Годишник на департамент „Природни науки“, ISSN 2367-6302, 2022
Annual of Natural Sciences Department, ISSN 2367-6302, 2022
Journal homepage: https://naturalsciences.nbu.bg/bg/godishnik-na-departament-prirodni-nauki

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Simultaneous TG/DTG-DSC analysis – application in ceramic artefacts

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Симултанен термичен анализ (TG/DTG-DSC) – приложение за изследване на керамични артефакти

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Abstract: The aim of this paper is to promote thermal analysis as a method for the study of archaeological ceramics. In order to achieve this goal, the nature of the thermal methods (thermal processes, types of thermal methods and their application) is described. Specific experimental measurements by simultaneous TG/DTG-DSC analysis of ceramic archaeological artifacts are also presented.

***Key words**: simultaneous TG/DTG-DSC analysis, archaeological chemistry, ceramic*

Резюме: Целта на работата е да се популяризират термичните анализи като метод за изследване на археологическа керамика. За постигане на целта е описана същността на термичните методи (термични процеси, видове термични методи и тяхното приложение). Представени са и конкретни експериментални измервания чрез симултанен TG/DTG-DSC анализ на керамични археологически артефакти.

***Ключови думи:** симултанен термичен анализ (TG/DTG-DSC), археологическа химия, керамика*

Introduction

Ceramic (pottery, brick, tile, etc.) is one of the most common archaeological artifact, since it is sustainable, produced over a long period of time and has a low cost. Its study provides information about the cultural aspects of the society from which it was created. Ceramics is also considered to be the first synthetic composite material. Its quality depends on both the raw material and the temperature at which it was processed, the gas atmosphere in the furnace and the specific production technology. The main object of modern research on ceramics is to precise the parameters that control its qualities. The complex of methods of archeological chemistry is used for its study, which includes: X-ray fluorescence (XRF) analysis for the determination of chemical composition; powder X-ray diffraction (PXRD), Fourier transform infra-red (FTIR) spectroscopy and thermal analysis for the study of phase composition. PXRD and FTIR are also

https://doi.org/10.33919/ansd.22.7.6

used to interpret the temperature and firing conditions by studying the differences in the mineral composition of the samples. Is it extremely important to determine the phase composition for ceramics from which metallurgical furnaces are built, since this is the main way to determine the maximum temperature that was reached in the ancient furnace. Thermal analysis is characterized as the leading method for defining the firing temperature of ceramics [Peacoc, 1970; Goffer, 2007; Palanivel et al., 2009; El Ouahabi et al., 2015].

In order to popularize thermal analysis for the study of archaeological ceramics, the nature of these methods is described and specific experimental measurements are presented.

The samples used for the experiments were collected by a project, funded by the Bulgarian Science Research Fund (grant number KP-06-N39/9). The used equipment (simultaneous TG/DTG-DSC analysis, Setline STA 1100, SETARAM, France) is purchased by the same project. The experiments are conducted in the temperature range “room temperature (RT) – 1100°C”; in air gas medium, static air, with a heating rate of 10°C min^{-1}. The operational characteristics of the TG/DTG–DSC- system were: sample mass of 25.0±1.0 mg (mass resolution of 0.05 µg) and alumina sample crucible with a volume of 100 µL.

1. Thermal processes

Solid crystals show different behavior under conditions of increasing and decreasing temperature, which is expressed in the course of different thermal processes. The course of a thermal process in a given crystalline substance is determined by the types of chemical bonds, atoms and molecular complexes that make it up. Depending on the chemical bonds, crystals are divided into molecular, covalent, ionic and metallic. Normally more than one type of chemical bond is established in some of them. When the temperature is increased, molecular, atomic or ionic movements in the crystal increase as well, leading to changes in the crystal structure, sublimation, melting, etc. A process of decomposition and subsequent formation of new structural phases can also take place. Some of the described processes take place with a general decrease in weight, and others - with an increase in the substance’s weight [Brown, 2004].

1.1. Thermal processes occurring with increasing temperature

- ***Oxidation***

When the temperature increases during a test, some chemical reactions occur that lead to a mass increase in the sample, such as oxidation. Oxidation is the process of electron removal from a species, where almost all elements and their compounds can undergo oxidation [Atkins et al., 2010]. Oxidation is a chemical reaction that occurs when energy is released (exothermic reaction).

Contrary to the previous reaction, the occurrence of some chemical reactions can lead to a sample’s mass decrease. Such reactions include: dehydration, dehydroxylation, decomposition, sublimation, melting, and pyrolysis. These reactions usually occur when energy is absorbed (endothermic reactions).

- ***Dehydration***

Dehydration of solids is the separation of adsorbed water molecules or water molecules included in their structure.

- ***Dehydroxylation***

Dehydroxylation is the process of adding hydrogen to a hydroxyl (alcohol) group leading to the creation of water and an alkyl group [Dembicki, 2017]. In crystalline solids, the hydroxyl

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group that is released during dehydroxylation is structurally bound, which determines the higher temperature of its separation compared to the temperature of dehydration.

- ***Sublimation***

Sublimation occurs when a constituent’s kinetic energy increases very rapidly and a direct transition to the disordered arrangement of a gas takes place, without a liquid phase forming intermediately. It’s generally normal for sublimation to appear together with thermal decomposition [Brown, 2004]. Sublimation leads to a mass loss in the sample and is an endothermic process that takes up energy.

- ***Decomposition***

Thermal decomposition occurs when the links of the constituent molecules are weaker than those between the atoms that constitute them. An increase in temperature may lead to bond redistribution and creation of a chemically different final product. When in liquid state, decomposition can proceed more rapidly than if it occurs in a crystalline state [Brown, 2004]. The reaction normally takes several steps to fully complete and is slow to begin at first [Gabbott, 2008]. A reaction’s decomposition rate can be slowed by diffusion of ejected gaseous species, thus causing the initial slow reaction rate, which then increases as the temperature rises. The result is a relatively broad endotherm [Speyer, 1994].

- ***Melting***

Melting is the process of a material changing its state from solid to liquid due to heating. When there is enough energy available, the attraction forces between constituents become inadequate to preserve the solid’s set arrangement which causes it to shift to a more relaxed state like that of the liquid. Depending on the complexity of the molecules involved, the shift from solid to liquid state may require several stages to complete. The intermediate order’s structures are referred to as “liquid crystals” [Brown, 2004].

- ***Pyrolysis***

When it comes to decomposition of organic matter, pyrolysis is a fundamental process. The reaction is responsible for the carbonization, combustion and gasification of coal and it can convert biomass into various biofuels. The first stages of pyrolysis comprise of the distillation of low molecular weight species. With the gradual raise of the temperature and the increased volatilization rate, the compounds begin to crack and may create volatile fragments. The study of pyrolysis kinetics is important in order to better understand this process and the kinetic parameters that are obtained from the thermal analysis can be useful for coal characterization [Brown, 2003]. Polymers are always lost from a sample during a TGA regardless of the type of atmosphere used or their chemical composition due to pyrolysis. This is because they have a high molecular weight, so they will pyrolyse before the increase in temperature is sufficient for them to volatise first [Gabbott, 2008].

- ***Phase transitions***

There are also chemical reactions that take place without any mass losses occurring. An example of this would be phase (polymorphic) transitions. In a phase transition, a new arrangement of constituents occurs which can be in a more stable state than its original one. The process takes place by absorbing energy.

1.2 Thermal processes occurring with decreasing temperature

Crystallization is another exothermic reaction that occurs without any mass change with decreasing temperature. A very common example of the process is glass crystallization, which unlike the α-quartz to β-quartz phase shift is an irreversible transformation.

https://doi.org/10.33919/ansd.22.7.6

2. Thermal analysis – types and application

A powerful method for the study thermal processes is thermal analysis. According to the International Confederation for Thermal Analysis and Calorimetry, Thermal Analysis (TA) represents a number of techniques in which a property of a sample is monitored against time or temperature while the sample's temperature is programmed in a specified atmosphere. TA can also be defined as the analysis of a change in a sample's property, which is related to an imposed temperature modification [Brown, 2004]. Thermal analyses suitable for the study of crystalline solids are thermogravimetry, differential thermal analysis, differential scanning calorimetry and simultaneous thermogravimetric analysis with differential thermal analysis/differential scanning calorimetry.

2.1 Thermogravimetry

- ***Introduction to the method***

Thermogravimetry (TG) is a method of thermal analysis in which a change in a sample's mass can be registered depending on the temperature. The mass of the sample is defined as a function of the temperature T or the time t:

$$m=f\,(T \text{ or } t). \tag{2.1}$$

There are three main types of thermogravimetry:

- isothermal (static) – the mass of the sample is measured in time at a constant temperature;
- quasistatic – the sample is gradually heated until it reaches a constant mass;
- dynamic – the temperature around the sample is changed according to an imposed law (normally with a constant speed).

The experimental curve which reflects the temperature dependency of the changes in a sample's mass is also known as thermolysis curve, pyrolysis curve, thermogram, thermogravimetric curve, thermogravimetric analysis curve, etc. This curve makes it possible to determine the thermostability and composition of a sample at the beginning and during the middle stages, as well as the composition of the sample that is left, if there is any. Other than the data regarding the sample's mass, the remaining information has an empirical character, since the temperatures of the monitored transitions depend greatly on the particular apparatus that is used [Fakirov, 1990]. The TG technique is mainly applied in transformations that involve the absorption or evolution of gases from a sample with a condensed phase. Most TG apparatuses are configured for vacuum and/or variable atmospheres and can be used for a wide range of analyses, from clay decomposition to a high temperature oxygen uptake in the analyzing of superconducting materials [Speyer, 1994].

Data from TG experiments can be presented graphically in multiple ways, depending on the requirements of the analysis. Usually the Y-axis of the graph represents the *mass* or the *mass percent* of the sample and the X-axis shows the *temperature* or *time.* Mass percentage could be preferable in some experiments as it gives the opportunity to compare separate experiments on normalized sets of axes. When time is used for the X-axis, a second temperature curve has to be plotted to indicate the temperature programme that is used for the experiment [Brown, 2004].

- ***TG curves***

There are a few possible TG curve types which can be classified as follows (Fig. 1):

- Type (i) curves – the sample does not go through decomposition and there is no noticeable loss of volatile products over the set temperature range. No information can be obtained whether the sample undergoes reactions such as solid phase transitions, melting,

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polymerisation or other that do not involve volatile products. In this case other techniques need to be applied in order to exclude such possibilities.

- Type (ii) curves – A rapid initial mass-loss occurs, which is due to either drying or desorption. Other reasons for this are the effects of convection or thermomolecular flow or even working at reduced pressures. In order to make sure that the mass-loss is real, the sample should be rerun, which in turn should produce a type (i) curve, unless there was moisture in the carrier gas or if it was reabsorbed at the lower temperature on the sample.
- Type (iii) curves – It only takes a single stage for the sample to decompose. The curve can be applied in determining the reactant’s limits of stability, the reaction’s stoichiometry and research its kinetics.
- Type (iv) curves – There are multiple stages of decomposition and relatively stable intermediates. Similar to curve (iii), this type can be used to define the reactant’s stability limits and that of its intermediates, as well as a better, more complex stoichiometry.
- Type (v) curves – Again, multiple stages of decomposition occur, however no intermediates are formed and only the stoichiometry offers more detailed information. The heating rate effect on the resolution needs to be verified, since type (v) curves resemble type (iv) curves at lower heating rates. At high heating rates both types (iv) and (v) resemble type (iii) curves in which case the detail of the complex decomposition is lost.
- Type (vi) curves – The sample reacts with the surrounding atmosphere which in turn causes the curve to show a gain in mass. An example of this would be the oxidation of a metal sample.
- Type (vii) curves – Such types of curves occur very rarely when the product of an oxidation reaction decomposes one more time at higher temperatures [Brown, 2004].

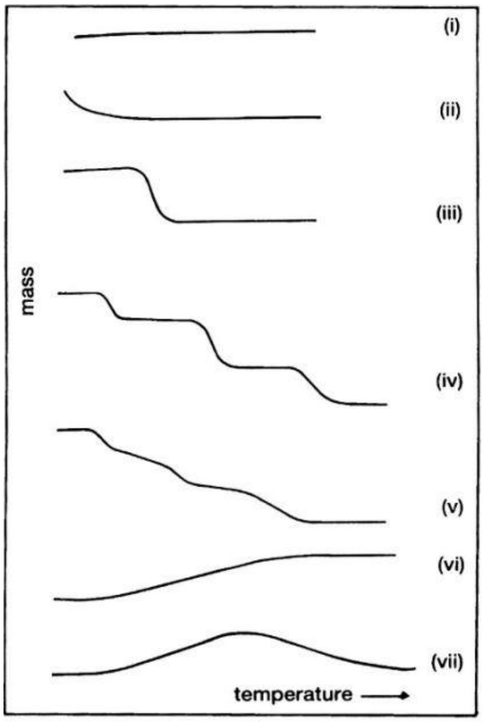

Fig. 1. Types of TG curves [Brown, 2004]

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- ***Buoyancy effect – correction in the TG curve***

According to Archimedes' principle, when a body is submerged (partially or completely) in a fluid, the fluid applies an upward force on it which is equal to the weight of the fluid being displaced by the body [Speyer, 1994]. This buoyancy effect can also be applied in the TGA measurements of a sample. Because of it, the initial TGA curve may sometimes appear as having a higher than a 100% mass when testing a sample or as having mass even though there is no sample in the crucible. The buoyancy effect greatly depends on the volume of the substance and the density of the gas in the atmosphere. The buoyancy effect can initially show a drastic rise in the TGA curve which occurs due to the design of the TGA apparatus. At low temperatures, heat is transferred from the furnace to the sample's thermocouple only though the process of convection. It takes a certain amount of time before the crucible is evenly heated, while the warm air that flows in the protective tube does not reach the crucible immediately, so the real temperature of the atmosphere is a lot higher than the sensor indicates. As a consequence the gas density changes very quickly in the beginning of the test and a false mass change is shown on the curve [Cement Science, 2013]. Buoyancy correction can be applied by running a blank test. During the test, the same temperature program and crucible are used, with the exception of the sample which is removed. The resulting curve is then subtracted from the original curve that included the sample. Such correction is especially important for tests that focus on ash content, since the residue at the end of the experiment has to be assessed correctly and where small mass losses are expected [Gabbott, 2008].

- ***Differential TG curve***

While normal thermogravimetry registers a sample's change in mass m as a function of temperature T or time t, differential thermogravimetry, also known as derivative thermogravimetry (DTG), registers the rate of mass change dm/dt as a function of temperature or time:

$$dm/dt=f\ (T \text{ or } t) \tag{2.2}$$

A DTG curve can be obtained from a thermogravimetric curve by graphical differentiation or by using a more effective way of differentiation. The latter may be achieved electronically as well – the TG's signal is differentiated and the derivative itself is registered. Modern devices can register both curves simultaneously – the integral curve (TG) and the differential one (DTG). While both curves provide the same information, the way this information is presented is different (Fig. 2). The DTG method has the following advantages:

- The curves can be obtained simultaneously with the analyses from the TG and DTA methods;
- The curves obtained by the TG and DTA methods can be compared with one another with the only difference being that the DTA curves are fixed with processes, not related to the sample's mass change;
- TG curves cannot separate stages that are close in temperature, unlike in DTG curves where they have sharp peaks and can be easily discerned;
- DTG curves are derived from the TG curves and as such the space beneath them correctly reflects the changes in mass, and because of this DTG curves can give accurate quantitative information;
- The DTG method can be applied for substances that for some reason cannot be analyzed by DTA.

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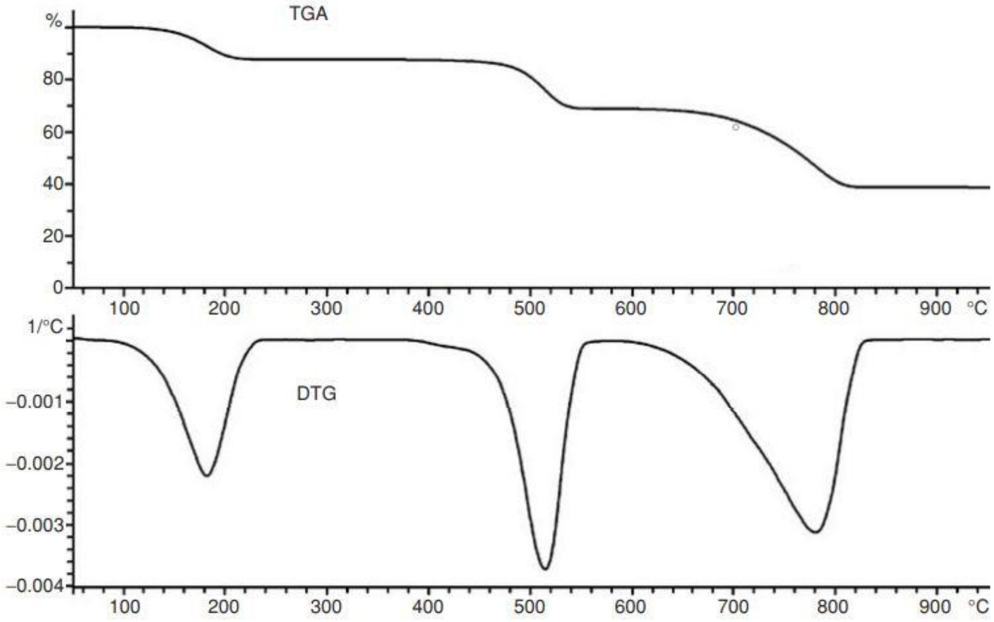

Fig. 2. Comparison of TGA and DTG curves [modified by Gabbott, 2008]

It should be noted, that the temperature which corresponds to the peak of the DTG curve must not be considered as “decomposition temperature”. The peak corresponds to the temperature, at which the mass’ rate change acquires its maximum value, but it is not the temperature, at which the sample’s mass begins to change [Fakirov, 1990].

2.2 Differential thermal analysis

A simple, popular TA method is the differential thermal analysis (DTA) technique. It records the difference in temperature ΔT between an analyzed sample and a reference material, while both substances are exposed to the same heating programme [Brown, 2004]. Unlike its sister technique, the DSC (Differential Scanning Calorimetry), DTA can operate in high temperatures up to 1500 degrees Celsius. However DTA cannot measure enthalpy changes accurately, it can only give an indication of the enthalpy changes involved when calibrated to do so [Gabbott, 2008]. A “differential” thermocouple is used to measure the differences in temperature between the sample and reference material, where each of the crucibles containing the substances is connected to a junction. When the analyzed material undergoes a transformation, it will either absorb (endothermic) or release (exothermic) heat. An example of this would be the melting of a solid material, which will result in heat absorption, meaning that the thermal energy is used to promote the phase shift. After this the instrument will pick up the change in temperature in the sample, which has become cooler than the reference material, and will indicate this transformation as an “endotherm” on a differential temperature (ΔT) versus time plot [Speyer, 1994]. In calorimetric DTA, the reference material and the analysed sample are put on separate bases with thermally conducting properties. The junctions of the thermocouple are then linked to the individual bases. Because of this, the output signal does not depend as much on the sample’s thermal properties, which is an advantage of the configuration, however this creates a slower response. The materials that are used for the thermocouples and furnace windings then determine the temperature range of the DTA [Brown, 2004].

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There are a few requirements that a reference material has to meet in order to be used in an analysis:

- No thermal events should occur over the set temperature range of the analysis
- The thermocouple and holder of the material should not react with it;
- The sample and reference should have a similar thermal conductivity and heat capacity.

One of the most frequently used reference materials for inorganic samples are alumina (Al_2O_3) and silicon carbide (SiC). Normally, the size of the particles of the samples and the conditions in which they are packed have an influence on the results of the analysis which is why both materials are used in the same form, which is mainly a powdered one. The reference material is often used as a diluent for the analysed sample in order to match its thermal properties. The sample should not react with the reference material [Brown, 2004].

Thermal events influence the DTA curve differently, depending on whether they are endothermic or exothermic. When the event that takes place within the sample is endothermic, the sample's temperature will lag behind that of the reference material and a minimum will be observed on the DTA curve. When the event is exothermic, the sample's temperature will rise above that of the reference, thus creating a maximum on the curve. The resulting curve from the endothermic or exothermic event is related to the change of enthalpy accompanying the thermal event [Atkinset al., 2010].

Fig. 3a shows the sample that is heated at a constant rate. The sample's temperature T_S varies linearly with time (Fig. 3b) which changes once an endothermic event occurs. While the event is being completed, the sample's temperature remains constant at $T_{C.}$ After its completion, the temperature increases quickly in order to catch up with the temperature required by the programmer. The result is a broad deviation from the sloping baseline (Fig. 3b). DTA is a rather insensitive method, since it cannot detect small heat effects and sometimes it can present spurious baseline variations triggered by fluctuations in the heating rate as an apparent thermal event. In Fig. 3c the sample and reference are placed together while separate identical thermocouples are connected to each of the materials. When the temperature is the same for both materials, the net output of the thermocouples is zero. This changes once a thermal event occurs in the sample and a temperature difference ΔT appears as a result. A third thermocouple monitors the temperature of the heating block and the results are shown as ΔT versus temperature (Fig. 3d). A horizontal baseline appears, which corresponds to $\Delta T=0$. In the curve, T_1 represents the temperature at which a deviation begins from the baseline and T_2 represents the peak temperature. Normally, the ΔT peak's size can be amplified so at to detect events with minor changes in enthalpy. The curve in (b) is clearly a less accurate and sensitive way of presenting data than (d), which is why (d) is the general method for presenting DTA results. DTA's main purpose is to be as sensitive as possible to thermal changes, however this creates a poorer calorimetric response as a result, where peak heights are only qualitatively related to the magnitude of the occurring enthalpy changes [West, 2014].

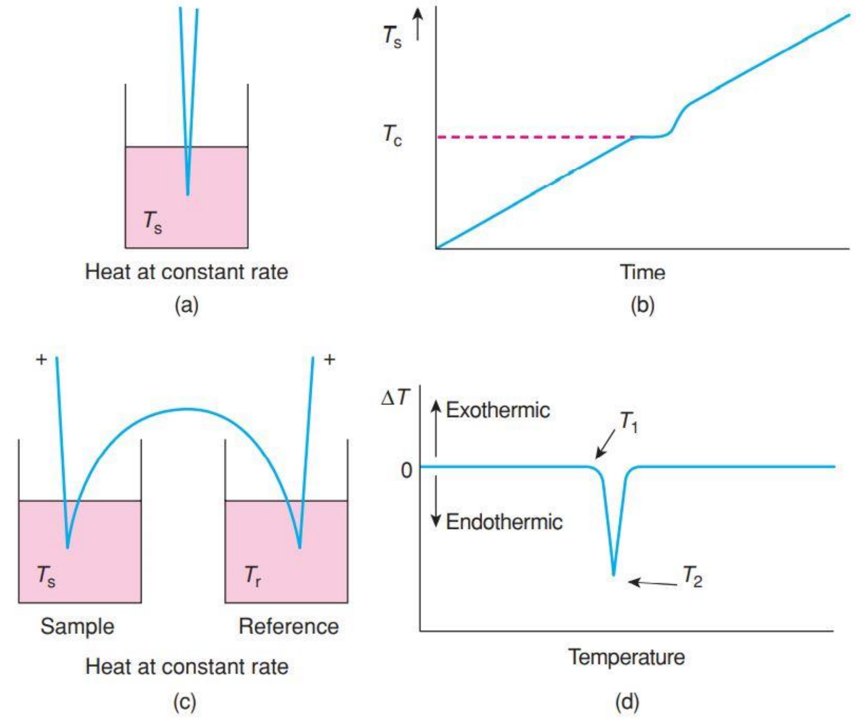

Fig. 3. The DTA technique: a) the set-up without reference; b) a typical DTA curve from the set-up shown in a); c) the set-up with reference (d) a typical DTA curve from the set-up shown in (c) [West, 2014].

2.3 Differential scanning calorimetry

As previously mentioned, a technique that resembles the DTA is the Differential Scanning Calorimetry (DSC). Both methods can be used to obtain similar information, with the difference being that DSC is used for lower temperatures and it provides more reliable quantitative data, such as the enthalpy of a phase change. Information regarding the enthalpy changes in transitions and temperatures can be obtained, like melting and structure change in the sample [Atkins et al., 2010]. The DSC method is based on the heat flow difference in the sample and reference material. The temperature is increased linearly with time, and it is maintained during the experiment for both the sample and the reference material. The technique aims to calculate the difference between the amounts of heat needed to for a thermal event to occur in one of the two materials being compared. The heat that is needed during the phase transition is either more or less than that of the reference [Kaushik, 2011]. Thermal events appear on the DSC curve as deviations from the baseline in the form of either exotherms or endotherms (Fig. 4). This depends on how much power is supplied to the sample relative to the reference; normally endothermic events are represented as positive deviations from the baseline, while exothermic events are shown as negative deviations from the baseline [Atkins et al., 2010]. DSC can be used for the analysis of processes such as polymerization, pyrolysis, crystallization, sublimation, purity evaporation, glass transition, phase changes and compatibility, etc. [Kaushik, 2011].

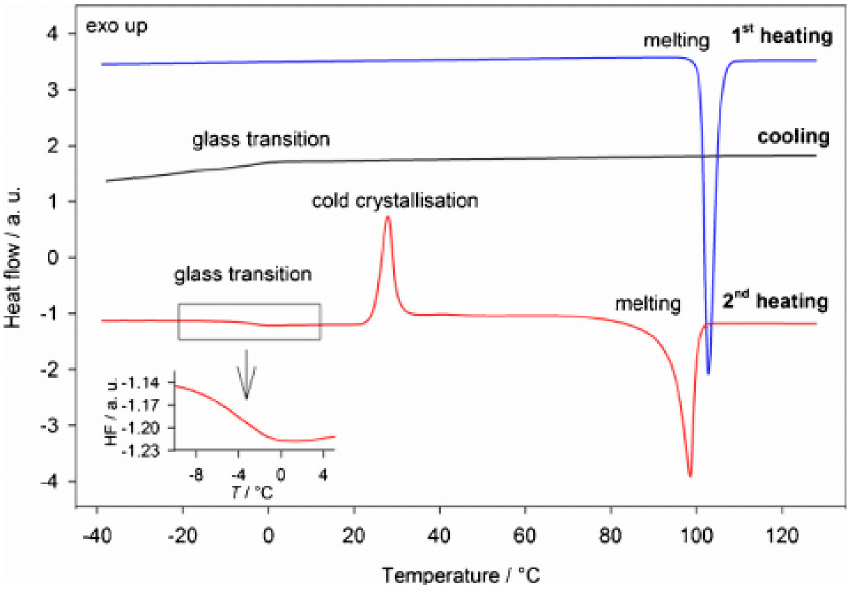

Fig. 4. Standard DSC curves [Skotnicki et al., 2014]

In DSC, the sample maybe heated in 2 different ways – via a furnace heater or infrared heating. The furnace represents an electrical resistive heater that can be positioned differently depending on the size of the furnace. Such heaters raise a sample’s temperature by conduction, which leads to large temperature gradients, particularly when dealing with inorganic glasses and polymers. A furnace should be capable of reaching 100 to 200°C above the maximum desired temperature, have a low heat capacity, not affect a mechanism’s balance via convection or radiation, have a uniform hot-zone and be non-inductively wound. As for the infrared heating, several halogen lamps are used, whose light is then focused onto the sample via parabolic or elliptic reflectors. The transfer of heat is practically instantaneous, with temperatures of over 1400°C being achieved at heating rates of up to 1000°C per minute. The use of such heating method however presents problems related to power control and temperature measurement [Brown, 2004].

- *Baseline correction*

Two additional aspects of the DTA and DSC curves include the baseline, which is normally measured without any samples, crucibles or with the crucibles empty. As for the baseline, it is constructed in a way so as to connect the measured curve as if no peak had formed, i.e. it links the curve before and after a peak (Fig. 5). The main point of interest in DSC and DTA curves are deviations of the signal from the baseline which occur due to some thermal event. However the baseline can sometimes prove to be difficult to establish. Factors such as asymmetry in the construction of the reference and sample holders, mismatch between the thermal properties of the two materials can create an initial displacement of the baseline. Such errors can even lead to the creation of a sloping baseline, which can be corrected via an electrical compensation. When the thermal properties of a sample are changing with the form of the sample (from low-temperature to high-temperature form) the response following a thermal event will not return to the original baseline. The baseline can be constructed in multiple ways, which can be integrated in the instrument’s software. A way to correct the baseline is to run a blank test with 2 empty crucibles and then subtract the result from the original analysis [Brown, 2004].

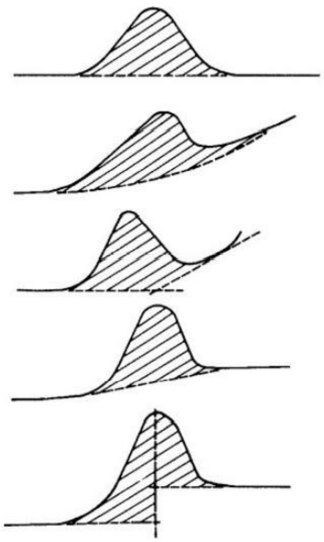

Fig. 5. Baseline construction procedures [Brown, 2004]

2.4 Simultaneous thermal analysis

A simultaneous thermal analysis method represents the measurement of two or more properties of the same sample during a single temperature programme. Those properties may be sampled in a repetitive sequence or they may be monitored in a continuous manner depending on the needs of the test [Brown, 2004]. The oldest combination of the Simultaneous Thermal Analysis (STA) methods is the TG-DTA. The technique is mainly applied over large temperature ranges, and unlike the DSC technique, it can even be used for very high temperatures. Frequently analysed products via this technique are the inorganic ones such as minerals. However due to the rapid increase in the DSC method's popularity and the need for quantitative measurements in multiple fields, the combination TG-DSC has also become a favored method. In TG-DSC, an open crucible is used during measurements which allows for both the evolved and reacting gases to flow. Experiments related to the TG-DSC method include pyrolysis, decomposition, dehydration and dihydroxylation. The mode is especially useful when analysing heterogeneous samples. If the test is run on 2 separate instruments (TG and DSC) with 2 separate samples, sampling reproducibility is generally not accomplished. However in a TG-DSC with only 1 sample, reliable TG and DSC data can be obtained. The same principle applies when investigating the decomposition if powders, explosives and polymeric materials. TG-DSC is also useful when investigating a gas' reaction with a powdered or solid sample, since many parameters need to be well defined, like the sample's grain size and surface. The size of the grains and the pores can influence the results obtained from different samples and as such, having only one sample instead of 2 separate ones is truly useful for the procurement of accurate data. The TG-DSC mode is helpful in investigations regarding surface reactivity, catalysis studies and all gas absorption types [Parlouer, 1987].

2.5 Application of TG and DTA/DSC for the study of thermal processes

For the processes of dehydration, desorption and decomposition, the most useful analysis is the thermogravimetric one, since it can accurately show the mass losses that occur during the processes [Atkins et a., 2010].

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The TG method has often been used to study the oxidation of materials in various atmospheres. Hot-stage X-ray diffraction is very practical for the study of the reaction as it can illustrate the development of different oxide products of corrosion during iron oxidation [Brown, 2003].

DTA can be used for the analysis of processes such as melting, sublimation, crystallization, heat capacity, pyrolysis, phase changes, purity evaporation, etc. [Kaushik, 2011].

Dehydration normally appears as an endotherm on a DTA curve and as an exotherm on a DSC curve. Dehydration is the first event that happens when a hydrated material is heated and it requires a heat input. Once the material becomes dehydrated, it undergoes a polymorphic transition that takes place at a higher temperature [West, 2014]. When in a moist atmosphere, dehydration can be reversible on cooling and before reheating. The presence of water vapour in the surrounding atmosphere influences the general rate of dehydration in a material. An additional technique known as hot-stage microscopy (HSM) could be used in order to provide more information on the mechanism of dehydration or decomposition.

Dexydroxilation is an endothermic process that is used for the characterisation and identification of minerals and their properties. In simple hydrates, dehydroxylation of hydrolysates may lead to special thermal effects occurring in the analysed sample. The process can also create heat changes in sulfates such as gypsum, kiesente, alunogen, morenosite and others. It occurs at 200-1000°C in Al-bearing phosphates (wavellite, turquoise, augelite), at 170-590°C in simple hydroxides, at 530-590°C in kaolin minerals, however this depends on the standardisation of the kaolin minerals themselves. In micas, dehydroxylation can occur in the temperature range of 700-1050°C and in chlorites, from 500°C to 860°C [Brown, 2003].

Different TA methods can be used for the analysis of sublimation with the most popular being TG and DSC. Concurrent sublimation can also give a false baseline in an analysis. The temperature of sublimation is influenced by the atmosphere and its temperature is a lot lower when in vacuum than in 1 atm argon or nitrogen pressure. Sublimation’s enthalpy values are derived from vapour pressure evaporation studies for most cases; however DSC curves can also be used to estimate those (Brown, 2003). Sublimation is also responsible for first order phase transformations in materials, along with boiling and solidification [Speyer, 1994].

Crystallization may be determined by both DSC and DTA and the sample is normally crystallized under a constant heating rate, since rapid heating will cause the reaction to proceed very quickly [Speyer, 1994].

Decomposition can be detected by endothermic and exothermic reactions in DTA and DSC.

A material can be decomposed both in DTA and DSC however when it is decomposed in a DSC, this can create a response with a lot of noise and the evolved volatiles will lead to system contamination. Because of this it is always better to first establish the decomposition temperature via a TGA analyser if possible. Since decomposition should be avoided when using a DSC, if it needs to be measured, an Oxidative Induction Time (OIT) test can be used. The test works by heating the sample to the desired temperature under inert conditions. Decomposition can sometimes occur simultaneously with another thermal event over the same temperature range. This however can be resolved by using fast scan rates, since the process is then displaced to higher temperatures, thus the previously obscured transitions can be properly measured. Another solution would be to reduce the pressure of the measuring cell [Gabbott, 2008].

One of the most commonly analysed transitions is the crystalline melt which appears as a peak on the heat flow trace. It is also considered a first-order transition and when it begins, the analysed material remains at the melting temperature while the liquid and solid are in equilibrium and the process progresses. The result is a peak with a straight leading edge while its slope corresponds to the energy transfer's rate to the sample. The maximum of the peak reflects the end of the equilibrium end region and its shape is asymmetrical and can look more like a triangular at slower rates. In a heat flux system, the signal that is reported as heat flow comes from the difference between the temperature of the sample and reference material. In a power compensation system, the same difference is still present and remains until melting is completed. Melting begins at the melting point (onset temperature) of the crystal, not at the peak maximum value. Some materials however do not consist of single crystals but of a range of crystals, whose stability is different and as such, they melt over a broad temperature range. In this case there is no point in calculating an onset temperature, which is why the peak maximum temperature of a broad melt is the most useful here. A 100% pure material is supposed to create a very sharp and narrow peak were it not for the thermal gradients across the sample. However this is only in theory, since in practice the energy that flows into the sample takes some time, causing the peak to broaden and become reduced in height. The slope of the leading edge can then be used to provide information about the maximum possible absorption rate of energy into a material, i.e., it is a measure of the thermal resistance to absorption of energy [Gabbott, 2008].

When the transition is from one solid state to another, it can be detected by both DSC and DTA, even though DSC is the preferred method [Brown, 2004]. The reaction is an endothermic one and can occur both with temperature increase or decrease. A very good example of the process would be the transition of α-quartz to β-quartz where the quartz undergoes a reversible crystalline inversion at around 573°C. This is accompanied by an expansion on heating and a contraction on cooling [Speyer, 1994].

3. TG/DTG-DSC analysis of ceramic samples

Figures 6 and 7 show the TG/DTG-DSC analysis results of two ceramic samples – No. 57 tile and No. 53 brick. The total mass loss (ML) of studied samples changed from 12.24% (No. 57) to 4.32% (No. 53). The thermal decomposition of the samples separates into five temperature ranges: RT - 220°C, 220 - 470°C, 470 - 720°C, 720-860, and 860 - 1100°C.

In the temperature range between RT - 220°C, the dehydration of: (i) hygroscopic water (humidity) [Papadopoulou et al., 2006] with ML changed from 0.51 (No. 53) to 0.6% (No. 57) and (ii) phyllosilicate minerals [Hatakeyama, 1998; Földvári, 2011] with ML from 0.36% (No. 57) to 1.78% (No. 53) occurs. (Phyllosilicate minerals include clays, micas, chlorite, serpentine, and talc.) The results show the same density of the two samples and different contents of phyllosilicates.

During the 220 - 470°C temperature range, an exothermic effect with DSC peaks at 340.1 (No. 57) and 391.6 (No. 53) registers, defined as organic decomposition [Imman et al., 2021] with ML of 1.13% (No. 53) and 0.64% (No. 57).

In the temperature range between 470 - 720°C, an endothermic effect occurs at 573.0°C (No. 57) and 571.3 (No. 53) without ML, assigned as the α-β polymorph phase transition of quartz [Moropoulou et al., 1995]. Additionally, phyllosilicate minerals dehydration occurs [Hatakeyama, 1998; Velosa, 2007; Földvári, 2011] with measured ML of 3.7% (No. 53) and 0.51% (No. 57).

In the temperature range between 720-860°C, the calcite decarbonation was established [Böke et al., 2006] with ML from CO2 - 3.62% (No. 57) and 0.51% (No. 53) and decarbonation temperature of 775.0°C (No. 57) and 847.8°C (No. 53). From the measured ML, the calcite content was calculated - 8.20% (No. 57) and 1.15% (No. 53). The sample No53 calcite

https://doi.org/10.33919/ansd.22.7.6

concentration would not be detected by PXRD (LOD - over 5% [Moropoulou et al., 1995]), but only by thermal analysis and probably by FTIR. The calcite registration is of importance for the determination of the firing temperature of the ceramic. Measured ML of CO_2 and calculated calcite amount define the raw clay as calcareous (No. 57) and non-calcareous (No. 53) [El Ouahabi et al., 2015].

In the last temperature interval (860-1100°C), the phyllosilicate minerals destruction was registered [Földvári, 2011; Hatakeyama, 1998; Papadopoulou et al., 2006] with ML of 0.37% (No. 57) and 1.59% (No. 53). The exothermic peak at 1051.8 (No. 53) was assigned to crystallization of new high-temperature phases [Hatakeyama, 1998; Papadopoulou et al., 2006].

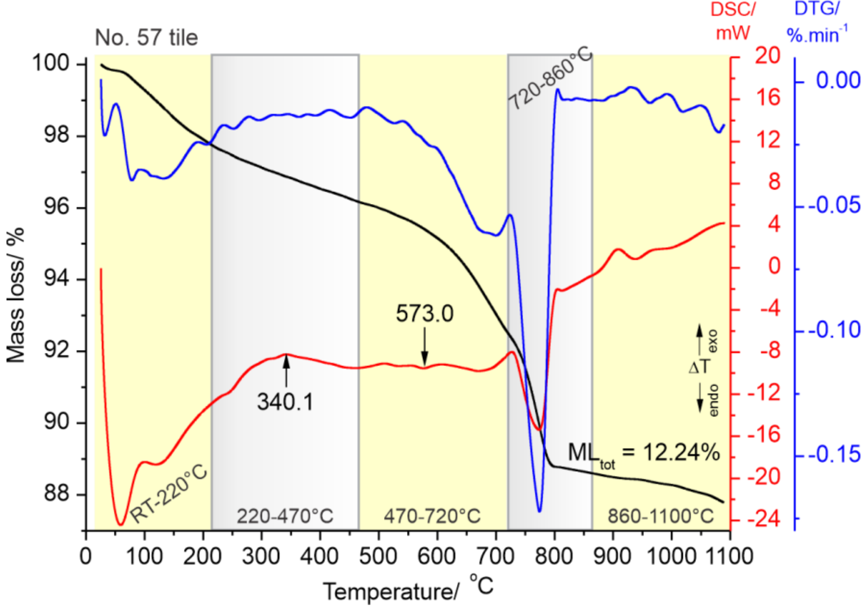

Fig. 6. TG/DTG-DSC curves of tile (sample No. 57 Dimitrievo Emporion Pizos, Roman age).

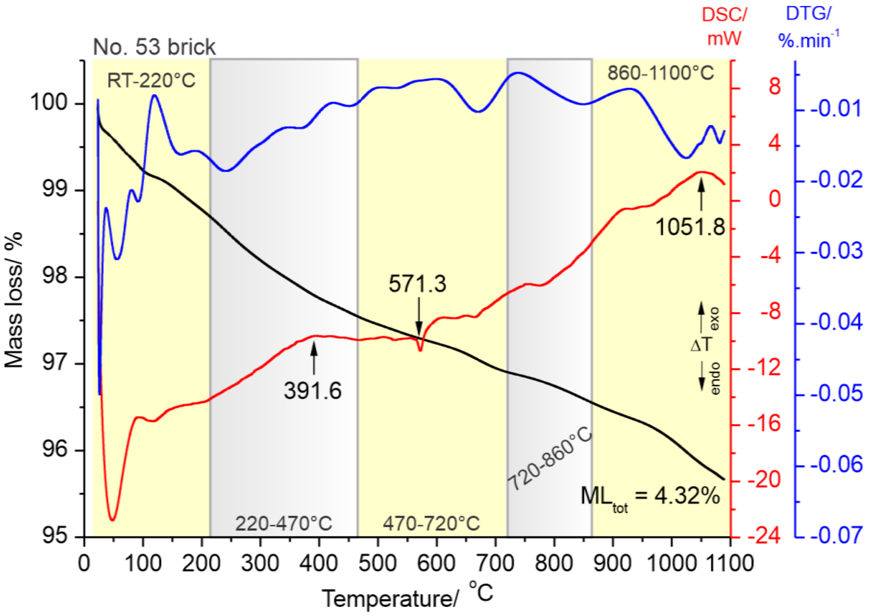

Fig. 7. TG/DTG-DSC curves of brick (sample No. 53 Dimitrievo Emporion Pizos, Roman age).

Conclusion

The results show two different types of clay for ceramic manufacturing - calcareous (No. 57) and non-calcareous (No. 53). The quartz is present in the clastic component of both raw clay types. The other minerals of a clastic part cannot be determined by thermal analysis since usual feldspars (plagioclase and potassium feldspar) are resistant to temperatures up to 1200°C and do not show thermal effects in the studied temperature range [Papadoloulu et al., 2006]. The thermal analysis results place an upper limit on the firing temperature of both samples, namely calcite decomposition temperature. For additional information on the raw clay composition - the type of phyllosilicates and clastic minerals, as well as to determine the lower firing limit, it is necessary to combine thermal analysis with FTIR and be supported by PXRD analysis. That defines the set of methods - thermal analysis supported by PXRD and FTIR as a powerful method for ceramic investigation.

Funding

This work was funded by the Bulgarian Science Research Fund (grant number KP-06-N39/9) (I.D., B.K.).

Acknowledgments

The authors are grateful to the Board of Trustees of NBU. This work is part of a bachelor's thesis (K.M.) developed in the Department of Natural Sciences.

Author contributions

K.M. and B.K. wrote the manuscript, which was read, revised and approved by all co-authors. The analyses were made by I.D.

Conflict of interest

The authors declared no conflict of interest.

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