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Preliminary Investigation of Ceramic Materials – Particularly Important Stage for Successful Conservation of Pottery

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The aim of this paper is to explore the potentialities of powder X-ray diffraction analysis (XRD) and infrared (IR) spectroscopy in assessing the chemical and mineralogical composition of ancient pottery, with the final goal of building up the possible sol-gel chemistry methodology for its conservation. Two samples of historical ancient pottery from different places of Lithuania (villages *Benaičiai* and *Turlojiškės*) were analyzed. For comparison, the latter-day ceramic sample (calcinated clay) was characterized as well.

Keywords: ancient pottery, ceramics, XRD analysis, IR spectroscopy, conservation.

INTRODUCTION

Scientists from the field "Preservation of cultural work" are currently dealing with the problem of conservation of glass, ceramics, paper, metals and alloys, without disturbing the structure of the raw material [1, 2]. Recently for the conservation of cultural values the coatings obtained by sol-gel technique has been suggested [3 – 5]. The development of reliable procedures for the conservation using sol-gel process offers potential advantages such as simplicity and effectiveness [6, 7]. However the preparation of low cost and environmentally benign technological procedures for the conservation of ancient pottery still is a big problem.

One of the traditional goals of inorganic materials research has been the preparation of new and useful materials, which combine the properties of coatings with those of ceramics. Recently in our laboratory a modified sol-gel method based on the carboxylate-alumoxanes [8 – 10] has been developed for the conservation of paper [11]. All the paper samples (untreated, impregnated with hexanato-alumoxane and treated-uncoated) were examined by SEM. The hexanato-alumoxane treated and treated-uncoated paper samples were visually indistinguishable from their untreated equivalents. These studies demonstrated that the carboxylate-alumoxanes can be successfully used for the fabrication of coatings for the protection of degradation of paper.

The successful development of sol-gel technique for the conservation of paper initiated the idea to prepare a novel sol-gel method to the conservation of pottery. We found interesting to modify the known sol-gel method for the preparation of aluminates [12, 13] and to transfer it to the conservation of pottery. However the conservation process can be greatly influenced by specific chemical reactions appearing due to the different chemical compositions in the object of conservation and protective coatings [14]. Thus, to avoid the possible interactions careful characterization of ceramic sample should be done [15, 16]. Moreover, the physical-chemical characterization of pottery used in ancient times could provide historical and technological information as regards their manufacture [17]. The knowledge of chemical and mineralogical compositions is mandatory in characterization studies of pottery: the former mainly depends on the raw materials used to produce the wares but also on processing and depositional changes, the latter on both the initial composition and the processing, as minerals are the "fingerprints" of the stable and also the metastable solid phases formed during firing [18]. Accordingly, the production processes of antique ceramics can be derived jointly with the changes in the manufacturing techniques; in this respect, maximum heating temperature, duration of firing and kiln redox atmosphere are important factors that help in understanding the transformations. In the present study, attention has been focused on the development of procedure for the characterization of unknown ceramic samples prior its conservation.

EXPERIMENTAL

Three types of ceramic materials were chosen for the characterization: (a) latter-day ceramic sample (calcinated clay) from the Kaunas pottery enterprise "*Jiesia*" (sample **I**), (b) historical ancient pottery found in Lithuanian village *Benaičiai* (sample **II**) and (c) historical ancient pottery from another Lithuanian place near village *Turlojiškės* (sample **III**).

The determination of water capacity of latter-day ceramic sample in different aqueous systems (bidistilled water and 0.1 M solution of acetic acid, CH_3COOH (Lachema)) and pycnometric density in 100 % ethanol were performed by well known and documented procedures [19] and [20], respectively. For the determination of water capacity the dried at 120 °C granulometric fractions were soaked for 48 h in an appropriate solution. The average particle size of the

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powdered samples (~0.1 g) was determined in bidistilled water (100 ml) by sedimentation analysis [20] using microbalance system.

The ceramic samples were characterized by powder X-ray diffraction analysis (XRD) performed with a D8 Bruker AXS powder diffractometer using CuKα_1 radiation obtained with multilayer Ni/C monochromator. The infrared (IR) spectra were recorded as KBr pellets on a Perkin Elmer Spectrum BX FTIR spectrometer. A pH meter Mettler-Toledo MP220 was employed for measuring pH values of solutions.

RESULTS AND DISCUSSION

As was mentioned in the introduction part, for the conservation of pottery we are planning to develop an aqueous sol-gel method. Therefore, the determination of water capacity of ceramics prior conservation procedure is necessary to avoid the contrary effect – destructive effect of the procedure of preparation protective coatings on the chemical composition of ancient pottery. Water capacity investigations were performed on differently powdered in agate mortar specimens of sample **I**. The results of determination of water capacity (W) and pycnometric density (ρ) for the same ceramics having different average particle size (φ) are presented in Table 1.

Table 1. Results for the determination of water capacity, pycnometric density and average particle size for the different granulometric fractions of ceramic sample **I** ($n = 5$)

Fraction	W^* (%)	W^{**} (%)	ρ (g/cm^3)	φ (μm)
1	16.6	17.2	2.131	18
2	16.4	17.2	2.096	22
3	16.9	17.0	2.080	25
4	16.6	17.5	2.070	45
5	16.7	17.3	2.044	90
6	16.5	17.2	2.018	200

*Water capacity in bidistilled water.
**Water capacity in 0.1 M CH_3COOH.

As seen, water capacity of the ceramics investigated shows very little variation by changing an aqueous system, consequently and pH of solution from ~6.0 to ~3.0. Also, water capacity does not depend on the particle size. The random distribution of the obtained results indicates that no correlation between water capacity, pH of solution and the particle size of the ceramic samples could be observed. These results are very important for the successful development of method of conservation.

However the determined pycnometric density of different granulometric fractions shows a little variation. As seen from Fig. 1, the pycnometric density of different granulometric fractions of ceramic sample **I** decreases almost linearly with increasing the average particle size.

The chemical composition and phase purity of the ceramic samples were investigated by powder XRD analysis and IR spectroscopy. A representative X-ray diffraction pattern for the calcinated clay specimen from granulometric fraction of 25 μm is shown in Fig. 2.

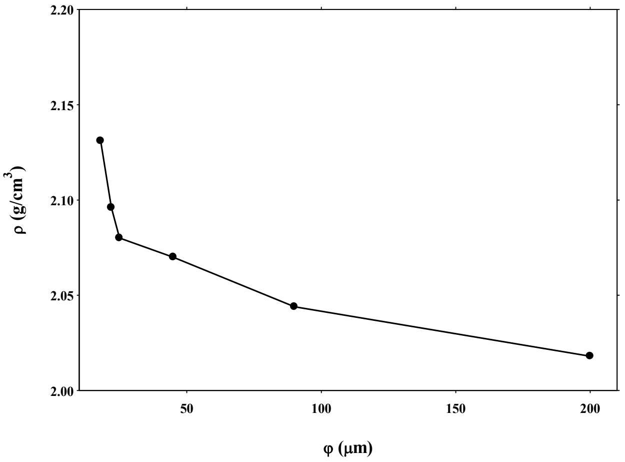

Fig. 1. Relationship between pycnometric density and average particle size of the ceramic sample **I**

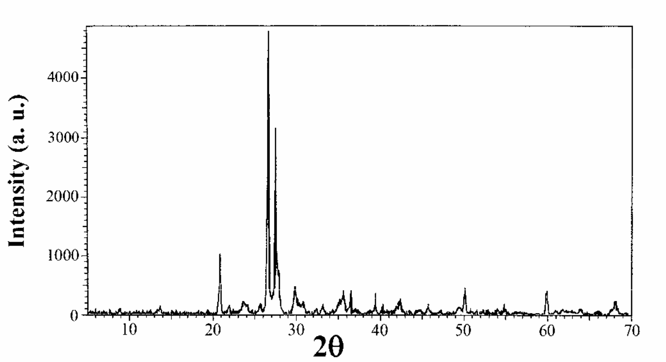

Fig. 2. X-ray diffraction pattern of the calcinated clay ceramic sample I from the granulometric fraction of 25 μm

As seen, the latter-day ceramic sample is fully crystalline. However, the XRD pattern also exhibits rather complicated chemical composition and multiphase character of the investigated polycrystalline sample. According to the XRD analysis, the sample **I** mainly (~76 %) is composed by triclinic anorthite ($Ca[Al_2Si_2O_8]$; PDF No. 41-1486) and monoclinic sanidines ($K[AlSi_3O_8]$ and $Na[AlSi_3O_8]$; PDF No. 10-357 and PDF No. 89-1455, respectively). Besides that, a large amount of hexagonal phase of quartz (SiO_2; PDF No. 46-1045) was found to be present in the ceramics. Additionally, smaller amounts of cubic magnetite (Fe_3O_4; PDF No. 89-0951), hexagonal hematite (Fe_2O_3; PDF No. 89-2810) and some unidentified phases could be also detected in the XRD pathern. Since the material investigated contains lot of different phases, they are not marked in the diffractogram presented in Fig. 2. It is interesting to note that X-ray diffraction patterns of different granulometric fractions (from 18 μm to 200 μm; see Table 1) of the ceramic sample **I** are almost identical (Fig. 3), i.e. independent on the particle size as well.

Quite different phase composition was determined for historical ancient pottery (sample **II** and sample **III**). A comparison between the XRD patterns for the ceramics from Lithuanian villages *Benaičiai* and *Turlojiškės* is reported in Fig. 4.

It is evident, that the *Benaičiai* pottery is characterized by the presence of quartz as a main phase, muscovite

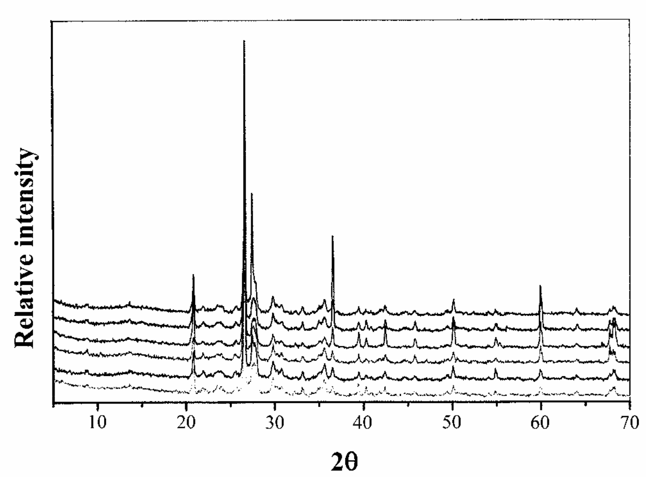

Fig. 3. X-ray diffraction patterns of the calcinated clay ceramic sample **I** from different granulometric fractions (from 18 μm to 200 μm)

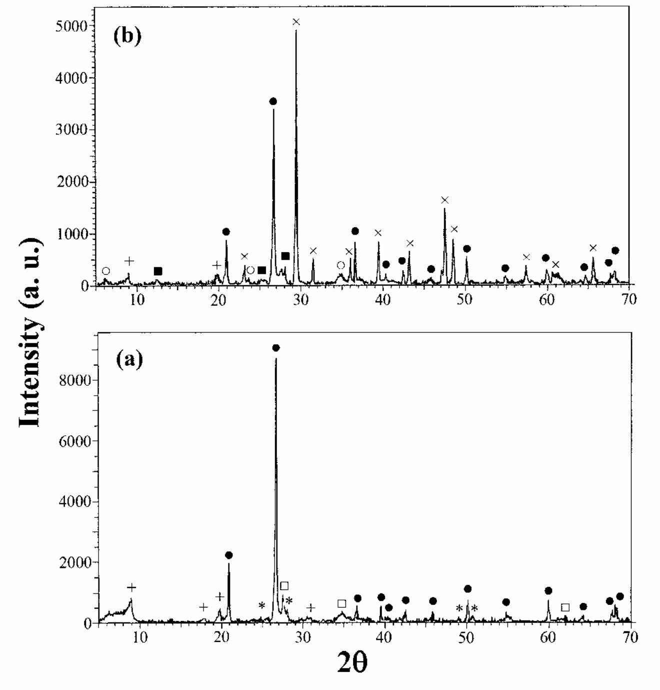

Fig. 4. X-ray diffraction patterns of the historical ancient pottery from: (a) *Benaičiai* and (b) *Turlojiškės*. The crystalline phases are marked: SiO_2 (●), $(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$ (✚), $CaCO_3$ (×), $CaTiO(SiO_4)$ (□), $(Ca,Na)(Si,Al)_4O_8$ (✱), $CaH_2(SO_4)_2$ (■), $Ca_{0.1}Fe_2(Si,Al)_4O_{10}(OH)_2{\cdot}4H_2O$ (○)

($(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$; PDF No. 07-0042), titanite ($CaTiO(SiO_4)$; PDF No. 25-0177) and sodium anorthite ($(Ca,Na)(Si,Al)_4O_8$; PDF No. 41-1481). The presence of large amount of quartz phase in the *Turlojiškės* pottery is seen as well. However, the main crystalline component of the ceramic sample **III** evidently is calcite ($CaCO_3$; PDF No. 05-0586). The secondary phases, such as muscovite, calcium hydrogen sulphate ($CaH_2(SO_4)_2$; PDF No. 39-0522) and nontronite ($Ca_{0.1}Fe_2(Si,Al)_4O_{10}(OH)_2{\bullet}4H_2O$; PDF No. 34-0842) could be also identified. Therefore, only two common phases, quartz and muscovite, were found to be in both ancient pottery ceramic samples obtained from different places of Lithuania. These results suggest different manufacture of two historical ancient pottery samples. The presence of calcium carbonate in the *Turlojiškės* pottery clearly confirms this assumption – apparently, the firing temperature of pottery from *Turlojiškės* is lower to compare with calcinations temperature of ceramic sample from *Benaičiai.*

Another important conclusion could be made, that the conservation process based on previous development of aqueous sol-gel processing for aluminates [12, 13] is not suitable to fabricate protective coatings for *Turlojiškės* pottery. This sol-gel chemistry approach ensures the high level of homogeneity only in slightly acidic medium [12, 13, 21]. Therefore, the degradation of ancient sample would be expected during the conservation procedure:

$$CaCO_3 + 2CH_3COOH \rightarrow (CH_3COO)_2Ca + CO_2 + H_2O. \quad (1)$$

Contrary, the acetate-tartrate sol-gel chemistry technique looks as promising method for the fabrication of protective coatings for *Benaičiai* pottery.

It is well known, that definite substances can be identified by their IR spectra, interpreted like fingerprints [22, 23]. To facilitate the interpretation of the XRD results the ancient pottery samples were also analyzed by FTIR spectroscopy. Fig. 5 shows IR spectrum for the ceramics from *Benaičiai.*

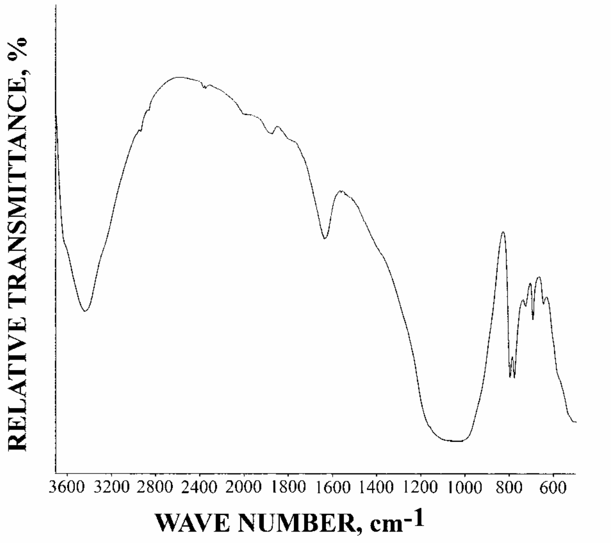

Fig. 5. IR spectrum of the historical ancient pottery from *Benaičiai*

A broad band between 3700 – 3000 cm^{-1} and less intensive absorption at 1635 cm^{-1} can be assigned to the adsorbed water (or water of crystallization) and O–H vibrations [22, 23]. The absorptions from the main quartz phase (Si–O) could be also easily identified (1160, 1082, 797, 778, 695, 512 cm^{-1}) [15]. The several intense bands in the range 800 – 550 cm^{-1} (725, 648, 595 cm^{-1}) are characteristic of the metal-oxygen vibrations in the ceramic samples [12]. Fig. 6 shows IR spectrum for the ceramics from *Turlojiškės*.

The similar bands attributable to the typical O–H (3700 – 3000 cm^{-1}; 1635 cm^{-1}), Si–O in quartz (1160,

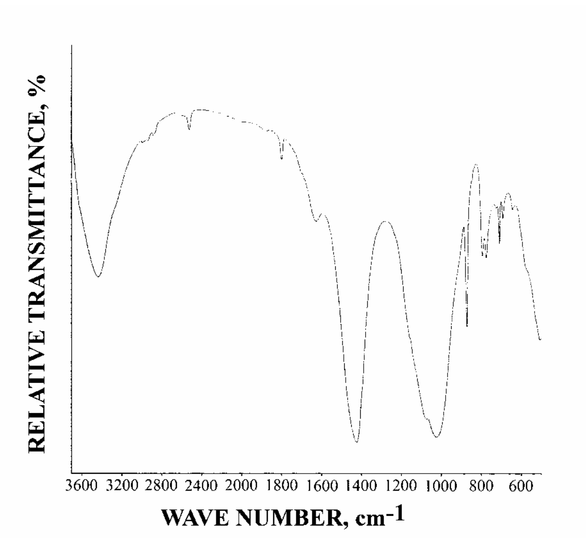

Fig. 6. IR spectrum of the historical ancient pottery from *Turlojiškės*

1082, 797, 778, 695, 512 cm^{-1}) and M–O (725, 645, 585 cm^{-1}) vibrations are very well resolved in the IR spectrum of pottery from *Turlojiškės*. However, additionally the characteristic carbonate (calcite phase) vibrations at 1797, 1420, 877, 714 cm^{-1} [15] and typical sulphate (calcium hydrogen sulphate phase) vibrations at 1105 ir 611 cm^{-1} [22, 23] could be also determined. Thus, the IR spectroscopy is indispensable tool for the characterization of materials and could be effectively employed for a qualitative characterization of ancient pottery and for the examination of different works of art.

CONCLUSIONS

Three types of ceramic materials (latter-day calcinated clay and historical ancient pottery samples from two places in Lithuania) were characterized by different methods. No correlation between water capacity, pH of solution and the particle size of the ceramic samples was observed. XRD analyses clearly showed that all investigated ceramic samples are polycrystalline materials and composed of different phases. Moreover, we demonstrated that IR spectroscopy is an indispensable tool for the characterization of ancient pottery. The results summarized in this paper are very important for the development of new method for the conservation of pottery.

REFERENCES

1. **Fairbrass, S.** Sticky Problems for Conservators of Works of Art on Paper *Int. J. Adhesion and Adhesives* 15 1995: pp. 115 – 120.
2. **Viart, N., Niznansky, D., Rehspringer, J. L.** Structural Evolution of a Formamide Modified Sol–Spectroscopic Study *J. Sol-Gel Sci. Technol.* 8 1997: pp. 183 – 187.
3. **Guglielmi, M.** Sol-Gel Coatings on Metals *J. Sol-Gel Sci. Technol.* 8 1997: pp. 443 – 449.
4. **Mackenzie, J. D., Bescher, E. P.** Physical Properties of Sol-Gel Coatings *J. Sol-Gel Sci. Technol.* 19 2000: pp. 23 – 29.
5. **Bescher, E. P., Pique, F., Stulik, F., Mackenzie, J. D.** Long Term Protection of the Last Judgment Mosaic in Prague *J. Sol-Gel Sci. Technol.* 19 2000: pp. 215 – 218.
6. **Caruso, R. A., Antonietti, M.** Sol-gel Nanocoating: an Approach to the Preparation of Structured Materials *Chem. Mater.* 13 2001: pp. 3272 – 3282.
7. **Chou, T. P., Chandrasekaran, C., Limmer, S., Nguyen, C., Cao, G. Z.** Organic-Inorganic Sol-Gel Coating for Corrosion Protection of Stainless Steel *J. Mater. Sci. Lett.* 21 2002: pp. 251 – 255.
8. **Landry, C. C., Pappe, N., Mason, M. R., Apblett, A. W., Tyler, A. N., MacInnes, A. N., Barron, A. R.** From Minerals to Materials: Synthesis of Alumoxanes from the Reaction of Boehmite with Carboxylic Acids *J. Mater. Chem.* 5 1995: pp. 331 – 341.
9. **Harlan, C. J., Kareiva, A., MacQueen, D. B., Cook, R., Barron, A. R.** Yttrium Doped Alumoxanes: a Chimie Douce Route to $Y_3Al_5O_{12}$ (YAG) and $Y_4Al_2O_9$ (YAM) *Adv. Mater.* 9 1997: pp. 68 – 71.
10. **Defriend, A. K., Barron, A. R.** Surface Repair of Porous and Damaged Alumina Bodies Using Carboxylate-Alumoxane Nanoparticles *J. Mater. Sci.* 37 2002: pp. 2909 – 2916.
11. **Kiuberis, J., Kazlauskas, R., Grabauskaite, L., Tautkus, S., Kareiva, A.** Scanning Electron Microscopy – a Powerful Tool for the Characterization of Materials. 2. Modified Sol-Gel Chemistry Approach to the Conservation of Paper *Env. Chem. Phys.* 25 2003: pp. 81 – 85.
12. **Veith, M., Mathur, S., Kareiva, A., Jilavi, M., Zimmer, M., Huch, V.** Low Temperature Synthesis of Nanocrystalline $Y_3Al_5O_{12}$ (YAG) and Ce-doped $Y_3Al_5O_{12}$ via Different Sol-Gel Methods *J. Mater. Chem.* 9 1999: pp. 3069 – 3079.
13. **Leleckaite, A., Kareiva, A.** Synthesis of Garnet Structure Compounds Using Aqueous Sol-Gel Processing *Opt. Mater.* 26 2004: pp. 123 – 128.
14. **Biscontin, G., Birelli, M. P., Zendri, E.** Characterization of Binders Employed in the Manufacture of Venetian Historical Mortars *J. Cultur. Heritage* 3 2002: pp. 31 – 37.
15. **De Benedetto, G. E., Laviano, R., Sabbatini, L., Zambonin, P. G.** Infrared Spectroscopy in the Mineralogical Characterization of Ancient Pottery *J. Cultur. Heritage* 3 2002: pp. 177 – 186.
16. **Lavat, A. E., Baran, E. J.** IR-spectroscopic Characterization of $A_2BB'O_6$ Perovskites *Vibr. Spectr.* 32 2003: pp. 167 – 174.
17. **Bakolas, A., Biscontin, G., Contardi, V., Franceschi, E., Moropoulou, A., Palazzi, D., Zendri, E.** Thermoanalytical Research on Traditional Mortars in Venice *Thermochim. Acta* 269/270 1995: pp. 817 – 828.
18. **Rice, P. M.** Pottery Analysis – A Sourcebook. The University of Chicago Press, Chicago, 1987.
19. **Mandeikytė, N., Šiaučiūnas, R.** Experiments of Ceramic Technology. Technologija, Kaunas, 1997 (in Lithuanian).
20. **Barkauskas, J., Kareiva, A.** Orthoboric Acid as a Densifying Agent for Graphitized Carbon Black *Mater. Res. Bull.* 38 2003: pp. 125 – 131.
21. **Baranauskas, A., Jasaitis, D., Kareiva, A.** Characterization of Sol-Gel Process in the Y-Ba-Cu-O Acetate-Tartrate System Using IR Spectroscopy *Vibr. Spectrosc.* 28 2002: pp. 263 – 275.
22. **Nakamoto, K.** Infrared and Raman Spectra of Inorganic and Coordination Compounds. John Wiley and Sons, New York, 1986.
23. **Schrader, B.** Infrared and Raman Spectroscopy: Methods and Applications. VCH, Weinheim, 1995.