si_30_{16'}$ and (z) – potassium aluminium trisilicate, $Kal_3Si_30_{11'}$



Fig. 8. XRD pattern of Sample No. 2 of historical ancient pottery. The main crystalline phases: (o) – quartz, $SiO_{2'}(*)$ – kilchoanite, $Ca_6(SiO_4)(Si_3O_{10})$, and (+) – sodium aluminium trisilicate, $NaAl_3Si_3O_{11}$







Fig. 10. XRD pattern of Sample No. 4 of historical ancient pottery. The main crystalline phases: (o) – quartz, SiO₂, (*) – kilchoanite, Ca₆(SiO₄)(Si₃O₁₀), (x) – calcite, CaCO₃, (z) – potassium aluminium trisilicate, KAl₃Si₃O₁₁, and (^) – microcline, KAlSi₃O₈



Fig. 11. XRD pattern of Sample No. 5 of historical ancient pottery. The main crystalline phases: (o) – quartz, SiO₂, (+) – sodium aluminium trisilicate, NaAl₃Si₃O₁₁, (s) – calcium pentasilicate, Ca₈Si₅O₁₈, (~) – sodium aluminium disilicate, NaAlSi₂O₆, (•) – sodium aluminium silicate, NaAlSiO₄, and (?) – unknown phase



Fig. 12. XRD pattern of Sample No. 6 of historical ancient pottery. The main crystalline phases: (o) – quartz, SiO₂, (x) – calcite, CaCO₂, and (?) – unknown phase

No. 2, we can propose that the observed characteristic metal-oxygen vibrations in the FTIR spectrum of ceramic Sample No. 2 could be attributed to Ca-O vibrations. The XRD pattern of pottery Sample No. 3 is given in Fig. 9, indicating that the dominating crystal phase in this sample again is quartz. According to the XRD results, the predominant compounds in pottery Sample No. 3 are kilchoanite, calcite CaCO₂ (PDF [5-586]), potassium aluminium trisilicate and microcline KAlSi₃O₈ (PDF [19-926]). Thus, the specific feature of Sample No. 3 is the existence of a small amount of calcite phase which is a very important constituent of building materials. Interestingly, the ionic carbonate phase in Specimen No. 3 was also determined by FTIR spectroscopy. The XRD pattern of pottery Sample No. 4 is displayed in Fig. 10. As seen, the determined main crystalline phases in Sample No. 4 absolutely coincide with those detected in Sample No. 3 (quartz, kilchoanite, calcite, potassium aluminium trisilicate and microcline). Therefore, the area of the monastery near the gate, at the top inside and outside the courtyard, was built using the bricks having the same composition. It is evident that the main crystalline component of Sample No. 5 again is quartz (see Fig. 11). This sample from ruin does not contain carbonate and contains sodium aluminium trisilicate as Sample No. 2. On the other hand, the kilchoanite phase was not determined in Sample No. 5. Besides, additional new phases, such as calcium pentasilicate Ca₈Si₅O₁₈ (PDF [29-368]), sodium aluminium disilicate NaAlSi₂O₆ (PDF [46-12]) and sodium aluminium silicate NaAlSiO₄ (PDF [44-1496]), were also detected in pottery Sample No. 5. The diffraction line located in Fig. 11 at about $2\theta = 41^{\circ}$ was not attributed to any crystalline phase. Apparently, the phase composition of Sample No. 5 is close to the previous ones which do not contain the calcite phase. The XRD pattern of pottery Sample No. 6 is shown in Fig. 12. It shows the presence of quartz, calcite and nonidentified crystalline phases in Sample No. 6. Clearly, there is only very little amount of non-identified crystalline phases in the sample.

| Table 2. XRD results obtained for the determination of main | crystalline phases in t | the ancient bricks from t | :he monastery of ! | San Fili | ippo |
|-------------------------------------------------------------|-------------------------|---------------------------|---------------------------|----------|------|
|-------------------------------------------------------------|-------------------------|---------------------------|---------------------------|----------|------|

| Dhace | Sample | | | | | | |
|---------------------------------------------------------------------------------------------------|--------|-------|-------|-------------|---|-------|--|
| rnase | No. 1 | No. 2 | No. 3 | No. 4 No. 5 | | No. 6 | |
| Quartz (SiO ₂) | + | + | + | + | + | + | |
| Calcite (CaCO ₃) | | | + | + | | + | |
| Calcium pentasilicate (Ca ₈ Si₅O ₁₈) | | | | | + | | |
| Microcline (KAlSi₃O ₈) | | | + | + | | | |
| Kilchoanite (Ca ₆ (SiO ₄)(Si ₃ O ₁₀)) | | + | + | + | | | |
| Potassium aluminium trisilicate (KAl ₃ Si ₃ O ₁₁) | + | | + | + | | | |
| Potassium aluminium trisilicate (K ₅ Al ₅ Si ₃ O ₁₆) | + | | | | | | |
| Sodium aluminium silicate (NaAlSiO ₄) | | | | | + | | |
| Sodium aluminium disilicate (NaAlSi ₂ O ₆) | | | | | + | | |
| Sodium aluminium trisilicate (NaAl ₃ Si ₃ O ₁₁) | + | + | | | + | | |
| Unknown phases | | | | | + | + | |

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Data from the XRD analysis of all investigated ancient bricks samples are summarized in Table 2. As seen, the investigated samples could be roughly divided in two groups. One group of samples contains the calcite phase (No. 3-4 and No. 6) and another one is free from calcite (No. 1-2 and No. 5). The essential phase composition of pottery Samples No. 3 and No. 4 is the same, however, Sample No. 6 contains unidentified phases instead of microcline, kilchoanite and potassium aluminium trisilicate. This is not surprising since the sampling area of Samples No. 3 and No. 4 was near the gate, at the top, just inside or outside the courtyard, respectively. The sampling area of Specimen No. 6 was inside the courtyard but not located near the gate. The sampling area of Specimens No. 1 and No. 2 is very similar, however, potassium aluminium silicates were determined only in Sample No. 1. On the other hand, the kilchoanite phase was detected only in Sample No. 2. The sampling area of Sample No. 5 was inside the courtyard, ruin. Despite different location, all three Samples (No. 1–2 and No. 5) contain sodium aluminium trisilicate phases. The calcium pentasilicate phase was identified only in pottery Sample No. 5. Since ancient brick samples from one group are rich of the calcium carbonate phase, for the successful conservation of this pottery the previously reported sol-gel method [19] is not suitable. However, the known polymeric method for the fabrication of coatings on the surface of ceramics [21] does not protect effectively pottery from degradation. Therefore, the search of new possible ways for the conservation of historical ancient pottery from different locations of the archaeological complex of San Filippo is necessary. Now the development of such methods which could be suitable for the conservation of most historical buildings is under investigation.

CONCLUSIONS

An elemental analysis of the ancient bricks of the monastery of San Filippo (Italy) showed that all six samples could be attributed to the pottery samples containing a low CaO content (0.1-2.3%). The amount of the main oxide silica varies between 51.9% and 58.4%. The concentrations of aluminium (17.6%-21.6% Al₂O₂) and iron (4.1%-6.2% Fe₂O₂) cover sufficiently narrow ranges. The determined amount of CaO and MgO in two samples is slightly higher in comparison with others. In conclusion, the elemental analysis data showed quite similar chemical compositions of all six investigated samples. The FTIR spectra of the corresponding ceramic samples contained broad bands due to the v(O-H) stretching and bending H–O–H vibration (δ) of H₂O adsorbed on the surface of pottery. The broad absorption bands located at ~1066 cm⁻¹ were attributed to the stretching vibrations of Si–O in the quartz phase. Some FTIR spectra contained very intensive absorption peaks of ionic carbonate. The main crystalline phases in the pottery samples were determined by the XRD analysis. These results were in a good agreement with the FTIR spectroscopic analysis data. Thus, the FTIR spectroscopic and XRD analysis data suggested that all investigated ancient bricks samples could be roughly divided in two groups. One group of samples contained the calcite phase and another one was free from calcium carbonate. Due to this reason, we concluded that new conservation routes for historical ancient pottery from different locations of the archaeological complex of San Filippo should be developed.

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SENOVINIŲ PLYTŲ, ESANČIŲ ISTORINIUOSE PAMINKLUOSE, IŠSAMUS APIBŪDINIMAS – BŪTINAS ETAPAS SĖKMINGAM KERAMIKOS KONSERVAVIMUI

Santrauka

Senovinės plytos iš šv. Pilypo vienuolyno (Italija) buvo tirtos elementinės analizės, infraraudonosios spektroskopijos (FTIR) ir rentgeno spindulių difrakcinės analizės (XRD) metodais. Parodyta, kad šie tyrimo metodai yra labai svarbūs norint nustatyti senovinės keramikos specifinius bruožus, cheminę bei fazinę sudėtį. Gauti rezultatai leido daryti išvadą, kad senovinių plytų, esančių istoriniuose paminkluose, išsamus apibūdinimas yra būtinas etapas sėkmingam keramikos konservavimui. Gauti keramikos pavyzdžių apibūdinimo rezultatai leido pateikti rekomendacijas sukurti galimą metodą istorinei keramikai konservuoti.