Thermal analysis – a powerful tool for the characterization of pottery

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Eight contemporary pottery samples were investigated by thermal analysis (TG-DTA) in order to define the effects of fabrication. The results of the measurements were shown to depend on firing conditions. In this article, the results of thermoanalytical characterization of two archaeological pottery samples from different regions of Lithuania are also presented. The samples of ancient pottery from Nikėlai and Jurgaičiai villages were investigated. The TG-DTA results for the historical pottery samples from different districts of Lithuania showed an analogous thermal behaviour, possibly due to similar fabrication conditions.

Key words: pottery, archaeological findings, thermal analysis, thermoanalytical characterization

INTRODUCTION

Pottery is the most numerous group of Bronze Age finds. Pottery analysis reveals important information about the daily life and the ethnical and cultural aspects of the society of the period. Therefore pottery studies are crucial for the reconstruction of the lifestyle of society during a period under consideration. It is well known that physical-chemical characterization of pottery used in ancient times provides historical and technological information as regards their manufacture [1–3]. Moreover, 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 [4–7]. A careful characterization of ancient pottery is a very important task not only for archaeologists, but also for people working in the field of conservation chemistry [10–12].

It is well known that thermal analysis (TG-DTA) is a very important characterization method used for the control of the reaction process and of the properties of the materials obtained. In this context, thermal analysis is a versatile group of techniques which can be used to aid preparatory studies [13–19]. The kinetics of solid decomposition reactions of various metal carbonates during calcination of different multimetallic precursors could be successfully investigated by thermogravimetric (TG) measurements [20, 21]. TG coupled with FTIR provides very important information about the decomposition products and the evolved gases. As an example of such study, a detailed investigation of the decomposition of oxalate precursors and the stability of the $YBa_2Cu_4O_8$ superconductor was reported by Mullens et al. [22]. Thermogravimetric experiments are very useful in solving the nonstoichiometry problem, which is a central one in solid state chemistry. Several oxygen-deficient ternary cuprates having different superconducting properties have been determined during TG study of the nonstoichiometric regions in the Y–Ba–Cu–O system [23]. Moreover, selected applications of various thermoanalytical techniques from medicine to construction have also been discussed by Mojumdar et al. [24].

However, until now only few thermoanalytical investigations of ancient ceramics have been published [25–28]. Therefore, in the present study attention has been focused on the characterization of different contemporary pottery samples by thermal (TG-DTA) analysis. The results of the measurements were used for the estimation of the firing temperature of two ancient pottery samples collected in archaeological complexes (Nikėlai and Jurgaičiai) located in different regions of Lithuania.

EXPERIMENTAL

Eight differently fabricated contemporary pottery samples were selected for the characterization: black pottery (sample I), fired at a high temperature, a fragment of pot (sample II) fired at high

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temperature glazed ceramics, containing CuO (sample III), ceramics with green glaze, manufacturing conditions unknown (sample IV), glazed ceramics, manufacturing conditions unknown (sample V), white ceramics fired at low temperature (sample VI), fired at low temperature glazed ceramics containing CuO (sample VII), and nonglazed ceramics fired at a high temperature (sample VIII). Besides, Bronze Age pottery samples found in the Lithuanian villages Nikėlai and Jurgaičiai were chosen for characterization.

In this study, the pottery samples were investigated by TG-DTA measurements in air atmosphere using Setaram TG-DSC12 and STA 490 analyzers. The mass of specimens was 29.65–32.47 mg. Thermogravimetric measurements were carried out in a temperature range of 25–1300 °C at a heating rate of 20 °C min⁻¹.

RESULTS AND DISCUSSION

Data on the thermal decomposition of eight differently fabricated contemporary pottery samples are summarized in Table. According to the specific features observed in the TG curves, the contemporary pottery samples can be roughly classified into several categories. However, such classification of pottery is fairly speculative. Pottery samples I and VIII show a very similar thermal behaviour (Fig. 1). As is seen from Fig. 1, no mass loss was observed between room temperature and 300–400 °C. Such thermal behaviour is characteristic of ceramics sintered in one time at a high temperature [29]. With the further increase of temperature, an abrupt one-step mass loss is seen in the TG curve of sample VIII. However, the TG curve of sample I shows a broad two-step weight loss between 385 °C and 780 °C. From this we may conclude that the phase composition of black pottery and nonglazed ceramics fired at a high temperature ceramic is quite different. This conclusion is also supported by different exothermic and endothermic peaks observed on the DTA curves.

Figure 2 shows the TG-DTA curves of pottery samples II and VI. One can see that the thermogravimetric curves of these two specimens are also very similar. The distinguishing feature is a rather low temperature of the beginning of mass loss. The main thermal decomposition for sample II starts at around 200 °C and for sample VI even at a lower temperature (105 °C). The most intensive decomposition of sample II proceeds continuously up to 510 °C. With the further increase of temperature, a negligible
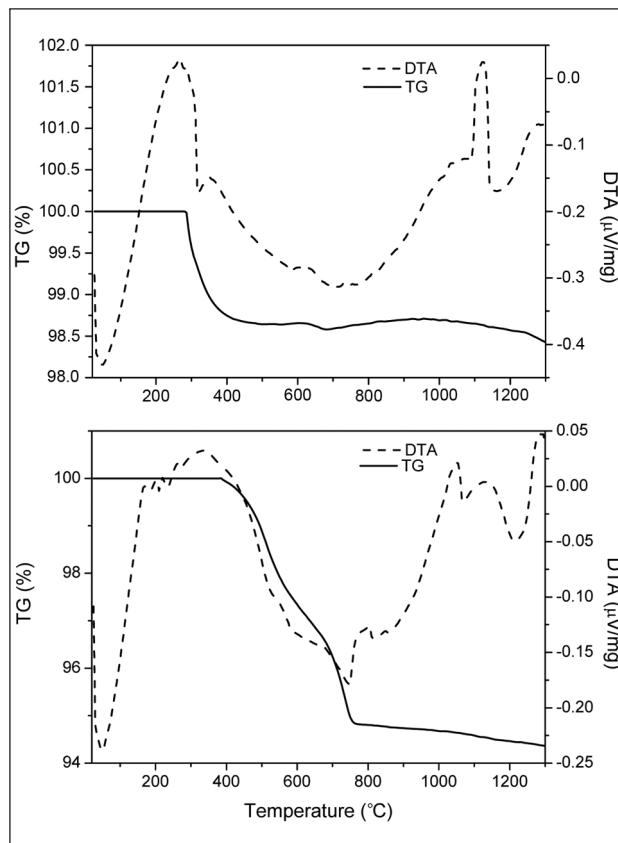

Fig. 1. TG-DTA curves recorded for pottery samples I (at bottom) and VIII (at top)
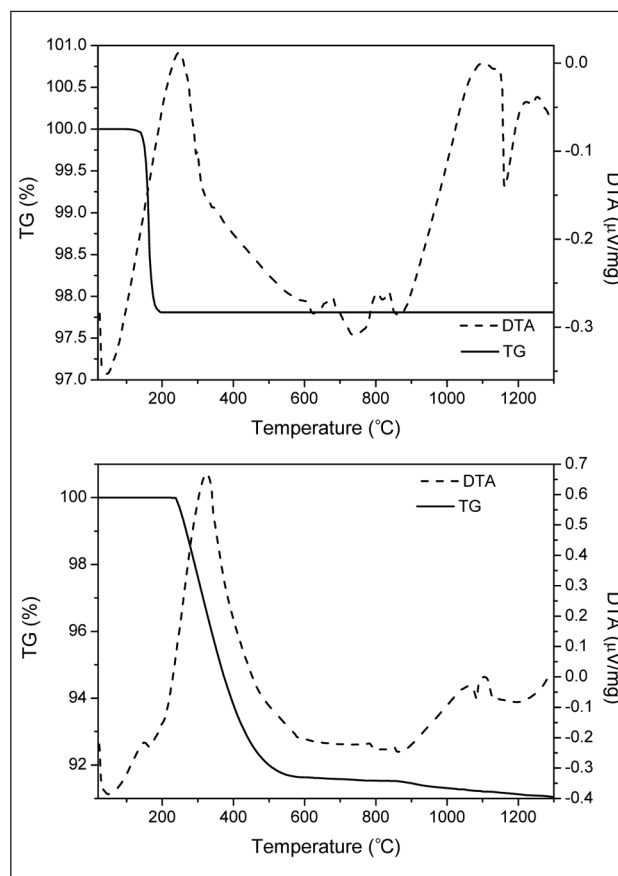
Fig. 2. TG-DTA curves recorded for pottery samples II (at bottom) and VI (at top)

Table. **TG data on differently fabricated contemporary and ancient archaeological pottery samples**

Sample	Main weight change	Total weight changes at 1300 °C
I	(385–780 °C), –5.2%	–5.7%
II	(230–510 °C), –8.1%	–9.0%
III	(175–350 °C), +0.8%	+1.1%
IV	(25–800 °C), +1.8%	+0.9%
V	(25–780 °C), +1.9%	+1.6%
VI	(105–200 °C), –2.2%	–2.2%
VII	(215–400 °C), +0.6%	–1.2%
VIII	(285–420 °C), –1.3%	–1.6%
Nikėlai	(110–515 °C), –5.2%	–5.9%
Jurgaičiai	(95–515 °C), –7.8%	–8.6%

weight loss could be observed even at up to 1300 °C. However, for sample VI a sharp weight loss was observed in a very narrow temperature range of 105–200 °C. With further increasing the temperature up to 1300 °C the weight remains stable. The difference in the total mass loss for these two samples is also evident. Apparently, in sample II there are more components that undergo thermal decomposition than in sample VI. Therefore, the phase composition of ceramics fired at a high temperature (sample II) and white ceramics fired at a low temperature (sample VI) is quite different. The most intensive decomposition of these two samples is associated with well pronounced exothermic peaks on the DTA curves. A sharp endotherm at ~1150 °C is clearly seen on the DTA curve of sample VI. However, this peak is not associated with mass changes on the TG curve. Thus, we can predict that sample VI contains crystalline or amorphous phase which undergoes polymorphic transformation.

The TG-DTA curves for the glazed ceramic samples (III and VII) containing CuO are presented in Fig. 3. Contrary to previous samples, the mass gain of 0.6–0.8% starting from 180–210 °C could be observed on the TG curves of samples III and VII. It is well known that heating Cu_2O in air or oxygen atmosphere the following reaction occurs [16, 17]:

$$Cu_2O + \tfrac{1}{2}\,O_2 = 2\,CuO. \qquad (1)$$

Moreover, a partial oxidation of Cu^{2+} to Cu^{3+} in solid state could also proceed [30]:
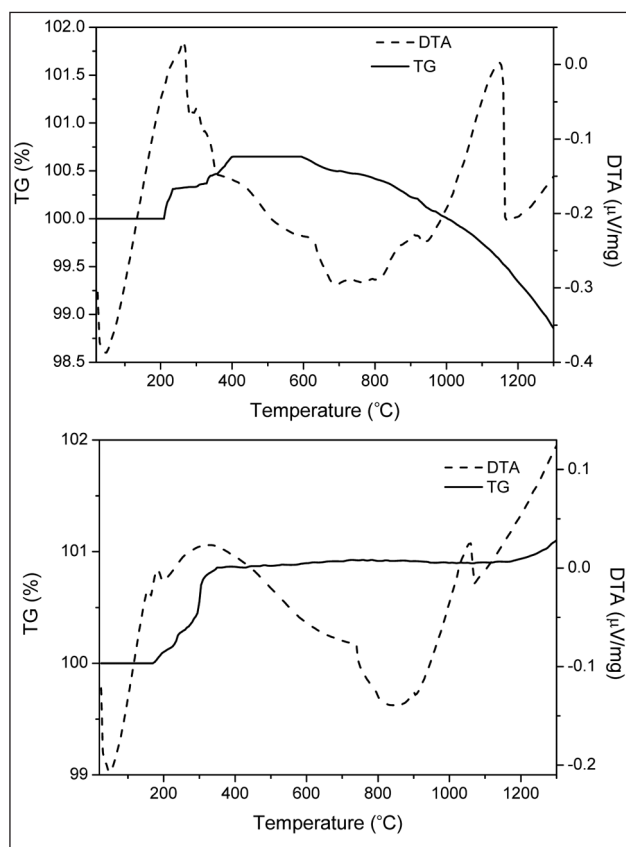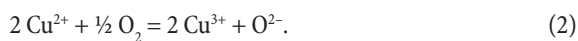
$$2\,Cu^{2+} + \tfrac{1}{2}\,O_2 = 2\,Cu^{3+} + O^{2-}. \qquad (2)$$

These processes are responsible for the weight increase that could be observed in TG curves while performing thermogravimetric measurements. Therefore, we can conclude that part of copper in the ceramic samples (III and VII) containing CuO exists in the Cu(I) oxidation state. With the further increase of temperature, the TG curve recorded for sample III remains almost steady. This is not surprising since this glazed ceramic sample is fired at a high temperature. On the contrary, with further heating the sample VII which was fired at a low temperature, a continuous mass loss up to 1300 °C is seen on the TG curve. Both DTA curves show the exothermic effect in the high temperature region (1050–1100 °C) which could be associated with a similar polymorphic changing presented in both ceramic samples.

Figure 4 shows TG-DTA curves recorded for pottery samples IV and V. Surprisingly, in both cases an abrupt increase in weight starts immediately at room temperature and lasts up to 200 °C. To our knowledge, such thermoanalytical behaviour of pottery samples has never been observed previously. Therefore, the explanation of the obtained TG curves could be possible only after additional X-ray diffraction measurements.

As was mentioned, the Bronze Age pottery samples found in Lithuanian villages Nikėlai and Jurgaičiai were also characterized by the TG-DTA method. The results of TG measurements of ancient archaeological samples are also listed in Table. The TG-DTA curves recorded for pottery samples excavated in the archaeological complexes Nikėlai and Jurgaičiai are shown in Fig. 5. As is seen, both TG and DTA curves recorded for two different specimens show a very similar behaviour. This observa-
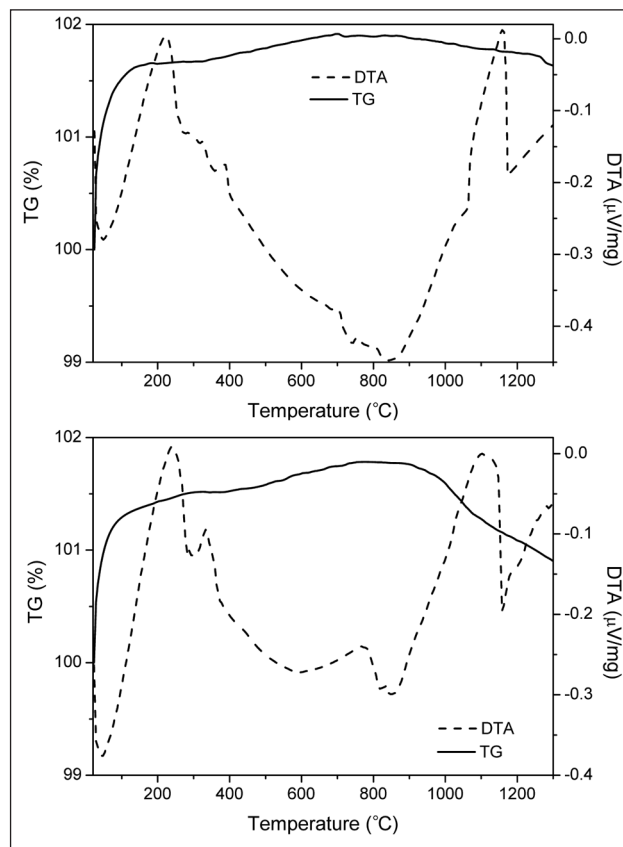

Fig. 3. TG-DTA curves recorded for pottery samples III (at bottom) and VII (at top)

Fig. 4. TG-DTA curves recorded for pottery samples IV (at bottom) and V (at top)
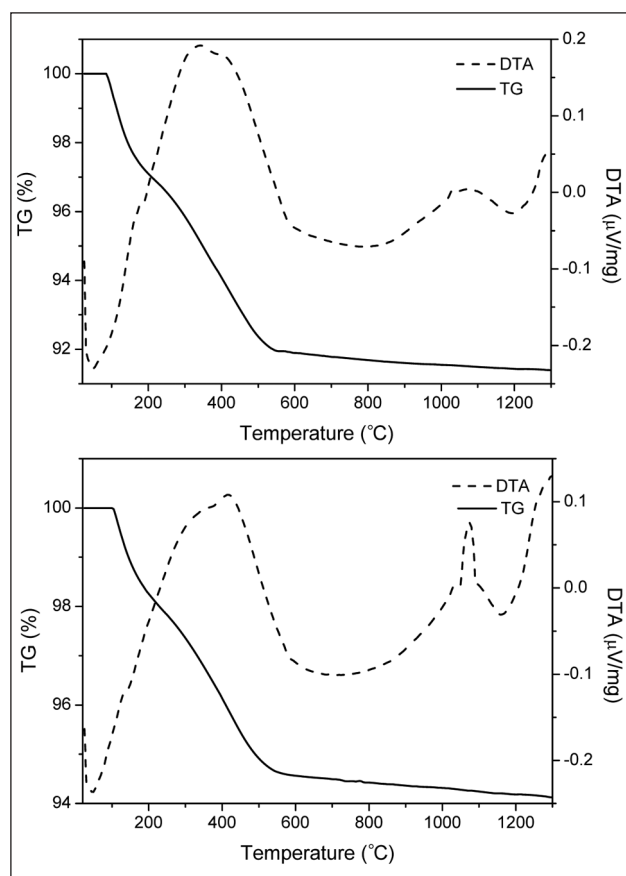
Fig. 5. TG-DTA curves of archaeological pottery samples from villages Nikėlai (at bottom) and Jurgaičiai (at top)

tion allows us to conclude that the chemical and phase composition, as well as the history of manufacture of these two Bronze Age pottery samples found in different archaeological complexes are also very similar. Moreover, the character of TG-DTA curves of ancient samples is very close to that of sample II (see Fig. 2, bottom). This allows us to conclude that the archaeological pottery was fired at relatively high temperatures [29]. The main conclusion that can be derived from the results of TG-DTA measurements is the possibility to predict the manufacturing conditions of ancient pottery. Such an approach originated from the characterization of the contemporary manufacturing of ceramics.

CONCLUSIONS

Eight contemporary pottery samples were investigated by thermal analysis (TG-DTA). The results of the measurements were shown to depend on firing conditions. TG-DTA analysis has clearly shown that the pottery samples are composed by different phases. Ancient ceramic findings from two different archaeological complexes of Lithuania (Nikėlai and Jurgaičiai villages) have been also studied by TG-DTA analysis. The results allow to conclude that the chemical and phase composition, as well as the manufacturing history of these to Bronze Age pottery samples found in different archaeological complexes are very similar. Besides, both archaeological pottery samples were fired at relatively high temperatures. The results

have demonstrated that TG-DTA analysis is an indispensable tool in discovering some special technological features of ancient pottery.

References

1. G. Biscontin, M. P. Birelli and E. Zendri, *J. Cultur. Herit.* **3**, 31 (2002).
2. G. E. De Benedetto, R. Laviano, L. Sabbatini and P. G. Zambonin, *J. Cultur. Herit.* **3**, 177 (2002).
3. G. Eramo, R. Laviano, I. M. Muntoni and G. Volpe, *J. Cultur. Herit.,* **5**, 157 (2004).
4. E. P. Bescher, F. Pique, F. Stulik and J. D. Mackenzie, *J. Sol-Gel Sci. Technol.* **19**, 215 (2000).
5. R. A. Caruso and M. Antonietti, *Chem. Mater.* **13**, 3272 (2001).
6. L. Nasdala, A. Banerjee, T. Hager and W. Hofmeister, *Eur. Microsc. Anal.* **3**, 11 (2001).
7. J. Perez-Arantegui, A. Larrea, J. Molera, T. Pradell and M. Vendrell-Saz, *Appl. Phys. A-Mater. Sci. Process.* **79**, 235 (2004).
8. A. Bakolas, G. Biscontin, V. Contardi, E. Franceschi, A. Moropoulou, D. Palazzi and E. Zendri, *Thermochim. Acta* **269/270**, 817 (1995).
9. F. E. Wagner and U. Wagner, *Hyperf. Interact.* **154**, 35 (2004).
10. P. M. Rice, *Pottery Analysis – A Sourcebook,* The University of Chicago Press, Chicago, 1987.
11. J. Kiuberis, A. Merkevicius, R. Juskenas and A. Kareiva, *Materials Science (Medžiagotyra)* **10**, 334 (2004).
12. M. Klein, F. Jesse, H. U. Kasper and A. Golden, *Archaeometry* **46**, 339 (2004).
13. 13. C. C. Landry, N. Pappe, M. R. Mason, A. W. Apblett, A. N. Tyler, A. N. MacInnes and A. R. Barron, *J. Mater. Chem.* **5**, 331 (1995).
14. J. Madarasz, T. Leskelä, J. Rautanen and L. Niinistö, *J. Mater. Chem.* **6**, 781 (1996).
15. J. Madarasz, T. Leskelä, G. Pokol and L. Niinistö, *J. Therm. Anal.* **49**, 1347 (1997).
16. A. Kareiva, *Thermochim. Acta* **298**, 155 (1997).
17. S. Tautkus, R. Kazlauskas and A. Kareiva, *Talanta* **52**, 189 (2000).
18. G. Nenartaviciene, K. Tonsuaadu, D. Jasaitis, A. Beganskiene and A. Kareiva, *J. Therm. Anal. Calorim.* **90**, 173 (2007).
19. R. M. Rojas, K. Petrov, G. Avdeev, J. M. Amarilla, L. Pascual and J. M. Rojo, *J. Therm. Anal. Calorim.* **90**, 67 (2007).
20. J. Mu and D. D. Perlmutter, *Thermochim. Acta* **49**, 207 (1981).
21. F. J. Gotor, N. Pellerin, P. Odier, E. Cazy, J. P. Bonnet, A. R. Fert and J. Ayache, *Physica C* **247**, 252 (1995).
22. J. Mullens, A. Vos, A. De Backer, D. Franco, J. Yperman and L. C. Van Poucke, *J. Therm. Anal.* **40**, 303 (1993).
23. J. Przyluski, K. Kolbrecka and K. Borowiec, *J. Therm. Anal.* **38**, 2067 (1992).

24. S. C. Mojumdar, M. Sain, R. C. Prasad, L. Sun and J. E. S. Venart, *J. Therm. Anal. Calorim.* **90**, 653 (2007).

25. L. Campanella, G. Favero, P. Flamini and M. Tomassetti, *J. Therm. Anal. Calorim.* **73**, 127 (2003).

26. S. Shoval and P. Beck, *J. Therm. Anal. Calorim.* **82**, 609 (2005).

27. D. N. Papadopoulou, M. Lalia-Kantouri, N. Kantiranis and J. A. Stratis, *J. Therm. Anal. Calorim.* **84**, 39 (2006).

28. V. A. Drebushchak, L. N. Mylnikova and V. I. Molodin, *J. Therm. Anal. Calorim.* **90**, 73 (2007).

29. P. Colomban, D. N. Khoi, N. Q. Liem, C. Roche and G. Sagon, *J. Cult. Heritage* **5**, 149 (2004).

30. A. Kareiva, J. Barkauskas and S. Mathur, *J. Phys. Chem. Solids* **61**, 789 (2000).

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TERMINĖ ANALIZĖ – VERTINGAS KERAMIKOS APIBŪDINIMO METODAS

S a n t r a u k a

Šiame darbe termogravimetrinės (TG) ir diferencinės terminės (DTA) analizių metodais ištirti aštuoni šiuolaikinės keramikos pavyzdžiai. Nustatyta, kad TG-DTA rezultatų pobūdis priklauso nuo keramikos sudėties bei gamybos sąlygų. TG-DTA metodais ištirti ir archeologinės keramikos pavyzdžiai, iškasti Nikėlų ir Jurgaičių archeologinėse radimvietėse. TG-DTA tyrimai parodė, kad archeologinės keramikos pavyzdžiai, rasti skirtingose Lietuvos vietose, pasižymi panašiu masės netekties priklausomybės nuo temperatūros pobūdžiu. Tai leido padaryti išvadą, kad abiejų archeologinės keramikos pavyzdžių cheminė ir fazinė sudėtis yra artima. Be to, lyginant gautus rezultatus su šiuolaikinės keramikos termogramomis, galima teigti, jog abi keramikos gamybos metu buvo degtos gana aukštoje temperatūroje. Padaryta išvada, kad terminė analizė yra itin vertingas archeologinių keraminių radinių tyrimo bei apibūdinimo metodas.