

Simultaneous Thermal Analysis

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Porcelain Clay Analysis using the STA 8000 Simultaneous Thermal Analyzer

Introduction

In a process known for millennia, clay is heated to yellow heat where the components are transformed in a series of processes, as the “mud” is transformed into a useful vessel, or a beautiful piece of art. Whether a porcelain clay formulation is being used in the production of a commercial product, or an artistic

creation, the ceramicist needs to ensure the quality of the finished product, and this depends in part upon the chemical and physical behavior of the formulation during the firing process. For example, in the firing of a porcelain clay object, such as shown above,¹ the physical and chemical properties of the clay formulation determines whether the structure slumps as it is fired, whether there is cracking around sharp edges, and whether the final product is bright and translucent. So what can thermal analysis in general, and Simultaneous Thermal Analysis (STA) specifically, tell us about such a clay formulation and about the firing process?^{2,3,4}



Figure 1. STA 8000 Simultaneous Thermal Analyzer.

The Technique

STA analyzes the weight change and transfer of energy to or from a sample while subjecting it to a controlled temperature and atmosphere. The STA 8000⁵ (Figure 1) offered by PerkinElmer Inc., combines the wide temperature range of a differential thermal analyzer (DTA), with the sensitive weight measuring capability of a microgram-capable thermogravimetric analyzer (TGA). The sample size varies from a few milligrams to a fraction of a gram; and the temperature range from ambient to 1600 °C, well above the firing temperature of the clay. For the data displayed here the conditions were typical, namely, the heating rate was 10 or 20 degrees per minute. Sample size was in the range of 50 to 150 milligrams, and the atmosphere was air diluted with nitrogen.

Determination of kaolinite

A typical analysis by STA of a dried porcelain clay can be seen in Figure 2, which shows the weight loss change on one axis, and on the other axis the heat flow, using the conventional DTA and Heat Flux DSC convention of endothermic (energy absorbing) activity in the downward direction.

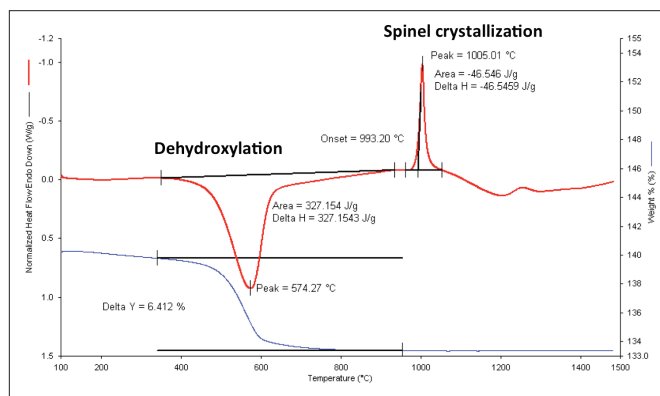
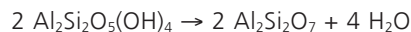


Figure 2. STA of a dried porcelain clay.

The initial endothermic weight loss process is due to the dehydroxylation of kaolinite to form metakaolinite by the process:



In the STA, quantifying this transformation allows relative determination of the kaolinite, the primary component in the porcelain clay formulation. This was done by comparison to a similar analysis of commercially refined kaolin. The weight loss of the porcelain clay yields a weight loss of 6.4% while that of the commercial grade kaolin the thermal curve of which looks qualitatively the same as that in Figure 1, gave a dehydroxylation weight loss of 12.7%. From the two weight loss calculations we determine that the percent commercial grade kaolin in the clay formulation in Figure 2 is 50.5%.

Alternatively, we could make the determination from comparing the STA dehydroxylation heat flow peak area data. From the ratio of the DSC peak areas the kaolinite analysis yields 51.9%. For these calculations an instrumental baseline was subtracted after having been generated by rerunning the method with only an empty capsule in the STA.

Again with reference to Figure 2 can be seen on the heat flow curve the exothermic peak due to a crystallization event that produces a spinel, an ordering of the substantially vitreous mixture into a crystalline lattice. Other exothermic events visible above 1200 °C in Figure 2 correspond to the formation of mullite and cristobalite, of interest to the ceramics industry.

Other major components of a dried porcelain clay formulation include silica, SiO_2 , known in its common crystalline form as quartz, and in its amorphous (non-crystalline form) as amorphous silica, commonly called glass, for example, window glass. Also in the formulation is another mined family of minerals, feldspar, which has the chemical composition: $\text{X-Si}_3\text{O}_8$, where X is sodium, calcium and/or potassium. Figure 3 shows STA data for the three refined components (not reagent pure) that, together with low composition additives, make up the porcelain clay formulation. Although the weight curves are not shown in this plot, from these analyses one can see that silica and feldspar show no weight loss other than from absorbed water.

Determination of silica

The silica shows the characteristic “inversion” peak at 573 °C which corresponds to the crystal lattice change in heating from the trigonal “alpha” form to the hexagonal “beta” form. From Figure 3 can be seen that this transition is reversible – the top blue curve is from the cooling data – provided the silica has not been heated up to the point of reaction with another component. The heat flow peak in silica is usually not observed in the STA thermal

curves of most clays because it is eclipsed by the much stronger dehydroxylation endotherm. However, the amount of crystalline silica in a clay formulation can be estimated by cooling and re-running the sample after heating it sufficiently to allow the dehydroxylation reaction to go to completion.

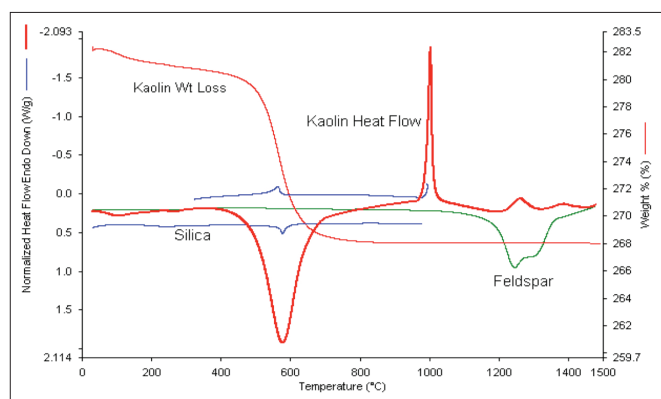


Figure 3. Three main components of porcelain clay run individually.

Figure 4 shows the heat flow signal from heating silica (top curve) and a cone 10 glaze after heating to 800 °C to eliminate the endothermic effect of dehydroxylation. Making certain assumptions, one can use the energy change of the solid-solid transition to determine the relative amount of silica in the formulation by comparison to the peak area of the silica sample. Here the calculation indicates 23% silica in this glaze.

A possibly relevant consideration here is that finely ground silica may have an amorphous content which in other finely ground crystalline materials can be detected by the change in specific heat capacity over the glass transition (T_g) region, where the amorphous solid softens. However, as can be seen in Figure 5, SiO_2 's T_g (as seen in a window glass sample also run in the STA 8000) closely overlaps the crystalline quartz inversion region where there is also a change in specific heat capacity, so the separation between amorphous and crystalline content is difficult.

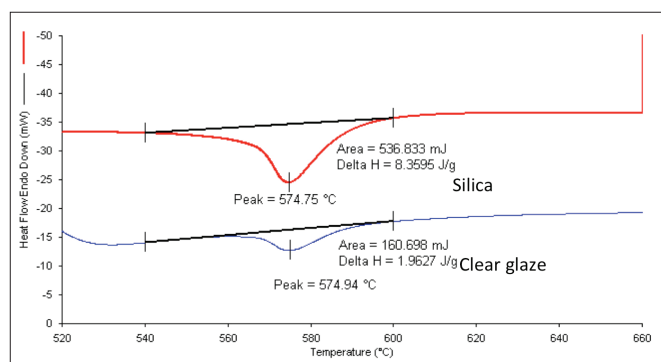


Figure 4. Inversion of SiO_2 in commercial silica and in a cone 10, clear glaze after heating to 800 °C.

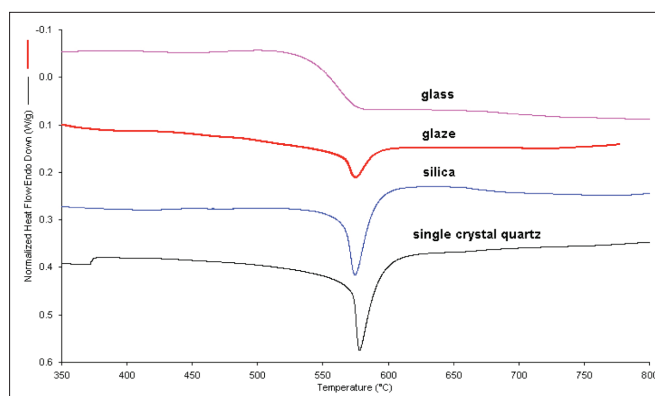


Figure 5. Thermal curves of SiO_2 in window glass, unfired ceramic glaze, commercial silica and single quartz crystal.

Detection of T_g of vitreous phases

For a clear glaze and for a translucent ceramic porcelain piece one would expect that a primary component would be amorphous, where crystallites are not scattering incident light. Figure 6 shows two STA heat flow curves for the first and second heat of the glaze sample of Figure 4. On the second heat after the sample has been heated to 1300 °C (roughly corresponding to cone 10 to set the glaze, i.e., to allow the components of the glaze to react and produce the amorphous phase desired for the ceramic finish), one sees an event which is a glass transition (T_g). The softening point of the vitreous component is indicated by the increase in the specific heat capacity, i.e., an endothermic shift in the heat flow curve, as the post-fired material is reheated in the STA. That this is truly a T_g and softening point was confirmed by running the sample by thermomechanical analysis in penetration mode.

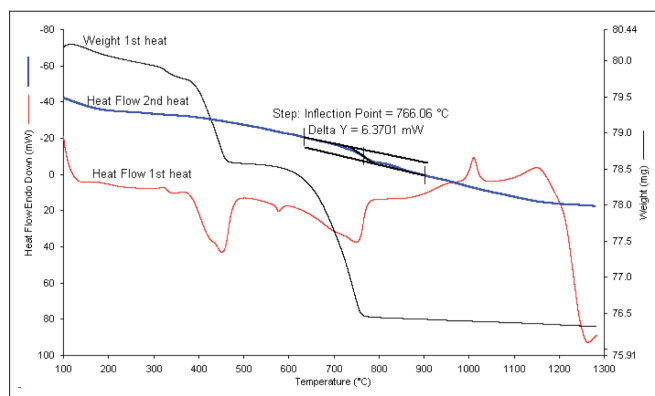


Figure 6. Glass transition in clear glaze after heating to firing temperature.

For the ceramic artist a thrown piece with a high amorphous content sitting in the kiln above T_g is likely to "slump", i.e., slowly flow under the pull of gravity. Another piece with the same nominal content but a different thermal history, a different time-temperature profile, may have a lower amorphous content, or a higher T_g , and thus be less likely to "slump".

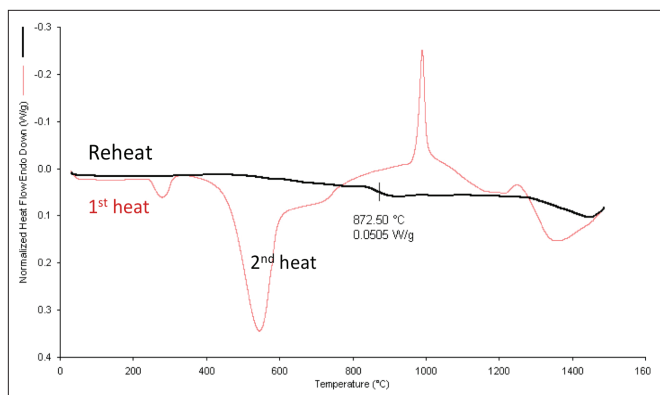


Figure 7. STA heat flow data of a translucent porcelain clay showing an apparent Tg on the reheat data.

Is it possible to detect Tg in a ceramic clay using the STA to heat the ceramic after firing? To find out, a clay known for producing translucent porcelain was “fired” in the STA and the results analyzed. Figure 7 shows the STA heat flow of the first and second heat with an indication of a Tg at 872 °C. Notice that the Tg is much higher in temperature than that for the glaze material. It is well known in potting circles that the glaze must be matched to the clay body to avoid crazing. This can be understood by the fact that the coefficient of thermal expansion changes going through the glass transition region, and a change in the differential expansion of the two layers could certainly lead to stresses in the piece. One could guess that matching the Tg of the clay to that of the glaze would lead to a more compatible combination. It is also known among polymer researchers that the glass Tg of a compatible polymer blend can be shifted higher or lower by the addition of components that dissolve in the blend.

Conclusions

There are many ways the STA can be utilized to elucidate the processes taking place in the firing of clay. From the observed weight loss profile one can follow dehydroxylation and carbonate decomposition. The kinetics of these reactions can be quantified. Melting and crystallization can be detected from the heat flow data. Furthermore, the observed glass transition can indicate the temperature range where amorphous phases are softening.

In conclusion, this technique is a viable tool for commercial ceramics formulators and users to better understand the firing processes and to control the quality of the raw materials. The small size, low cost and ruggedness of this sensitive STA analyzer makes it a good fit for both commercial and educational settings.

Moreover, thermal analysis of clay offers an overlap between art and science that could be exploited at universities and trade schools to introduce artistically inclined students to concepts of chemistry, thermodynamics, and kinetics.

References

1. “Flame Vessel” by Jennifer McCurdy, co-author; photo by Gary Mirando.
2. C.M. Earnest, in “Compositional Analysis by Thermogravimetry”, ASTM® STP 997, C.M. Earnest editor, ASTM®, Philadelphia, October 1988, pp 274-277.
3. C.M. Earnest, Perkin-Elmer Thermal Analysis Application Study TAAS 30, “The Application of Differential Thermal Analysis and Thermogravimetry to the Study of Kaolinite Clay Minerals”, Norwalk, CT, 1980.
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5. PerkinElmer STA 6000/8000 Brochure Order No. 010452_01