J Therm Anal Calorim (2010) 102:393–398
DOI 10.1007/s10973-009-0226-x

Thermal analysis of Romanian ancient ceramics

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Received: 20 May 2009 / Accepted: 16 June 2009 / Published online: 9 July 2009

Abstract The present work is focused on thermoanalytical investigations as thermogravimetric analysis (TG) and derivative thermal analysis (DTG), applied for the characterization of some samples collected from archaeological sites (Brasov and Trofeum Traiani) located in different regions of Romania. New informations derived about ceramic technologies concerning raw materials and binding materials (mineralogical components) have been obtained. All these experimental results have been correlated with related techniques as X-ray diffraction (XRD), energy-dispersive X-ray fluorescence (EDXRF) and inductively coupled plasma—atomic emission spectrometry (ICP-AES). By progressive heating in static air atmosphere and in the temperature range of 20–800 °C, all investigated materials exhibit three main successive processes, associated with the dehydration and thermo-oxidative degradations. The rate of the first thermooxidative process, temperatures corresponding to the maximum rate of the second thermooxidative process and shrinkage temperature were associated with the damage of the investigated materials due to environmental impact. Heating also affects the contact between the fine-sized clay matrix and mineral clast fragments, appearing in reaction rims, sometimes showing newly formed phases. The temperature at which ancient ceramics and pottery were fired varies over a wide range (600–800 °C) depending on the type of clay used, although firing temperatures not above 30–400 °C have also been suggested. Clay minerals, as the main material for production of ceramics and pottery, show some characteristic reactions (dehydroxylation, decomposition, transformation) in the course of firing (heating effects) and several thermoanalytical criteria can be used for reconstruction of former production conditions.

Keywords Cultural heritage · TG · DTG · XRD · EDXRF · ICP-AES

Introduction

Pottery is the most numerous group of Bronze Age artifacts. For pottery characterization, it is an enormous advantage to know from where this artifact or its raw material has come. It is well known that physical–chemical characterization of pottery used in ancient times provides historical and technological information as regards their manufacture [1, 2]. Provenance studies of pottery analysis are based on patterns of elements, which vary in geological materials as a result of their different histories, all these revealing important information about the daily life and the ethnical and cultural aspects of the society of the period. Moreover, the knowledge of chemical and mineralogical compositions could be as “fingerprints” of the stable and also the metastable solid phases formed during firing [3, 4].

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Many analytical methods have been applied by historians and restorers to solve complicated problems of chemical composition and classification of artefacts and museal pieces. Among these techniques, we decided in this paper to use thermogravimetric analysis (TG) and derivative thermal analysis (DTG), coupled with EDXRF (energy dispersive X-ray fluorescence) and ICP-AES (inductively coupled plasma atomic emission spectrometry), which offered to us the privilege to determine a high number of elements and to learn many things about the chemical composition and morphological structure [5]. EDXRF results from medieval ceramics are examined and the derived informations on ceramic technologies, concerning raw materials and production conditions are validated by ICP-AES observations, with regard to the extent of vitrification, as well as by the compositional data provided by mineral measurements. Also, X-ray diffraction (XRD) was used to determine the oxidic components present in such artefacts.

Clay minerals, as the main material for production of ceramics and pottery, show some characteristic reactions (dehydroxylation, decomposition, transformation) in the course of firing (heating effects—20–800 °C) and several thermoanalytical criteria can be used for reconstruction of former production conditions, knowing that the temperature at which ancient ceramics and pottery were fired varies over a wide range (600–800 °C) depending on the type of clay used.

It is well known that TG and DTG, is a very important characterization method used for the control of the reaction process and of the properties of the materials obtained [6–8].

The results of the measurements were used for the estimation of the firing temperature of some pieces from ancient pottery samples collected in archaeological complexes (Brasov and Trofeum Traiani) located in different regions of Romania.

Experimental data

Methods and apparatus

The samples were examined by a TG (Du PontTGA) thermobalance connected to a PC running Du Pont data processing software. About 15 mg of gently ground stones are subjected to analysis in a Pt crucible in a temperature range 35–1,000 °C (10 °C min^{-1}).

X-ray fluorescence analysis was performed with an energy dispersive spectrometer, EDXRF PW4025, type Minipal-Panalytical, with a Si-PIN detector with a beryllium window having 255 eV resolution at 5.9 keV (Mn–Ka-line), cooled by thermo-electric means to about −18 °C. An air-cooled side window Rh-tube (maximum power 9 W, maximum voltage 30 kV, maximum current 1 mA) was used for excitation. The spectrum is accumulated in a 2048-channel analyzer. Due to varying surface structures and inhomogeneities in the surface composition of the artefacts, analysis was performed on both sides of the objects and a mean value was calculated.

A Varian Liberty 110 Series spectrometer was used for the ICP-AES analysis. For the ICP-AES measurements, sub samples were cut off from the original sherds and were finely powdered in an agate mortar. Multielement, matrix matched standards were used for the quantitative determinations.

Microwave assisted digestions were performed in a Berghof microwave oven with the use of high-pressure closed Teflon PFA vessels and online pressure and temperature control. In particular, 0.1 g of each sample was placed in the Teflon PFA digestion vessels and a mixture of 5 mL HF 40% and 5 mL HNO_3 67% was added.

The XRD patterns were recorded on a DRON 2 diffractometer using CoK_α and CuK_α radiation with an iron filter.

Sampling and experimental procedure

Sampling, reported in Table 1, was performed at the ruins of the Schneckenberg culture (sixteenth century), Dealul Melcilor, Brasov, Romania. It is interesting that in this region concervived many cultures (Vatina, Garla Mare, Luciu de Sus, Wietenberg and Otomani). All the ceramic samples contain as degreasing agent limestone shell. Ten differently fabricated contemporary pottery samples were selected for the characterization (Table 1).

Table 1 Pottery samples used for the study

No.	Sample	Observation
1	Ceramic	Black
2	Ceramic	Grey
3	Ceramic	Red
4	Ceramic	White
5	Ceramic	Green
6	Ceramic	Brown
7	Ceramic	Brasov
8	Ceramic	Teracota Brasov site
9	Ceramic pot	Brasov
10	Ceramic pot	Trofeum Traiani site

Results and discussion

Thermal analysis—a powerful tool for the characterization of pottery allows us to conclude that the chemical and

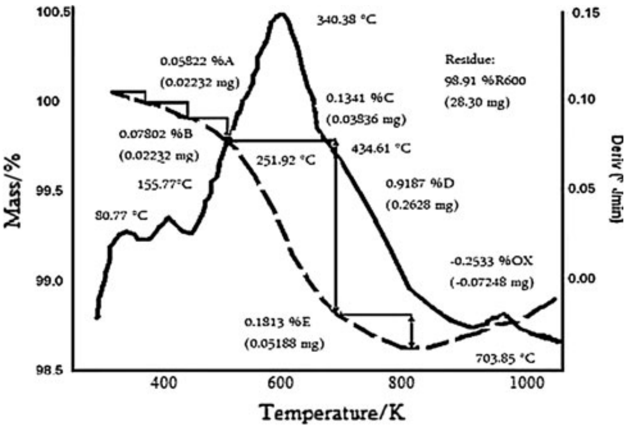

Fig. 1 DTG diagramm for the white ceramic sample

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. This allows us to conclude that the archaeological pottery was fired at relatively high temperatures [9, 10].

It is noted that the thermal behavior of such samples is coherent with their chemical and mineralogical composition. By analysing the samples, we could decide that the first six samples show quite similar thermal diagrams (Fig. 1).

Few weight loss events are seen in the TG and DTG curves [11]:

- The first one at 50–70 °C, related to the evolution of the physically adsorbed water by the particles;
- The second one at 300–400 °C, with a large exothermic peak around 325 °C due the organic matter decomposition was observed for all studied samples.
- The last one at 400–450 °C, whose total weight loss is in the 1–3% range. This peak could be responsible for Kaolinite whose dehydroxylation is seen at 400–450 °C where metakaolinite is generated. By loosing the hydroxyl groups, metakaolinite transforms into three phases—mullite, a transition alumina phase and silica [12].
- The most common clay minerals (kaolinite, illite, smectite) could be responsible for the strong endothermic effects within the range 550–650 °C (somewhat higher for chlorite) in the ceramic samples from Brasov not coloured, but glazed. These results confirm the predominance of the kaolinite clay mineral in the studied samples, and are consistent with XRD (Fig. 2).

Gypsum, if present, also shows endothermic effects within the range 120–160 °C. The TG curve of sample I shows a broad two-step weight loss between 300 °C and 780 °C. From this we may conclude that the phase composition of black pottery and not-glazed ceramics fired at a high temperature ceramic is quite different.

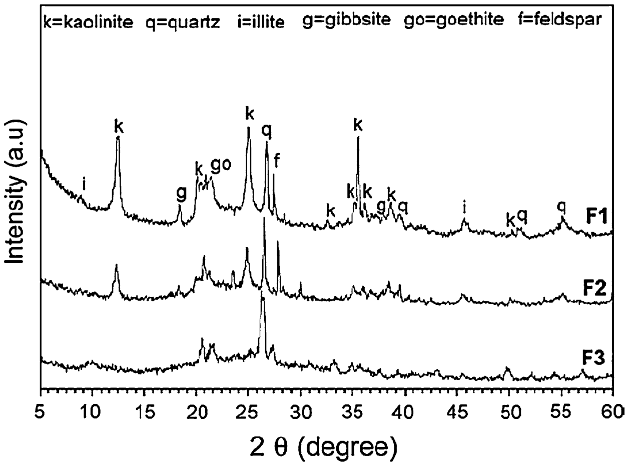

Fig. 2 XRD spectrum of different clay minerals

The presence of these characteristic thermic effects indicates that the primary minerals survived the firing processes required to destroy the structure of the minerals. On the other hand, several peaks may be due to secondary phases (as carbonates, gypsum, salts, etc.).

In the case of the last two samples, belonging to the Trofeum Traiani area, in both cases an abrupt increase in weight starts immediately at room temperature and last up to 200 °C. To our knowledge, such thermoanalytical behaviour of pottery samples has never been observed previously (Fig. 3).

The TG/DTG curves of salts are complex and their interpretation needs familiar experience with the technique, to be coupled with energy dispersive X-ray fluorescence (EDXRF).

An important factor is the carbonate content (Ca-rich or Ca-poor raw clays). Quartz, feldspars are mainly preserved in Ca-poor ceramics. The decomposition of calcite (in an oxidizing atmosphere) occurs at a lower temperature than for illite. As a consequence, there is free CaO until about 800 °C and it can react at higher temperature with clays and SiO_2, forming new silicate phases [13]. In a reducing atmosphere the breakdown of illite and calcite runs almost

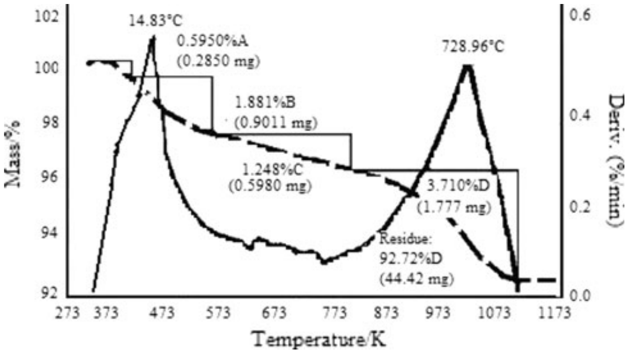

Fig. 3 The DTG diagramm of Trofeum Traiani ceramic sample

parallel, and due to increased CO_2, partial pressure, the dissociation of calcite is shifted to higher temperatures (as well as the formation of CaO).

The *Ca-rich* (Fig. 4) ceramic fragments present a CaO content of over 5% (according to CO, weight loss). They show hygroscopic water –2% at about 80 °C and some of them intense gypsum peaks at 145 °C. The peaks from 580 to 640 °C show the decomposition of the most common clay minerals (kaolinite, illite, chlorite) recognizable by XRD (Fig. 2).

The *Ca-poor* (Fig. 5) characteristic DTG profile, apart from the moisture water, shows peaks at about 640 °C, where clay minerals decomposition occurs. Most of the samples present very low firing temperatures (740 °C) and fragmented vitrification at the initial stage, according to recent publications, which reveal the composition and texture of the different calcite and calcium aluminosilicate crystalline phases which might explain the difference in vitrification and in behaviour [14].

By analysing the EDXRF data, could be observed that SiO_2 values vary from 63.5 to 70.8 wt% (the average of each ceramic temper), and those from Al_2O_3 from 14.7 to 17.4 wt %, and together comprise more than 80 wt% of whole ceramic chemical composition (Table 2).

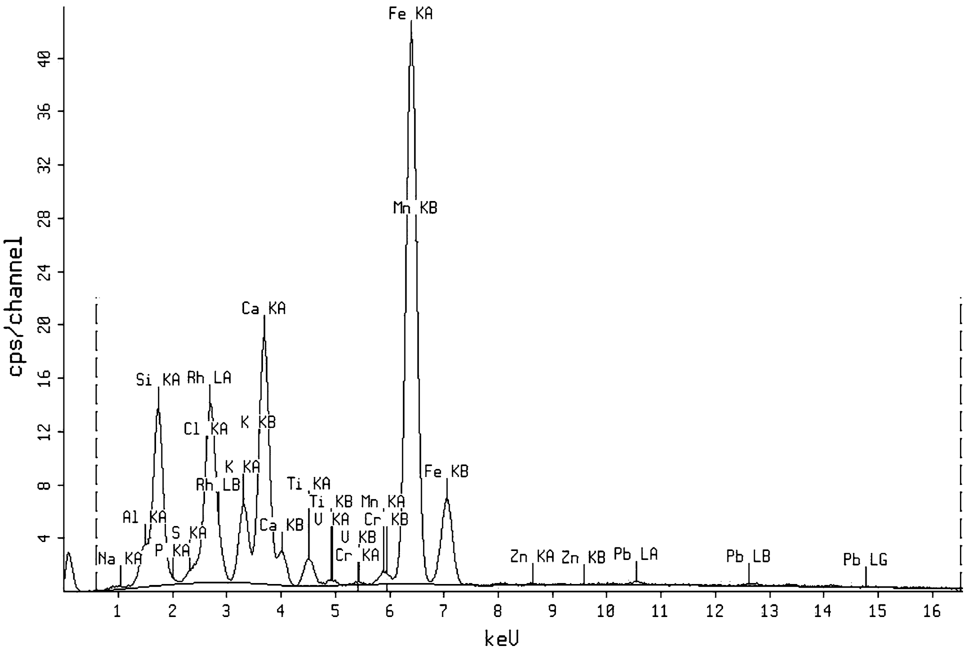

Fig. 4 EDXRF spectrum of Ca-rich ceramic

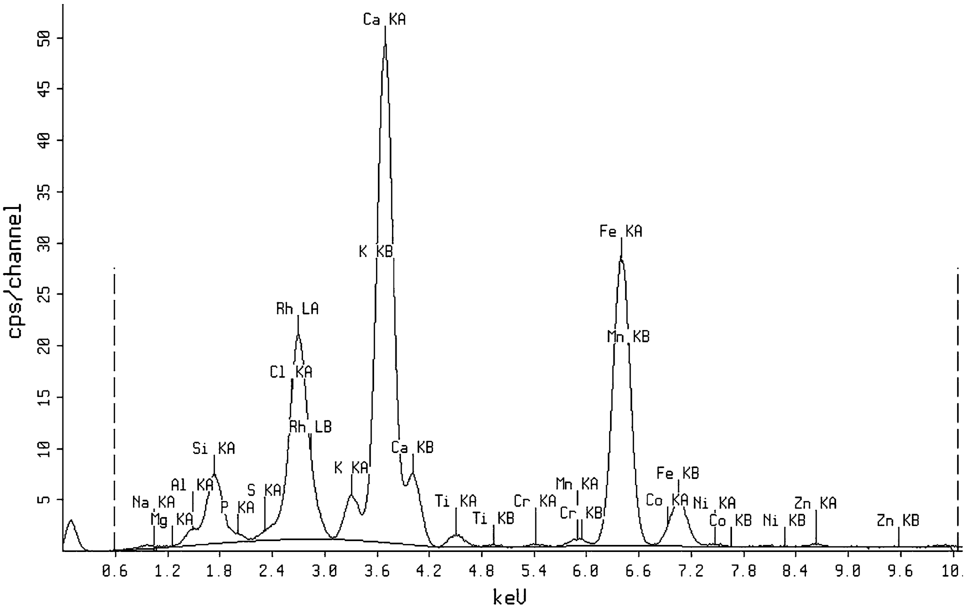

Fig. 5 EDXRF spectrum of Ca-poor ceramic

Table 2 Metal oxides composition of ceramic samples (Sample 4)

Element	Ceramic (surface)	Ceramic (in depth)
Na_2O	4.9	4.9
Al_2O_3	20.5	4.9
SiO_2	56	55.7
P_2O_5	0.59	0.95
Cl	1.7	1.7
K_2O	2.44	2.75
CaO	1.52	0.976
TiO_2	1.09	1.12
Cr_2O_3	0.044	0.051
MnO	0.11	0.11
Fe_2O_3	10.6	10
others	1.78	1.7
Zr	–	0.6

Table 3 Chemical elements from ceramic samples (Sample 10)

Element	Ceramic (surface)	Ceramic (in depth)
Si	25.3	23.9
Ti	10.1	3.52
Al	3.34	1.69
Fe	3.05	1.06
K	1.21	0.36
Na	1.19	1.06
Ca	0.28	8.31
Ba	0.11	908 ppm
Mg	702 ppm	0.13
Zr	147 ppm	76.5 ppm
Mn	355 ppm	356 ppm
Cr	85.3 ppm	17.3 ppm
Zn	71.2 ppm	20.6 ppm
Sr	46.4 ppm	73.1 ppm
Li	24.9 ppm	–
Ag	1.99 ppm	2.52 ppm
Pd	–	7.65 ppm
Pb	–	0.18

Fe_2O_3 is the third most abundant element and reaches 5.79 wt% on average. The alkali elements (as K_2O, Na_2O, CaO and MgO) constitute together less than 3 wt%. On the other side come out the relative high contents of P_2O_5, 2.37 wt% in average. The H_2O values reach 7.54 wt% on average, which is still high for burned ceramic material (mainly clay material). The Al_2O_3 and H_2O contents explain the great abundance of clay-derived minerals. The relative high contents of H_2O confirm the abundance of partial dehydroxylation of clay-material derived from kaolinite as main mineral of the ceramics and the neo-formation of kaolinite. It means that the fragments reabsorbed water along its discarded and incorporation into soil formation. The extremely high SiO_2 contents correspond, besides clay-derived material and the abundance of quartz, as sand grains and rock fragments. The iron contents represent hematite and goethite, and some maghemite, minerals also identified in the studied ceramic fragments. K_2O, Na_2O and CaO built the feldspars (microcline and albite) and together with MgO indicate the presence of illite in the raw material. The predominance of SiO_2, Al_2O_3 and H_2O plus Fe_2O_3 (together they make up more than 93 wt% of whole sample) confirm clay-derived minerals, quartz and some iron oxyhydroxides as the main minerals of ceramic fragments. The chemical and mineralogical data, as well as textural aspects, leave one to conclude that the main raw material for ceramic elaboration comes from fine-grained clay quartz rich material. The P_2O_5 contents, however, are relatively high for clay material normally used for ceramic purpose.

The higher contents of Zr, Sc and Sn might have been promoted by weathering processes forming the saprolite, confirmed by the decreasing of Cl, Co, Cu, V, Mn and heavy rare earth elements (Sm, Gd, Dy, Ho, Er, Yb and Lu) as demonstrated before (Table 3). The addition of feldspars, which obviously contributes with K, Na and Ca into raw material improves the firing temperature. The firing of the potteries occur in open atmosphere, possibly in the same primitive way. The firing temperature did not exceed 600 °C, as demonstrated by partial dehydroxylation of clay material and the formation of maghemite. This phase formed *the ceramic minerals*: dehydroxylation of clay giving rise to burned clay, maghemite and recrystallization of anatase. Maghemite promotes the slightly brown to red color of the potteries [15].

After much firing potteries were used for daily purposes as cooking and conserving foods. At this phase they get in contact with meals, fishes, roots and so on, in boiling water, become contaminated and form minerals like aluminum phosphates and Ba–Mn oxyhydroxides mineral equivalents (post-ceramic minerals), which may contain the elements Mg, Ca, Ba, Zn, Pb, Y, and so on. Finally the potteries after several uses become old, break down and are discarded together with many other organic (vegetal and animal) material waste.

Chemical elements such P, Mg, Ca, Mn, Ba, Zn, Pb, etc. are fixed partly and concentrated in the organic humus of soils and possibly is partly absorbed in the ceramic fragments, contributing to formation of phosphates and Mn oxyhydroxides in less extension. During this phase the clay derived materials and hematite/maghemite rehydrated and form kaolinite and goethite, respectively. The high content of organic matter of the sample explains its gray color, caused the deferrugination the outer skin of the ceramic fragments, which become yellowish gray.

The main conclusion that can be derived from these results is the possibility to predict the artefacts composition and manufacturing conditions of ancient pottery, as a historical proof for some population.

Conclusions

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, all archaeological pottery samples were fired at relatively high temperatures. The results have demonstrated that TG-DTG analysis is an indispensable tool in discovering some special technological features of ancient pottery.

The carbonate content (Ca-rich, Ca-poor or marly clays of intermediate Ca content) discriminates between the paragenesis in the ceramic body, while the type of CaO transformations in the ceramic matrix could inhibit or enhance vitrification according to augite formation.

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