

VILNIUS UNIVERSITY

Aušra Krapukaitytė

**INVESTIGATION AND DESCRIPTION OF MODERN AND
ARCHAEOLOGICAL CERAMICS**

Summary of doctoral dissertation

Physical sciences, chemistry (03 P)

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The dissertation is available at the library of Vilnius University and the library of Institute of Chemistry.

VILNIAUS UNIVERSITETAS

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**ŠIUOLAIKINĖS IR ARCHEOLOGINĖS KERAMIKOS
TYRIMAS IR APIBŪDINIMAS**

Daktaro disertacijos santrauka

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INTRODUCTION

Ceramics is the oldest material created by the human hand and articles thereof: from small articles, household ware to architectural elements, decorative plastics and insulating devices, laboratory vessels and fireproof products. It exerted great influence on human civilisation; without ceramics, today it would be impossible to melt metals and launch cosmic apparatus. It is a craft, science and art at the same time. Particularly great are artistic possibilities of ceramics. It is a universal branch of applied decorative arts with features of sculpture, graphic and design, and architecture. The ceramics manufacturing technology is quite interesting and varied, on account of which it is called "the art of fire".

Ceramics, as an oldest craft, maintains its value in the material and spiritual culture of the present day. The specific purpose of ceramics, as its millennial feature, currently is not one and only, and crucial. Its social and artistic function today is much wider and more complex than ever before.

Ceramic articles are analysed in various laboratories. Analysis is performed seeking to find out the components of ceramics and its manufacturing technologies. According to the obtained data it is possible to identify from which region the articles are or to what period they belong. These data are later used by restorers wishing to recreate or revive ancient ceramic articles.

The bulk of ceramics discovered in Lithuania is from the Bronze Age. Analysis of ancient ceramics provides information about the-then everyday life, reveals the ethnic and cultural aspects of that period. In addition, the physical-chemical characteristics of archaeological ceramics provide the historic and technological information on its manufacturing, and the knowledge of its chemical and mineralogical composition is indispensable for further characterisation of the ceramics. The ceramics chemical composition depends on the original raw materials used, processing and changes over time. The mineralogical composition 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. Therefore, information about ancient ceramics is important not only for archaeologists, but also for materials scientists and people working in the field

of conservation chemistry.

Lithuanian archaeologists mainly use only visual analysis of ancient ceramics. They define the shapes of pottery, surface decorations, ornaments, the thickness of the walls and the base, etc. Visual description of ceramics is necessary, but represents the first stage of examination only. For subsequent examinations, a more detailed physical and chemical characterisation of ceramics is lacking.

The purpose of the work

The purpose of the scientific research generalised in this doctoral thesis is to explore the possibilities of different methods in establishing the morphology, elemental and phasic composition of ceramics samples, and to apply these methods in describing archaeological ceramics of historical value.

The tasks of the dissertational work:

- To find reliable methods for establishing the elemental composition of ceramics samples.
- To establish the possibilities of X-ray diffraction (XRD) and infrared ray spectroscopic (IR) analyses for defining samples of ceramic materials.
- To establish the possibilities of the Scanning Electron Microscope (SEM) in defining the morphology of ceramic materials and establishing their elemental composition.
- To explore the possibilities of thermal analysis for the characterisation of ceramics samples.
- To define comprehensively ten samples of modern ceramics of artistic value.
- To define comprehensively the archaeological ceramics of historical value from the Stanaičių, Turlojiškių, Žvainių, Jurgaičių and Nikėlų archaeological villages.

Statements of the thesis to be defended

The results of the work allow defending the following key statements:

- The X-ray dispersion analysis (EDX) is fast, reliable and perfectly suitable for establishing the basic elemental composition of modern and archaeological ceramics. The flame atomic absorption spectroscopy (FAAS), combined with

titrimetric and spectrophotometric methods, enables not only to establish the key metals of ceramics but their traceable amounts as well.

- The X-ray diffraction and infrared spectroscopic analysis enable to identify precisely the phasic composition of samples of modern and archaeological ceramics. The results of ceramics characterisation received enable to reveal the technological features of its manufacturing.
- The Scanning Electron Microscope provides a possibility to explore the morphological features of ceramic articles. With SEM photographs, it is possible to establish the shape, morphology, size and distribution of pores, and manufacturing conditions of the ceramics.
- The nature of the results of thermogravimetric (TG) and differential thermal analysis (DTA) depends on the ceramics composition and manufacturing conditions. Thermal analysis is a particularly valuable method of examination and description of modern and archaeological ceramic findings.

2. INSTRUMENTATION

For the determination of metals by the flame atomic absorption spectrometry (FAAS) method, an atomic absorption spectrometer of model 170-50 of the Japanese firm *Hitachi* was used.

To determine silicon and titanium by the spectrophotometric method, a photometer KFK-3 and a 10 mm cuvette were used; optic density was measured at $\lambda = 597$ nm and $\lambda = 410$ nm.

The X-ray diffraction analysis of examined samples was performed with a PANalytical X'Pert PRO diffractometer, using a $\text{CuK}\alpha_1$ radiation source and a Fe monochromator.

The infrared 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 morphology, microstructure and elemental composition of all pottery samples were examined using scanning electron microscopy and energy dispersive X-ray analysis. The measurements were recorded under vacuum in the specimen chamber of

the scanning electron microscope EVO 50 (United Kingdom) equipped with energy dispersive X-ray spectrometer (Oxford Instruments) and operating at secondary electron mode. The used accelerating voltage – 20 keV; working distance – 10 mm. The cation content was analyzed using L, K lines.

Thermal analysis was carried out using the Setaram TG-DSC12 and STA 409 (Netzsch) thermal analysers. Samples of 29.65 – 32.47 mg were examined. Thermogravimetric measurements were performed at a temperature regime of 25-1300° C, the heating rate of 20° C/min, with air as the carrying gas.

3. RESULTS AND THEIR DISCUSSION

3.1 Analytical characterization of modern ceramics

For the characterization of modern ceramics, ten different ceramic samples of artistic value, obtained from P. Gudynas Restoration Centre in Vilnius and from the stock of the National Art Museum of Lithuania, were used. All samples were examined using the energy-dispersive X-ray, flame atomic absorption spectroscopy, X-ray diffraction, IR spectroscopy, and thermal analysis methods. The surface morphological examinations were performed with a scanning electron microscope.

3.1.1 Elemental analysis

3.1.1.1 Energy-dispersive X-ray analysis

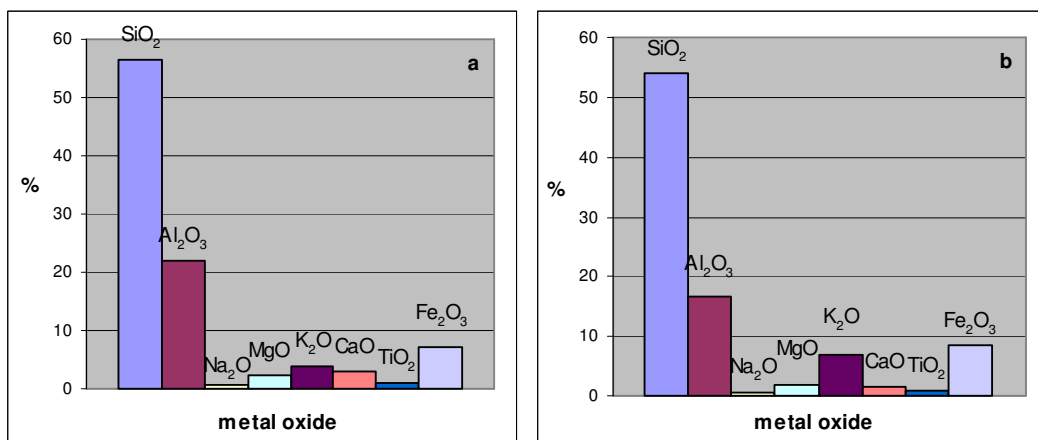


Fig.1. Prevailing metal oxides (%) discovered in the ceramic samples: (a) black ceramic; (b) fragment of a pot

The elemental composition of the ceramic samples was first determined using energy-dispersive X-ray analysis. The average ratio of metals in the samples, expressed

as metal oxides, determined by the EDX method, is presented in Fig.1. As can be seen, the prevailing metals detected in all the samples are silicon and aluminium. In different samples, the discovered amount of SiO_2 was 48%–56% and that of Al_2O_3 – 17%–33%. In all the samples, smaller amounts of sodium, magnesium, potassium, calcium, titanium and iron were also discovered.

3.1.1.2 Atomic absorption spectroscopy

Energy-dispersive X-ray analysis is quantitative analysis, which enables to determine not only the prevailing metals whose amounts in ceramics exceed 0.5%. Therefore we used flame atomic absorption spectrometry to detect small amounts of metals in modern ceramics.

The largest amounts discovered were iron oxide (1.5–10.8%), sodium oxide, magnesium oxide, potassium oxide and calcium oxide (1.0–7.5%). In all samples, small amounts of lead and zinc compounds were discovered, whereas cobalt, manganese, copper, nickel, strontium and chrome were discovered not in all samples. There are no tin and cadmium compounds in the ceramics, or their amounts are below the limit of detection.

The amounts of aluminium were determined by the titrimetric method. Al_2O_3 is one of the main compounds in the ceramics, its amount ranging between ~ 18% and ~ 33%.

To determine the amounts of silicon and titanium, spectrophotometric methods were used. It has been established that the amount of SiO_2 in the examined samples ranges between ~ 46% and ~ 58% and this is the main component of the ceramics. The discovered much smaller amounts of TiO_2 range at around 1%.

3.1.2 X-ray diffraction analysis

The phase composition of the ceramics was determined by X-ray diffraction analysis. The samples of modern ceramics are characterised by multiphase composition. Quartz (SiO_2) is the prevailing phase in almost every ceramic. In the ceramics quartz is often discovered along with alkaline feldspars. From the diffractogrammes in Fig. 2 it has been established that the black ceramics (a) and the fragment of a pot (b) contain albite ($\text{NaAlSi}_3\text{O}_8$) and microcline (KAlSi_3O_8) assigned to feldspars, and the black ceramics –

additionally kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$.

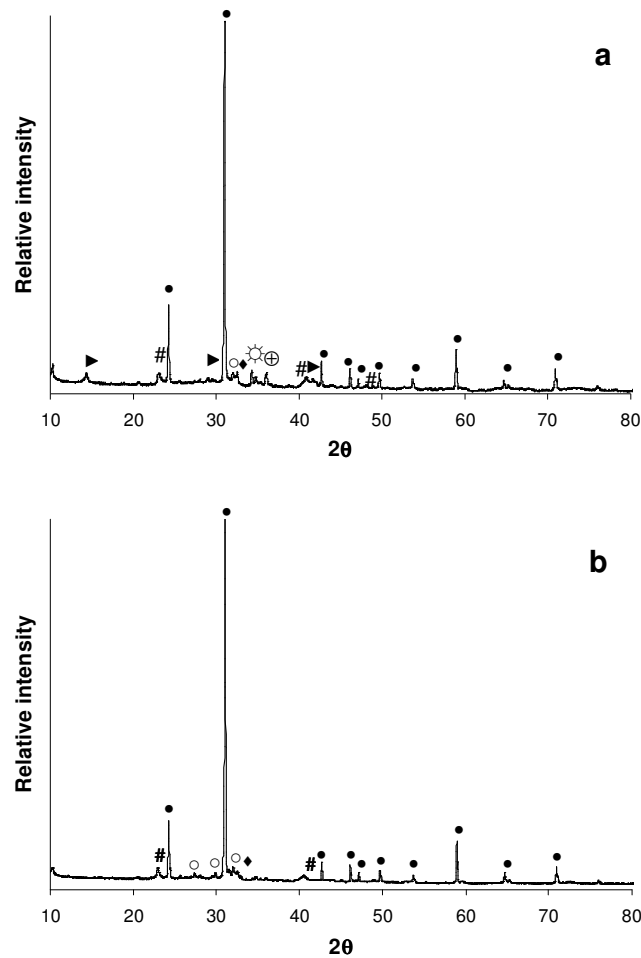


Fig. 2. X-ray diffractograms of the ceramic samples: (a) black ceramics; (b) fragment of a pot. The phases are marked as follows: SiO_2 (●), $\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$ (#), KAlSi_3O_8 (o), CaCO_3 (☼), $\text{CaMg}(\text{CO}_3)_2$ (⊕), $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (►), $\text{NaAlSi}_3\text{O}_8$ (◆)

The diffractograms not only provide information about the composition of the ceramics but also can be used for the interpretation of the technological features of its manufacturing. The carbonates contained in the black ceramics – calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) suggest that the ceramics was fired at low temperature, because raising temperature to 800°C makes all carbonates transform into other compounds. The presence of kaolinite in the black ceramics also confirms that it was fired at low temperature or at least not higher than 800°C . The ceramic of the fragment of a pot most likely was also fired at low temperature, because its composition, apart from quartz, also

contains the initial pottery materials: albite, microcline and muscovite ($\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$).

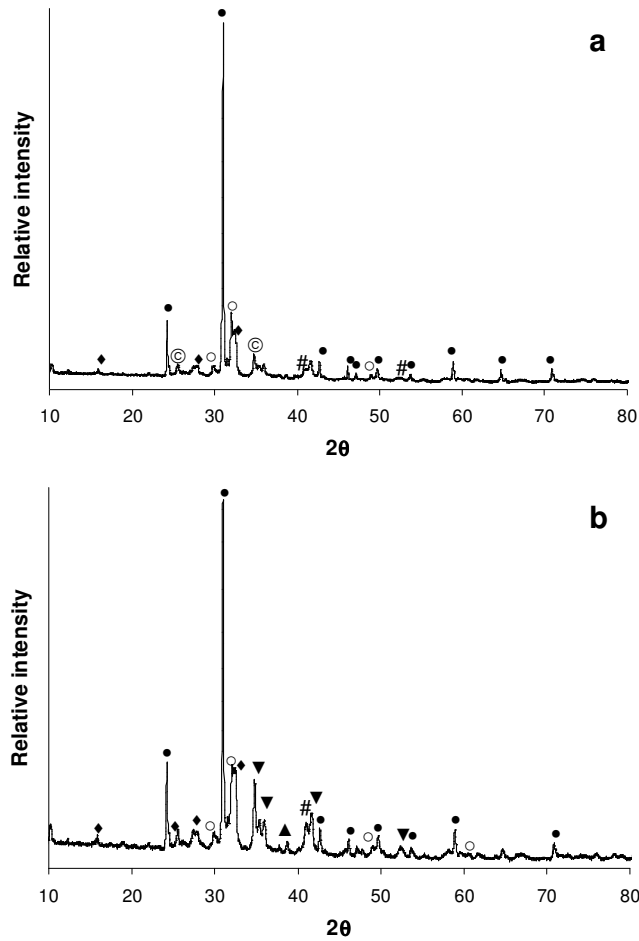


Fig. 3. X-ray diffractogrammes of the samples of modern ceramics: (a) glazed red clay; (b) Kozlov vase's red clay fragment. The phases are marked as follows: SiO_2 (●), $\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$ (#), KAlSi_3O_8 (o), $\text{NaAlSi}_3\text{O}_8$ (◆), $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ (⊙), Fe_2O_3 (▲), $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ (▼), $\text{Al}_6\text{Si}_2\text{O}_{13}$ (◄)

In the glazed red clay ceramic (Fig. 3 a) and in the fragment of the Kozlov vase's red clay ceramic (Fig. 3 b), secondary phases were identified: albite ($\text{NaAlSi}_3\text{O}_8$), microcline (KAlSi_3O_8), muscovite ($\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$), diopside ($\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$), hematite (Fe_2O_3). In the glazed red clay, cordierite ($\text{Mg}_2\text{Al}_3[\text{AlSi}_5\text{O}_{18}]$), and in the Kozlov vase's red clay fragment – mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) were additionally found. In literature there are data that thermal decomposition of calcite begins at around 600°C and completes at $800\text{--}850^\circ\text{C}$, with new high-temperature

aluminium-calcium-silicates forming. One of such high-temperature compounds is diopside ($\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$), which was found in both ceramics presented in Fig.3. The presence of diopside provides data that these ceramics were fired at a temperature not lower than 850°C , as no carbonate compounds have been detected any more.

The Kozlov vase's red clay ceramic most likely was fired at a still higher temperature – $1000\text{--}1050^\circ\text{C}$, as in its composition mullite was found, which only begins forming when the firing temperature is 950°C . The presence of muscovite in the ceramic shows that its firing temperature did not exceed $\sim 1050^\circ\text{C}$, because at 1100°C muscovite peaks are no longer observed in the diffractogrammes.

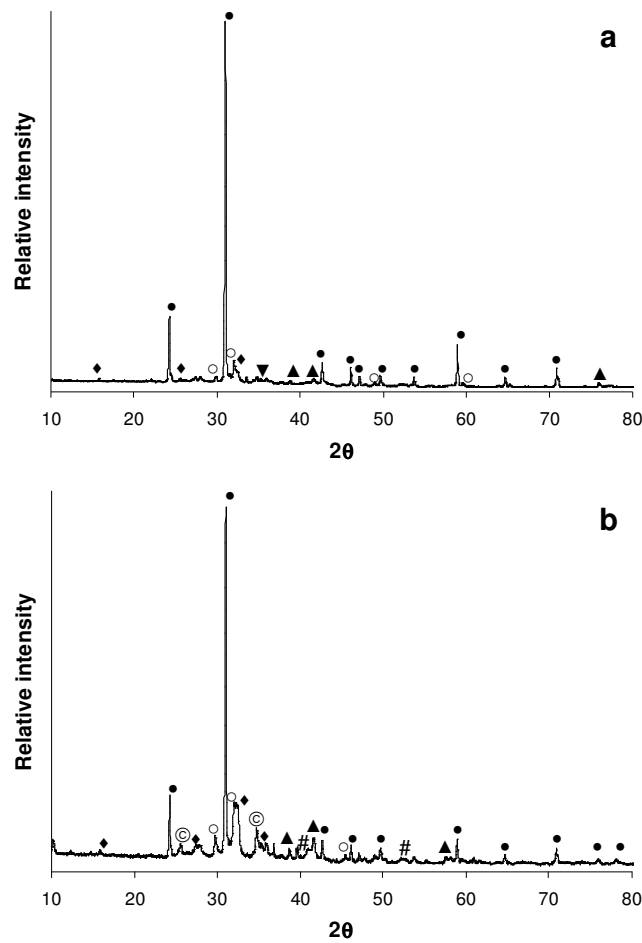
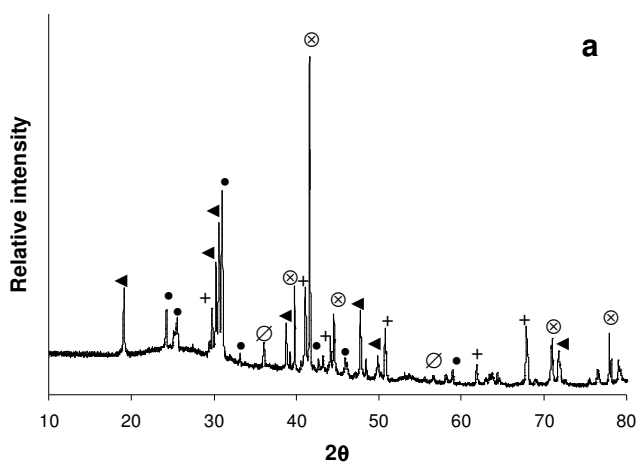


Fig. 4. X-ray diffractogrammes of the modern ceramic samples: a) colour-glazed tile; b) fragment of green-glazed ceramic. The phases are marked as follows: SiO_2 (●), $\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$ (#), KAlSi_3O_8 (○), $\text{NaAlSi}_3\text{O}_8$ (◆), $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ (⊙), Fe_2O_3 (▲), $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ (▼)

In the colour-glazed tile (Fig. 4 a) and in the fragment of green-glazed ceramic (Fig. 4 b), the following was found: albite ($\text{NaAlSi}_3\text{O}_8$), microcline (KAlSi_3O_8), diopside ($\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$) and hematite (Fe_2O_3), and in the green-glazed ceramic – muscovite ($\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$) and cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) were additionally found. The presence of these phases suggests that these ceramics, like the glazed red clay sample in Fig. 3 a, were fired at a temperature not below 850°C .

The phase composition of the fired CuO-saturated glazed ceramic consists of quartz, albite, microcline, mullite, diopside, muscovite, and hematite. In the CuO-saturated glazed ceramic, cordierite was also found. Since the composition and diffractogrammes of these two ceramics are similar to the composition of the Kozlov vase's red clay ceramic (Fig. 3, b), the technological features of their manufacturing are probably the same.

In the fragment of white clay from *Panevėžys* (Fig. 5, a) and in the fragment of the *Tern* of white clay (Fig. 5, b), only small amounts of quartz (SiO_2) were found, however in both ceramics cristobalite (SiO_2) was identified, which forms firing ceramic at a high temperature of $1200\text{--}1300^\circ\text{C}$. Firing ceramic at the temperature of 950°C and above, another crystal phase – mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) is formed. As in both ceramics of white clay cristobalite and mullite were found, we can claim that these ceramics were fired at high temperature. Apart from these phases, in both ceramics korundum (Al_2O_3) was also found. In the white clay from *Panevėžys*, large amounts of carborundum (SiC) were discovered. Since the SiC compound is only formed at very high temperature, this only confirms that the white clay from *Panevėžys* was fired at high temperature.



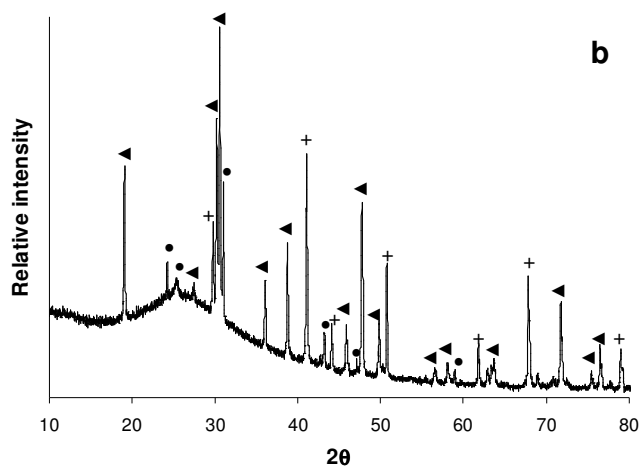


Fig. 5. X-ray diffractogrammes of the modern ceramic samples: (a) white clay from *Panevėžys*; (b) fragment of a *Tern* of white clay. The phases are marked as follows: SiO_2 (●), SiC (⊗), Al_2O_3 (+), $\text{Al}_6\text{Si}_2\text{O}_{13}$ (◄), $(\text{Fe}_2,\text{Mn})_3\text{Al}_2(\text{SiO}_4)_3$ (⊗)

3.1.3 Investigation of surface morphology

The morphology of the ceramics was investigated with a scanning electron microscope. As can be seen in Fig. 6 a, the black ceramic is comprised of plate-like particles. Such composition of ceramic is characteristic of the ceramic which has been fired at the low temperature of $\sim 600^\circ\text{C}$. The ceramic of the fragment of a pot (Fig. 6 b) is also comprised of plate-like particles, however here the “threads” of the melting phase are also visible. The visible inserts of the melting phase allow us to establish that the ceramic of the fragment of a pot was fired at a temperature higher than the black ceramic.

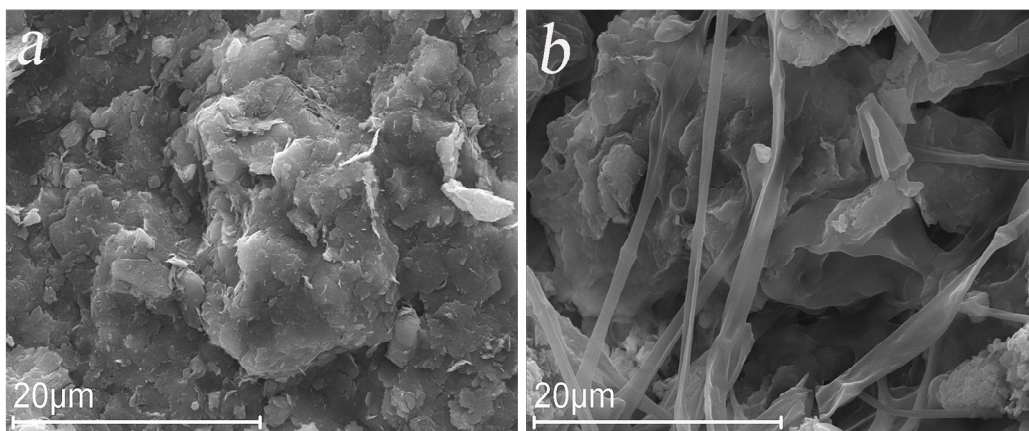


Fig. 6. SEM images of the modern ceramics: (a) black ceramics; (b) fragment of a pot

The ceramic from *Panevėžys* (Fig. 7) is comprised of molten planes of the liquid phase between which spherical and oblong pores are visible. This morphological structure is characteristic of ceramic that has been fired at high temperature. The structure of the ceramic in Fig. 7 (b) is characteristic of that which has been fired at a very high temperature. The ceramic body is comprised of a solid hardened mass inside which spherical pores sized 1–50 μm are. Increasing the firing temperature to 1300–1350°C, the porosity of the ceramic lowers, although the size of the pores increases accordingly.

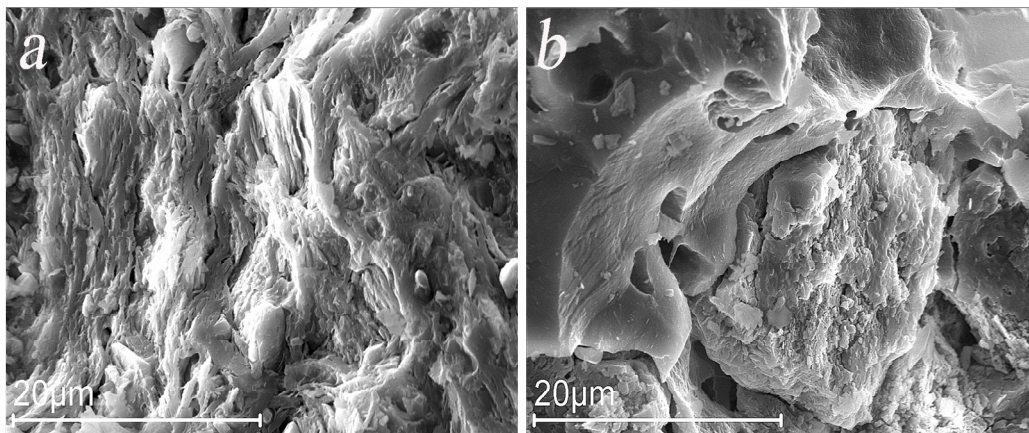


Fig. 7. SEM images of the modern ceramics: (a) white clay from *Panevėžys*; (b) fragment of a *Tern* of white clay

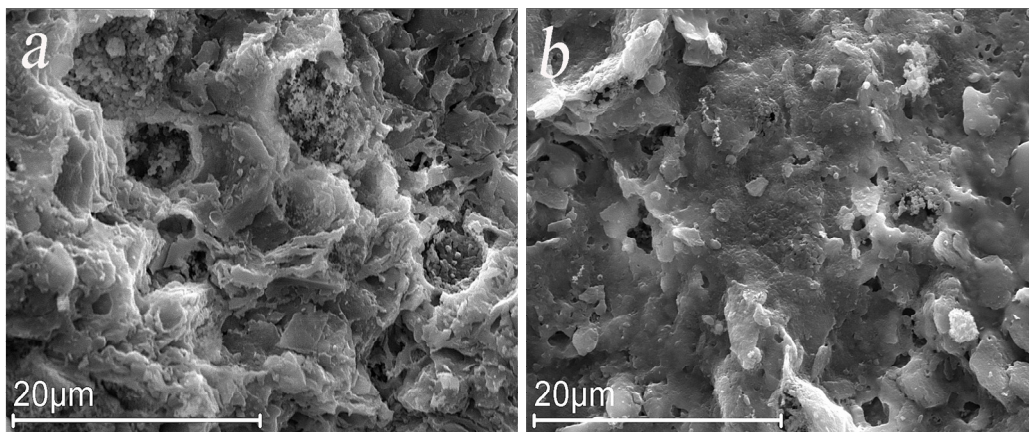


Fig. 8. SEM images of the modern ceramics: (a) glazed red clay; (b) the Kozlov vase's red clay fragment

The red clay ceramic (Fig. 8 a) is comprised of razor-edge planes, among which round cavities sized 5–10 μm with crystals are visible. Such crystals can emerge when new phases are formed at firing. The Kozlov vase's red clay fragment (Fig. 7 b) is comprised of unmelted particles of clay distributed across the liquid phase. Pores sized several μm are visible in the ceramic. This morphology is typical to ceramic which has been fired at the temperature of $\sim 1000^\circ\text{C}$.

In Fig. 9 (a) it can be seen that the tile ceramics is comprised of particles which have coalesced into agglomerates. The particles are characterised by porous structure. This surface morphology suggests that the ceramic was fired several times gradually increasing the temperature.

The morphology of the green-glazed ceramic, fired colourless-glaze ceramic and the fired CuO-saturated (Fig. 9 b) glaze ceramic is uniform. In all the three ceramics, a hardened liquid phase with hollow pores of different size and shape are visible. In the ceramic bodies, pores with mullite crystals that probably have formed in them were also found. These ceramics are also characterised by high density of the pores in the body. Such porous structure can emerge if the initial raw materials contained over 10% of calcite. Due to the abundance of the pores and the presence of the diopside phase one can claim that these ceramics were fired at medium temperature from initial raw materials containing many carbonate compounds.

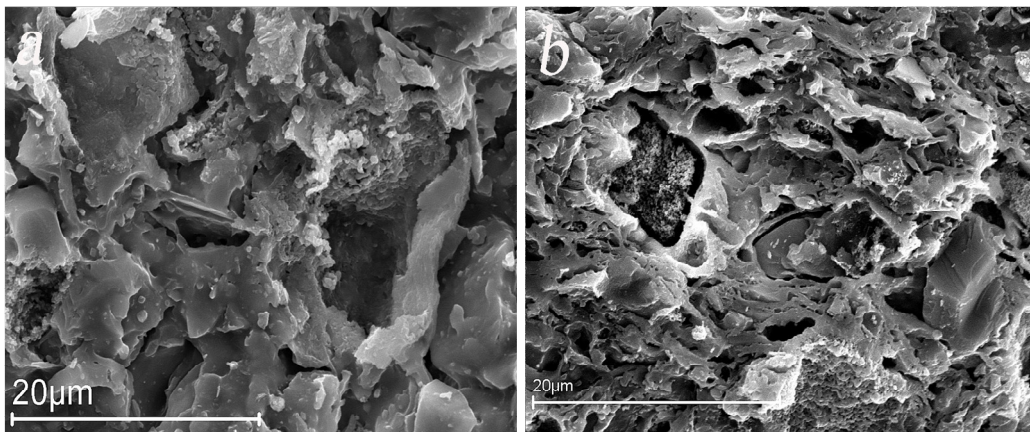


Fig. 9. SEM images of the modern ceramics: (a) colour-glazed tile; (b) fired CuO-saturated glaze

3.1.4 Infrared spectroscopy

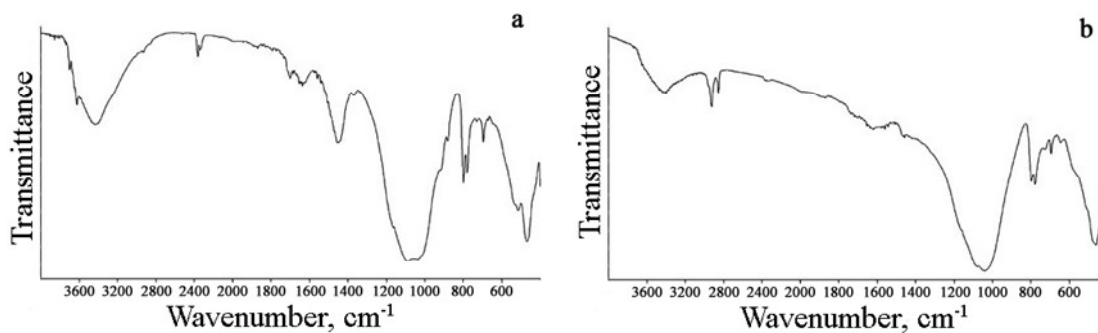


Fig. 10. IR spectra of the modern ceramics: (a) black ceramic; (b) fragment of a pot

The phase composition of the ceramics was established using also infrared spectroscopy. The wide band observed in all the samples, in the IR spectrum at 3700–3000 cm^{-1} , and less intensive absorption at 1635 cm^{-1} , is assigned to adsorbed or crystallization water (O–H vibrations). The main quartz phase can easily be identified by the absorption peaks observed in IR spectrum at 1160, 1082, 797, 778, 695, 512 cm^{-1} . The quartz peak, however, is mainly identified in the IR spectrum at peaks 797 and 778 cm^{-1} , which correspond to the symmetric valence Si–O–Si vibrations. The absorption bands at $\sim 1083 \text{ cm}^{-1}$ are too wide to enable to assign them in a credible manner to a certain compound. At 1200–1000 cm^{-1} , characteristic groupings belonging to quartz, feldspars or other clays overlap.

In the IR spectrum of the black ceramic (Fig. 10, a), on the wide absorption band 3700–3400 cm^{-1} , two peaks at 3700 and 3620 cm^{-1} , characteristic of kaolinite, are observed. In this spectrum, peaks of low intensity 880 and 720 cm^{-1} and peak of high intensity 1456 cm^{-1} , assigned to C-O_3^{-2} vibrations, are also visible. The absorption bands visible in the ceramic of the fragment of a pot (Fig. 10, b) at 2922 and 2852 cm^{-1} , obtained due to C–H vibrations, are assigned to organic compounds having groupings – CH_2 and – CH_3 .

The bands present within the range 1200–400 cm^{-1} can be attributed to other silicates: albite, microcline, muscovite, mullite, and cordierite. Several intensive bands in the wave number area 800–550 cm^{-1} (725, 648, 595 cm^{-1}) are the characteristic peaks of

the metal-oxygen (M-O) stretching vibrations. The absorption bands observed in Figures 10–11 at 470–600 cm^{-1} can also be assigned to iron oxide (hematite).

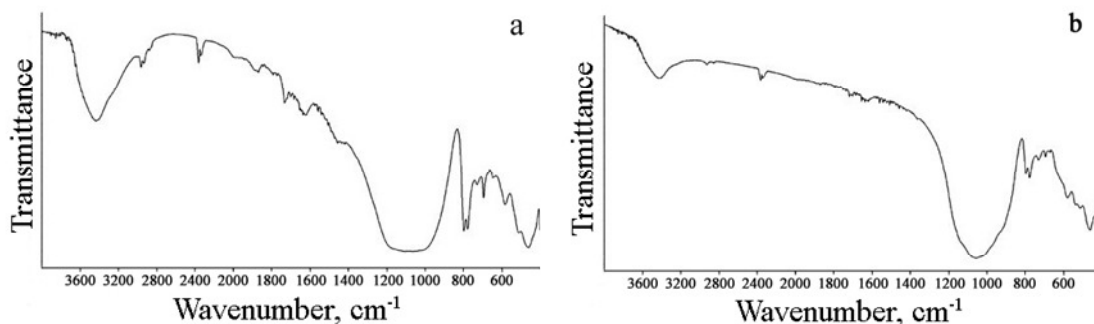


Fig. 11. IR spectra of the modern ceramics: (a) glazed red clay; (b) Kozlov vase's red clay fragment

3.1.5 The use of thermal analysis for the characterisation of ceramics

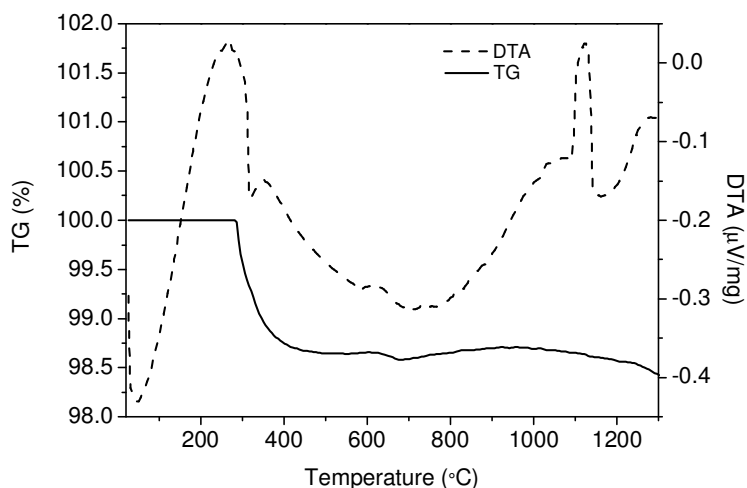


Fig. 12. TG/DTA curves of the Kozlov vase's red clay fragment

As can be seen in Figures 12 and 13, raising the temperature from room temperature to 300–400° C, no loss of mass is observed. This thermal dependence is characteristic of ceramics that have been sintered once at high temperature. Raising the temperature further, the thermogravimetric curve in Fig. 34 shows a sharp one-leap loss of mass (~ 1.3%). In the thermogravimetric curve of the black ceramic, a wide two-step loss of mass at 385° C to 780° C is observed, which accounts for some 5,2% of the loss of mass. The obtained results report that the phase composition of the black ceramic and of

the Kozlov vase fragment's ceramic is quite different. Different exothermic and endothermic peaks obtained by differential thermal analysis also enable to confirm this conclusion.

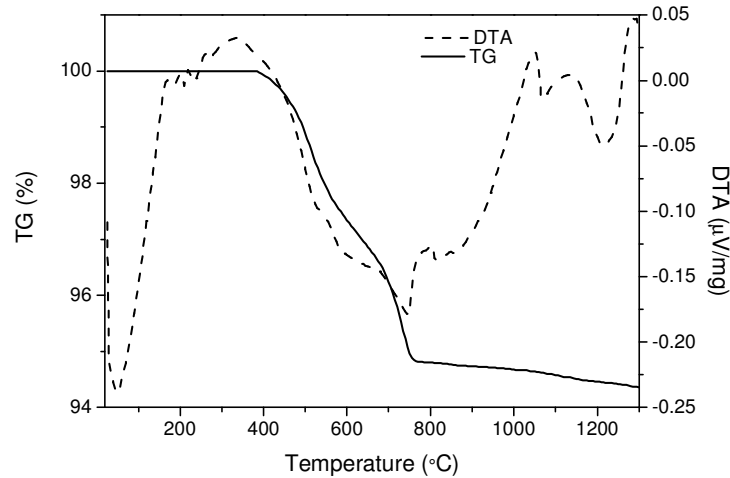


Fig. 13. TG/DTA curves of the black ceramic

The TG/DTA curves of the fired glazed CuO-saturated ceramic are presented in Fig. 14.

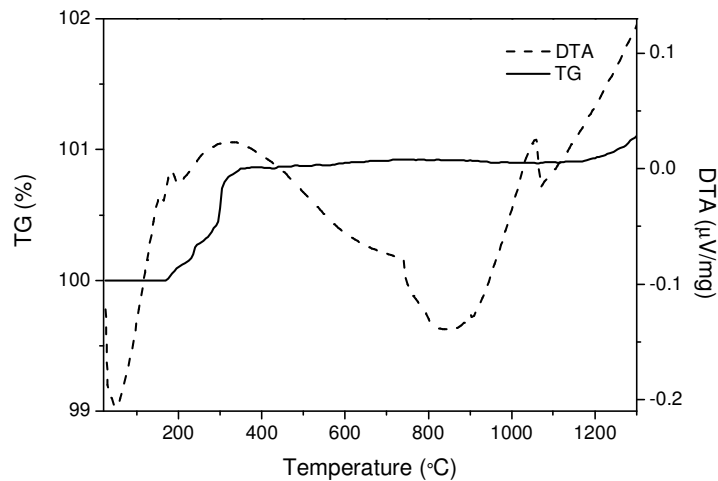
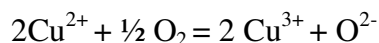
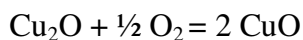


Fig. 14. TG/DTA curves of the fired glazed CuO-saturated ceramic

Differently from the ceramic samples examined before, here we see not the loss of mass but an increase in the mass of 0.8% on the temperature reaching 180-210°C. Heating Cu_2O in air or oxygen atmosphere, mass increases as a result of the following reactions:



Raising the temperature further, changes in the TG curve are observed no more. The absence of changes in the TG curve at a higher temperature and previous examinations confirm this ceramic to have been fired at high temperature.

3.2 Analytical characterization of archaeological ceramic

Among all items of cultural heritage and ancient articles in Lithuania, very important are archaeological ceramic findings. To characterize archaeological ceramics, six ceramic samples of the Bronze Age discovered in different Lithuanian villages (Fig. 15) were used in this work. The samples were discovered carrying out archaeological excavations of *Stančiaiai*, *Turlojiškės*, *Žvainiai*, *Jurgaičiai* and *Nikėlai* burial grounds. By the origin of the different articles found in the graves, they were assigned to the end of the Early and Late (second millennium B.C.) Bronze Age. The ancient ceramic samples from *Stančiaiai*, *Turlojiškės* and *Žvainiai* were excavated and their historical value was established by the archaeologists of the Department of Archaeology of the Faculty of History of Vilnius University. The ancient ceramic samples from *Jurgaičiai* and *Nikėlai* were obtained from the Pranas Gudynas Restoration Centre in Vilnius.



Fig. 15. Location of archaeological complexes in Lithuania

3.2.1 Elemental analysis

3.2.1.1 Energy-dispersive X-ray analysis

The average ratio of metals expressed as oxides in the ceramic sample, determined by the EDX analysis method, is presented in Fig. 16. In the samples, silicon, iron and aluminium oxides prevail. In all the samples, sodium, magnesium, potassium, calcium, and in the ceramics of *Nikėlai* and *Jurgaiėiai* – additionally titanium were found.

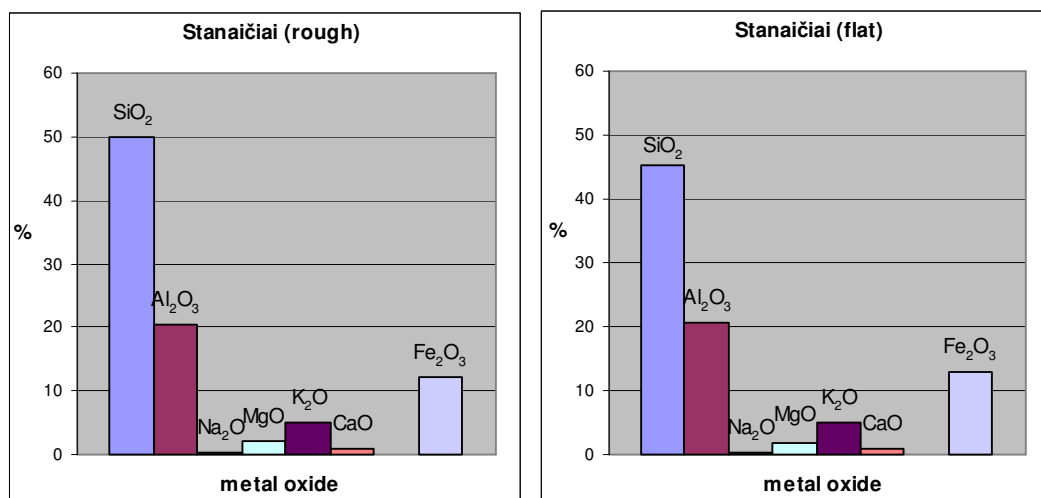


Fig. 16. Prevailing metal oxides (%) found in the ceramic samples

3.2.1.2 Atomic absorption spectroscopy

In the case of ancient archaeological ceramics, like in the case of modern ceramics, the elemental analysis was carried out by the flame atomic absorption spectroscopy, titrimetric and spectrophotometric analysis methods.

As can be seen from the results obtained, the amount of silicon in different ceramic samples ranges between 47.3% and 60.4%. The smallest amount of aluminium (18.0%) was found in the ceramic from *Turlojiškės*, whereas the ceramic from *Žvainiai* and *Nikėlai* contained the smallest amount of iron (~8.5%). The Table shows that the amount of potassium oxide ranges between ~4.56% and 6.92%; the amounts of magnesium and calcium oxides found ranged between ~1.0% and 2.0% and 1.0% to 7.5% respectively; the amount of sodium oxide found was still smaller (0.24%– 0.63%). Titanium was only found in the ceramic from *Jurgaiėiai* and *Nikėlai*. In all the samples, small amounts of cobalt, manganese, zinc, copper, lead, nickel and chrome compounds

were detected. In addition, it was established that the analysed ceramic samples contained no strontium, cadmium and tin, or the concentrations of these metals were lower than the limit of detection used for these methods.

3.2.2 X-ray diffraction analysis

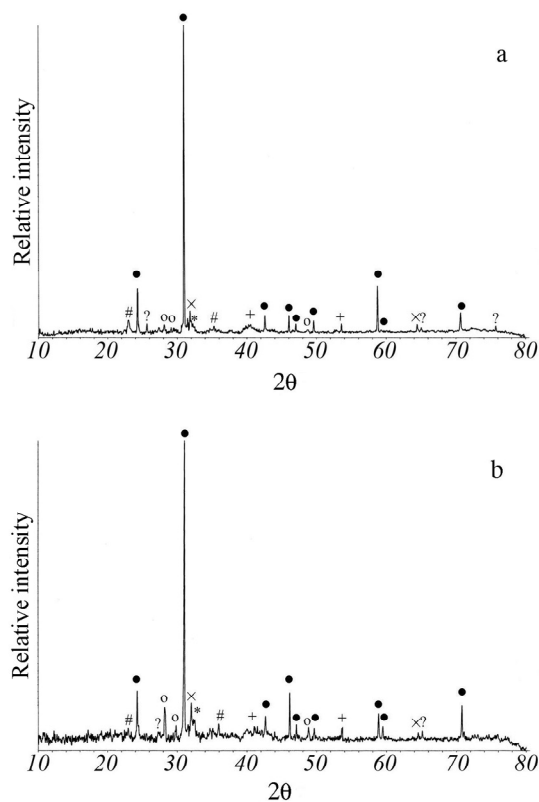


Fig. 17. X-ray diffractogrammes of the archaeological ceramic samples: a) *Stanaičiai* rough ceramics and b) *Stanaičiai* flat ceramics. The phases are marked as follows: SiO_2 (•), $\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$ (#), $\text{CaTiO}(\text{SiO}_4)$ (×), KAlSi_3O_8 (o), Al_2O_3 (+), $(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$ (*).

Fig. 17 shows that the rough (a) and the flat ceramics (b) from *Stanaičiai* have the same main phase – quartz (SiO_2), and a few common phases: titanite ($\text{CaTiO}(\text{SiO}_4)$), microcline (KAlSi_3O_8), muscovite ($\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$), corundum (Al_2O_3) and sodium anorthite ($(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$). The same main and secondary phases (except microcline) were also discovered in the ancient ceramic samples from *Žvainiai* (Fig. 43 a) and *Turlojiškės*. However, nontronite ($\text{Ca}_{0.1}\text{Fe}_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2 \bullet 4\text{H}_2\text{O}$) and calcite (CaCO_3)

were only identified in the ceramic from *Turlojiškės*. The secondary phase – calcium hydrogen sulphate ($\text{CaH}_2(\text{SO}_4)_2$) and sodium aluminium silicate (NaAlSiO_4) were identified in the ceramic from *Žvainiai*.

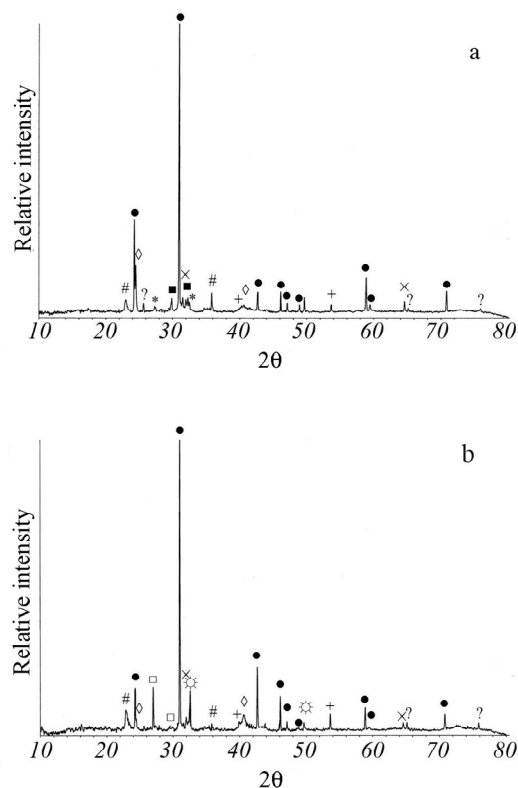


Fig. 18. X-ray diffractogrammes of the archaeological ceramic samples a) *Žvainiai* and b) *Turlojiškės*. The phases are marked as follows: SiO_2 (●), $\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$ (#), $\text{CaTiO}(\text{SiO}_4)$ (×), Al_2O_3 (+), $(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$ (*), NaAlSiO_4 (♦), CaCO_3 (⊙), $\text{Ca}_{0.1}\text{Fe}_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (□), $\text{CaH}_2(\text{SO}_4)_2$ (■).

The main phase of the ceramics from *Jurgaičiai* and *Nikėlai* (Fig. 19) is quartz. Apart from it, microcline, albite, and muscovite were discovered. In both ceramics, amphibolite ($\text{Ca}_2(\text{Fe},\text{Mg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$) was discovered as well. The phase composition of these two ceramics is almost identical; the difference in the amounts of the detected phases is negligible. These results enable us making an assumption that the ceramics

from *Jurgaičiai* and *Nikėlai* were both manufactured using the same initial raw materials and firing technologies.

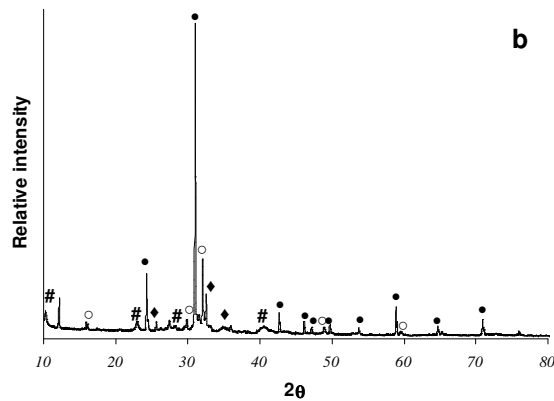


Fig. 19. X-ray diffractogramme of the *Nikėlai* archaeological ceramic samples. The phases are marked as follows: SiO_2 (●), $\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$ (#), $\text{NaAlSi}_3\text{O}_8$ (◆), KAlSi_3O_8 (○)

3.2.3 Investigation of surface morphology

SEM images of the two ceramic samples (rough and flat) found in *Stanaičiai* village are presented in Fig. 20. The rough ceramic (Fig. 20 a) is composed of plate-like particles, which suggests it has been fired at a relatively low temperature. In Fig. 20 (b) we see “molten” surface on which sharp edges are visible. This microstructure suggests this ceramic has been fired once, but at high temperature.

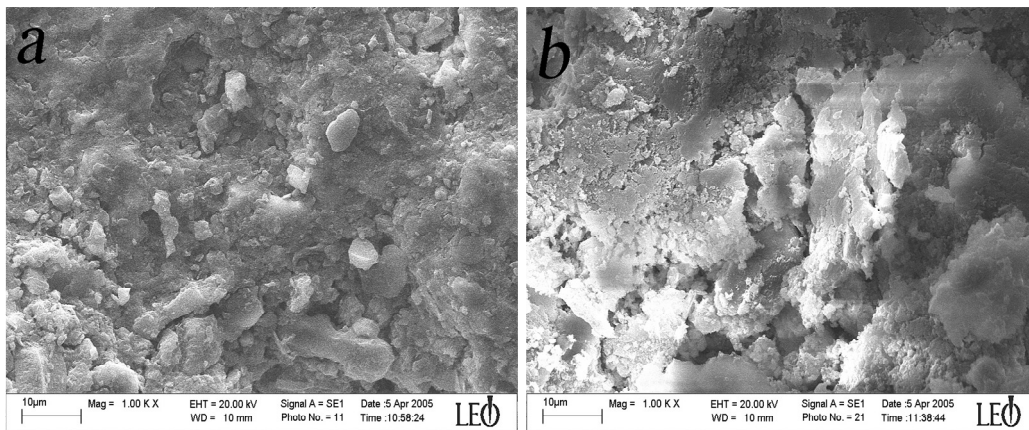


Fig. 20. Scanning electron micrographs of pottery samples from *Stanaičiai* village: (a) rough sample and (b) flat sample.

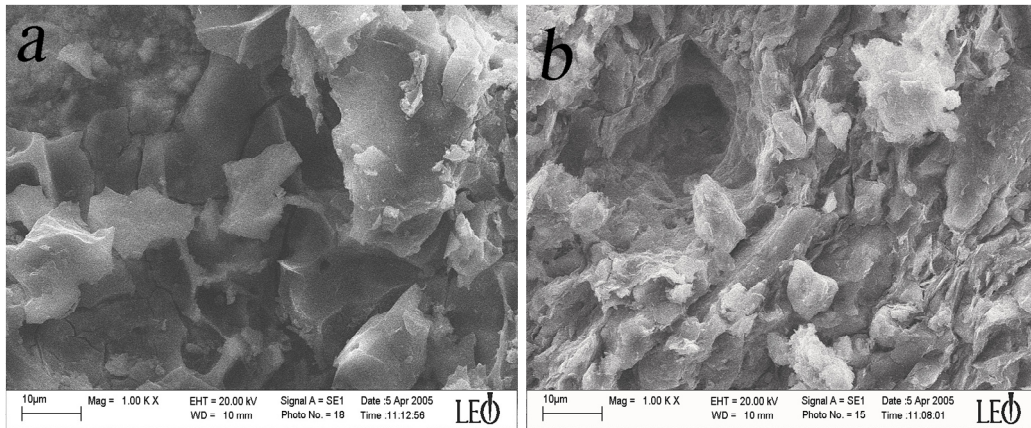


Fig. 21. Scanning electron micrographs of pottery samples from a) *Turlojiškės* and b) *Žvainiai* villages.

Fig. 21 presents SEM images of two ceramic samples found in *Turlojiškės* and *Žvainiai* villages. The microstructure of these two ceramics is very similar. Small particles, smaller than 10 micrometres, were formed, which have coalesced into agglomerates. These particles are characterised by porous structure. The cavities formed are large (sized 10 micrometres) and varying in shape. This surface morphology suggests the ceramics were fired several times, raising the temperature gradually.

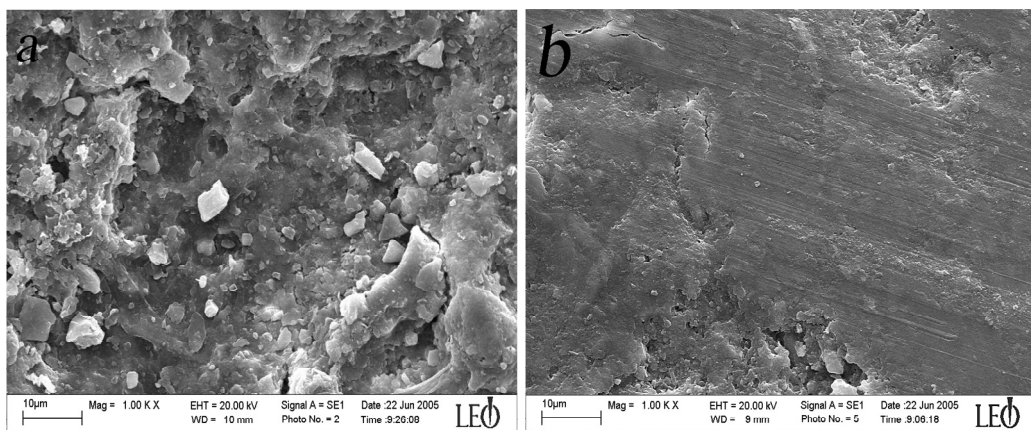


Fig. 23. Scanning electron micrographs of pottery samples from a) *Nikėlai* and b) *Jurgaičiai* villages.

Fig. 23 presents SEM images of two ceramic samples found in *Nikėlai* and *Jurgaičiai* villages. On the surface of the ceramic from *Nikėlai*, separate, differently shaped, micro-sized particles are visible (Fig. 23, a). This shows that most particles do

not melt in the matrix, but expand independently, forming a different phase. By contrast, in the ceramic sample from *Jurgaičiai* archaeological site, “molten” and dense microstructure is observed (Fig. 23, b). This shows that that the particles melt totally in the matrix, which forms a network maintaining “glass-smooth” surface with no inner pores. These data report that the ceramic sample from *Nikėlai* has been sintered at a much lower temperature, and the sample from *Jurgaičiai* has been sintered once, but at a very high temperature.

3.2.4 Infrared spectroscopy

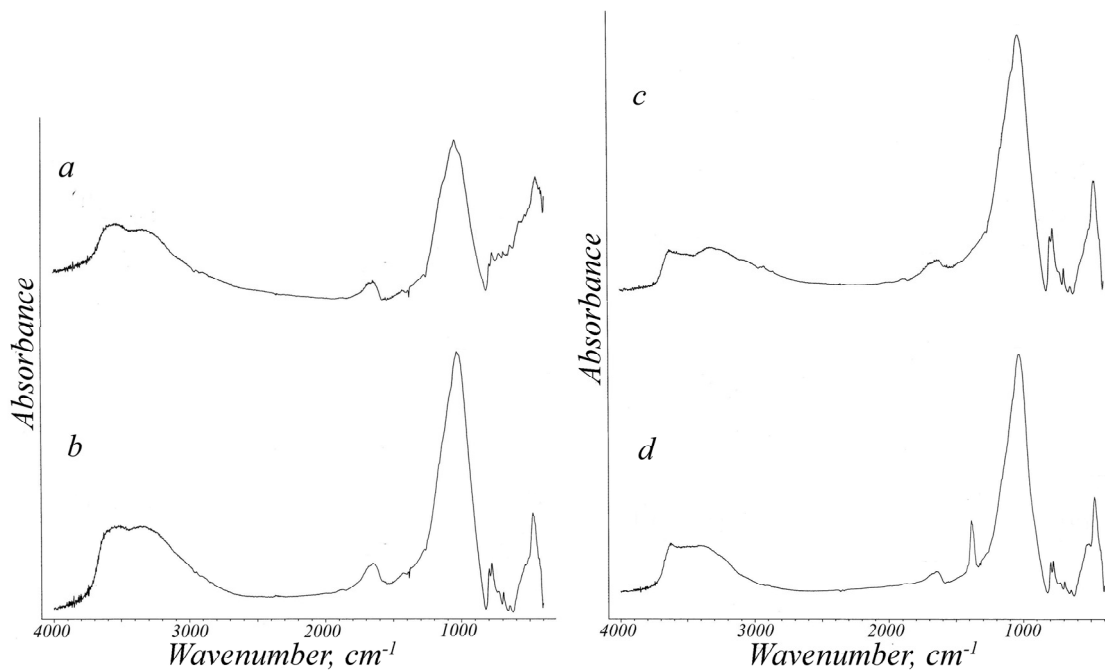


Fig. 24. IR spectra of the ceramic samples from *Stanaičiai*: (a) rough, (b) flat, (c) *Žvainiai*, (d) *Turlojiškės*

As can be seen in Fig. 24, the IR spectra of the rough (a) and flat (b) ceramics from *Stanaičiai*, (c) ceramics from *Turlojiškės* and (d) ceramics from *Žvainiai* are similar. In both IR spectra, intensive peaks at 3700–3100 cm^{-1} and at around 1640 cm^{-1} , corresponding to O-H vibrations (absorbed water and OH groupings in muscovite), were obtained. Si-O vibrations were detected within the range of 1100 to 419 cm^{-1} – they correspond to quartz and other silicates (muscovite, microcline, titanite, anorthite). In the spectrum of *Žvainiai* (Fig. 24 , c), S-O vibrations at 1105 cm^{-1} were additionally identified, which correspond to the calcium hydrogen sulphate phase. In the spectrum of

Turlojiškės ceramic (Fig. 24, d), the absorption band 1420 cm^{-1} is clearly visible, which is assigned to C-O vibrations and corresponds to the calcite phase.

The IR spectra obtained examining the ceramics from *Jurgaičiai* and *Nikėlai* (Fig. 25 (a) and (b) respectively) are almost identical. The absorption bands at $3600\text{--}3000\text{ cm}^{-1}$ and 1630 cm^{-1} visible in both spectra are assigned to water, muscovite and amphibolite. The presence of quartz is proved by the distinct absorption bands in the spectrum at $1100\text{--}1000\text{ cm}^{-1}$, 797 and 778 . The bands within the range $400\text{--}1200\text{ cm}^{-1}$ could be assigned to other silicates (albite, microcline, muscovite). Thus, based on the results obtained, we can claim that infrared absorption analysis can be used for the qualitative analysis of ancient ceramic.

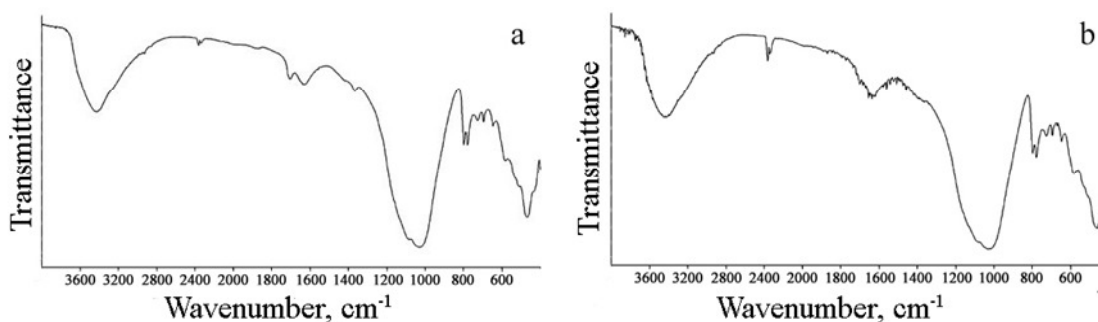


Fig. 25. IR spectra of the ceramic samples from (a) *Jurgaičiai*; (b) *Nikėlai*

3.2.5 The use of thermal analysis for the characterization of ceramics

For the characterization of archaeological ceramics from *Stanaičiai*, *Turlojiškės* and *Žvainiai*, thermogravimetric analysis was employed. As can be seen in Fig. 26, in all TG curves loss of mass at up to 120°C is observed (0.6% – 1.3%). This could be explained by elimination of humidity and/or desorption of crystallized water. Heating further up to 1000°C , loss of mass is no longer observed in the ceramic samples from *Stanaičiai* and *Žvainiai* (Fig. 26 a, b and d). This reports that the samples are stable in thermal terms. In the ceramics from *Turlojiškės* (Fig. 26, c), however, loss of mass ($\sim 0.45\%$) is additionally observed when heating at 665°C to 840°C . This is related to the calcite phase and its decarbonisation.

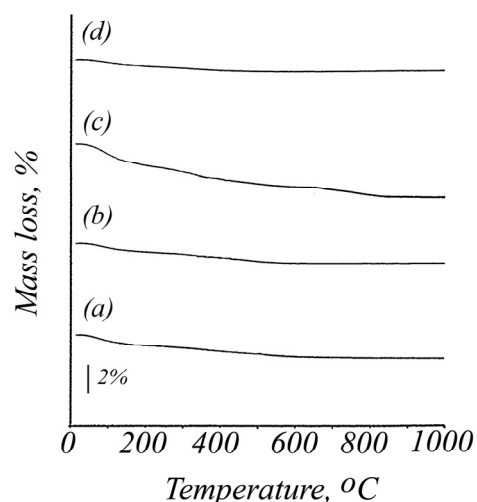
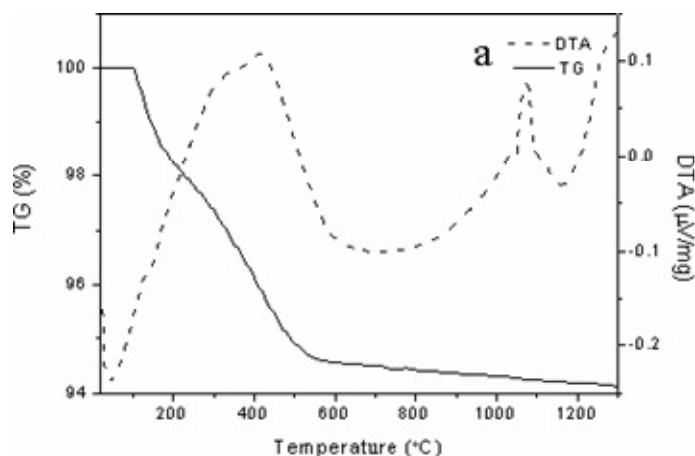


Fig. 26. TG curves of the ceramic samples from *Stanaičiai*: (a) flat, (b) rough, (c) *Turlojiškės* and (d) *Žvainiai*

As can be seen in Fig. 27, the TG and DTA curves of both the ceramics from *Nikėlai* and *Jurgaičiai* are shaped almost identically. In the ceramics from *Nikėlai*, major loss of mass is observed at 110–515°C and in that from *Jurgaičiai* (-7.8%) – at 95–515°C. This shape of the curves enables interpreting that these archaeological ceramics have been sintered at sufficiently high temperature, and their chemical and phase composition and manufacturing conditions are similar, although the samples have been discovered in different archaeological complexes.



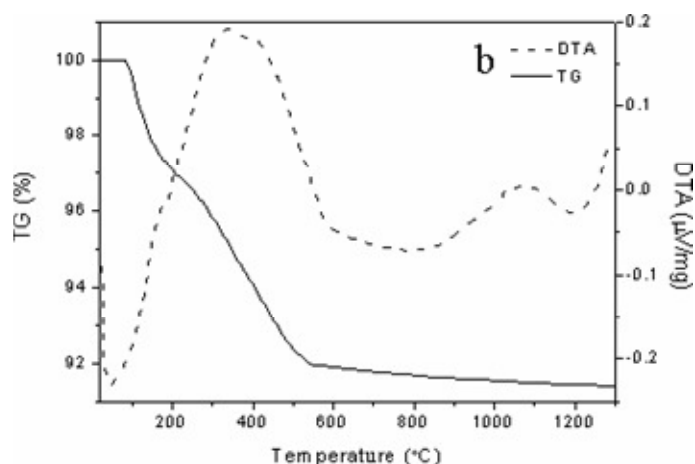


Fig. 27. TG/DTA curves of the ceramic samples from (a) *Nikėlai* and (b) *Jurgaičiai*

CONCLUSIONS

1. The elemental composition of the samples of modern and archaeological ceramics was determined using the energy dispersive X-ray analysis, flame atomic absorption spectrometry, titrimetric and spectrophotometric analysis methods. It has been shown that the qualitative and quantitative composition of all the samples is different. It has been established that silicon and aluminium are the main elements in all the samples. SiO_2 accounts for 46–60 % of the composition of the ceramics, Al_2O_3 – for some 17–33%. The amounts of Fe, Na, Mg, K, Ca and Ti discovered in the samples are several times lesser. EDX analysis can successfully be used in determining the main elements whose amounts exceed 0.5% of the overall elemental composition. In order to determine the exact composition of ceramics one has to employ the FAAS analysis method. To determine in a credible manner the amount of aluminium in ceramics, one can use the titrimetric method, and the amount of silicon and titanium – spectrophotometric methods.
2. Upon examination of the modern and archaeological ceramics by diffraction analysis it has been established that the main phase of all the samples is the same – quartz SiO_2 , however their phase composition varies. In different samples the following phases have been discovered: calcite, dolomite, kaolinite, albite, microcline, muscovite, mullite, hematite, rutile, diopside, corundum, titanite, and sodium anorthite. Being aware of the phase composition, it has been established that the

samples of modern ceramics were fired at the temperatures of 600–1300° C, and the archaeological pottery – at the temperature of up to 1000° C.

3. The scanning electron microscope provides a possibility to examine the morphological features of ceramic items. Being aware of the shape and morphology of ceramic items it is possible to determine their manufacturing conditions. From the photographs made by a scanning electron microscope it can be seen that the samples of modern ceramics are characterised by different morphology – the size of their particles and pores, shapes and distribution are different. The surface features, chemical and phase composition of the archaeological pottery discovered in different locations are different too: this is related with the technological manufacturing features of the pottery.
4. FTIR analysis can facilitate interpretation of the results obtained by XRD and TG. In IR spectra, intensive peaks are observed at 3700–3000 and 1635 cm^{-1} , corresponding to the O-H vibrations (adsorbed water). The Si–O vibrations observed at 1200–1000, 797 and 778 cm^{-1} are assigned to SiO_2 . Employing FTIR analysis, other silicates and carbonates, earlier determined by XDR analysis, have also been identified. Infrared ray spectroscopy, jointly with X-ray diffraction analysis, can be successfully used for the qualitative analysis of ancient pottery.
5. The modern and archaeological ceramics has been examined using the methods of thermogravimetric and differential thermal analysis. It has been established that the nature of the TG–DTA results of modern ceramics depends on its composition and manufacturing conditions. Using the data of the thermal analysis it has been established that the ceramics, excavated in different archaeological complexes, was manufactured at different firing temperatures. The obtained results of the thermal analysis are in good agreement with the XRD and FTIR results, and are a valuable method of examination and description of ceramic findings.

The List of Original Publications by the Author

Articles in journals

1. **A. Krapukaityte**, I. Pakutinskiene, S. Tautkus, A. Kareiva. SEM and EDX characterization of ancient pottery. Lithuanian journal of physics. **46** (2006) 383-388.
2. **A. Krapukaityte**, S. Tautkus, A. Kareiva, E. Zalieckiene. Thermal analysis – a powerful tool for the characterization of pottery. Chemija. **19** (2008) 4-8.
3. **A. Krapukaityte**, J. Senvaitiene, A. Merkevicus, S. Tautkus, A. Kareiva. Characterization of the Bronze Age pottery from different archaeological complexes of Lithuania. Chemine Technologija. **49** (2008) 11-18.

Published contributions to academic conferences

1. **A. Krapukaitytė**, I. Pakutinskiene, S. Tautkus. Investigation of ancient pottery by SEM (EDS) and FAAS methods. Konferencija „Chemija ir cheminė technologija“. Kaunas, (2006) 57-58.
2. **A. Krapukaitytė**, I. Pakutinskiene. Senovinės keramikos tyrimai XRD metodu. Vilniaus universiteto jaunųjų chemikų konferencija „Neorganiniai junginiai: sintezė, savybės ir panaudojimas“. Varėnos raj., Burokaraistėlės km., (2006) 11.
3. **A. Krapukaitytė**, S. Tautkus. Senovinės keramikos tyrimai XRD, FTIR ir TG metodais. Konferencija „Chemija ir cheminė technologija“. Kaunas, (2007) 97-98.

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SANTRAUKA

Šioje daktaro disertacijoje pirmoje dalyje nustatyta šiuolaikinės, o antroje dalyje – archeologinės keramikos gaminių elementinė ir fazinė sudėtis, bei ištirta morfologija. Šiuolaikinės ir archeologinės keramikos pavyzdžių elementinė sudėtis nustatyta Rentgeno spindulių dispersinės analizės (EDX), liepsnos atominės absorbcinės spektrometrijos (LAAS), titrimetrinės ir spektrofotometrinės analizės metodais. Parodyta, kad visų keraminių pavyzdžių kokybinė bei kiekybinė sudėtis yra skirtinga. Nustatyta, kad visuose keramikos mėginiuose pagrindiniai elementai yra silicis ir aliuminis. SiO₂ sudaro 46 – 60% keramikos sudėties, Al₂O₃ – apie 17 – 33%. Fe, Na, Mg, K, Ca ir Ti mėginiuose rasta kelis kartus mažiau. EDX analizė gali būti sėkmingai naudojama nustatant pagrindinius elementus, kurių kiekiai viršija 0,5 % bendros elementinės sudėties. Norint nustatyti tikslią keramikos sudėtį ir pėdsakinius elementus reikia naudoti LAAS analizės metodą. Aliuminio kiekį keramikoje patikimai galima nustatyti titrimetriškai, o silicio ir titano kiekį – spektrofotometriniais metodais.

Ištirus šiuolaikę ir archeologinę keramiką Rentgeno spindulių difrakcine analize (XRD), nustatyta, kad visų keramikų pagrindinė fazė yra vienoda – silicio dioksidas SiO₂, tačiau jų bendra fazinė sudėtis skiriasi. Skirtinguose keramikos pavyzdžiuose buvo aptikos šios fazės: kvarcas, dolomitas, kaolinas, albitas, mikroklinas, muskovitas, mulitas, hematitas, rutilas, diopsidas, korundas, titanitas, natrio anortitas. Žinant fazinę sudėtį, nustatyta, kad šiuolaikinės keramikos pavyzdžiai degti 600 – 1300°C temperatūroje, o archeologinė keramika – iki 1000°C.

Skenuojantis elektroninis mikroskopas (SEM) suteikia galimybę ištirti keramikos gaminių morfologinius ypatumus. Žinant keramikos formą ir morfologiją galima nustatyti keramikos gamybos sąlygas. Iš nuotraukų, gautų skenuojančiu elektroniniu mikroskopu, matyti, kad šiuolaikinės keramikos pavyzdžiai pasižymi skirtinga morfologija – skiriasi keramikos dalelių ir porų dydis, forma bei pasiskirstymas. Archeologinės keramikos, rastos skirtingose vietovėse, paviršiaus ypatumai, cheminė bei fazinė sudėtis taip pat skirtinga – tai susiję su keraminių dirbinių gamybos technologiniais ypatumais.

XRD ir TG gautų rezultatų interpretavimą palengvina Furjė infraraudonųjų spindulių spektroskopinė analizė (FTIR). Visuose šiuolaikinės ir archeologinės keramikos IR spektruose stebimos intensyvios smailės 3700 – 3000 ir 1635 cm^{-1} srityje, atitinkančios O–H jungties virpesius (adsorbuotas vanduo). 1200 – 1000, 797 ir 778 cm^{-1} srityje stebimi Si–O jungties virpesiai priskiriami SiO_2 . FTIR analize identifikuoti ir kiti silikatai, karbonatai, anksčiau nustatyti XRD analize. Infraraudonųjų spindulių spektroskopija kartu su Rentgeno spindulių difrakcine analize gali būti sėkmingai naudojama kokybinei senovinės keramikos analizei.

Šiuolaikinė ir archeologinė keramika iširta termogravimetrinės (TG) ir diferencinės terminės (DTA) analizių metodais. Nustatyta, kad šiuolaikinės keramikos TG–DTA rezultatų pobūdis priklauso nuo keramikos sudėties bei gamybos sąlygų. Naudojant terminės analizės duomenis, nustatyta, kad keramika, iškasta iš skirtingų archeologinių vietovių, buvo gaminama naudojant skirtingas degimo temperatūras. Gauti terminės analizės rezultatai gerai derinasi tarpusavyje su XRD ir FTIR rezultatais ir yra vertingas archeologinių keraminių radinių tyrimo bei apibūdinimo metodas.