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The contribution of thermoanalytical techniques to the conservation treatment of cuneiform tablets in the British Museum

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Abstract

The British Museum's collections contain artefacts composed from almost the whole range of materials known to mankind prior to this century. For more than 70 years, analysis has been a vital tool in the conservation of the museum's collections and recently thermoanalytical techniques have been shown to complement techniques existing within the museum's laboratories. Their major contribution to date has been in a project re-examining the firing process used as part of the conservation of an important collection of unfired clay tablets bearing cuneiform script from ancient Mesopotamia. Differential scanning calorimetry (DSC) has shown that the 130 000 plus tablets from 22 major sites should be treated with the same firing schedule. Together with thermogravimetyric analysis (TGA) and thermomechanical analysis (TMA), the results have indicated several beneficial modifications to the present firing schedule, the most important being the lowering of the firing temperature to avoid a damaging calcite decomposition reaction.

Keywords: Cuneiform tablets; Firing temperature; Thermoanalytical techniques; British Museum collection; Conservation treatment

1. Introduction

The collections of the British Museum number in excess of six million objects and encompass artefacts made from almost every material utilised during human history. This presents many challenges for their continued preservation and conservation. The nature of such problems can be highly complex, the materials and construction methods of artefacts are often not well characterised and their nature can be altered dramatically by many centuries of burial or interaction with the environment. Sir Alexander Scott first applied scientific analysis to the museum's artefacts in order to solve conservation problems in 1919. Instrumental analysis plays a vital role in the characterisation of materials, deterioration processes and the testing, development and evaluation of conservation treatments. Whilst the museum's laboratories are relatively well equipped and its scientists have extensive experience of the application of many techniques to conservation and archaeometric studies, the introduction of techniques from other fields offers new and exciting opportunities.

Thermoanalytical techniques were first applied in the museum to the study of busts, by the artist Roubiliac, which were undergoing repair and cleaning [1]. Analysis had identified that several busts undergoing a cleaning treatment were formed from the clays kaolinite and illite. The degree of firing of the clay was of

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vital importance as unfired clays would react very adversely to water based cleaning treatments. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) indicated that the busts had only undergone low temperature firing and non-aqueous cleaning methods were employed.

Recently thermogravimetric analysis has assisted in characterising a novel pale blue corrosion product affecting Egyptian copper alloy statuary and tools [2]. The technique was applied to determine the acetate to carbonate ratio in a previously unidentified sodium copper acetate carbonate corrosion product.

An involved study improving the firing treatment for cuneiform tablets is nearing completion. This joint project with the Thermal Methods and Conservation Science Laboratory at Birkbeck College, University of London, has utilised three techniques to characterise the thermal behaviour of the tablets during firing and to modify the schedule to minimise damage. This paper reports the results of this study as an illustration of the contribution that a well suited instrumental technique can bring to the often involved problems of artefacts' conservation.

2. Cuneiform tablets

Cuneiform tablets were formed by incising script onto unfired clay and an example from the site of Sippar in present day Iraq and dated between 630 and 450 BC is shown in Fig. 1. They document many important aspects of the ancient Mesopotamian culture. The British Museum has a collection in excess of 130 000 tablets, which originated from 22 major sites. The collection forms an important archive for scholars of ancient Mesopotamia and is intensively studied by over 250 visitors each year on top of the research undertaken by the museum's academic staff. In order

Fig. 1. Cuneiform tablet detailing sale of land, from Sippar, 630–450 BC. ©The Trustees of The British Museum.

Table 1
Firing schedule used for conservation of cuneiform tablets

	Start temperature (°C)	Heating/cooling rate (°C/h)	Finish temperature (°C)	Soak time (h)
Stage 1	20	19	150	48
Stage 2	150	50	740	2
Stage 3 (cooling)	740	29	20	0

to read the complex script researchers need to handle the tablets and rotate them so that the different lighting angles reveal the script for translation. This intensive handling, coupled with the weakening action of soluble salts existing in high concentrations in some of the tablets, means that many of them require strengthening before they can be safely studied. The conservation process involves firing using the schedule shown in Table 1, followed by desalination in running water to reduce the soluble salt concentrations in the tablets. This process would only be considered for the conservation of other artefacts in extreme circumstances as it irreversibly alters the nature of the material. The over-riding importance of the text on the tablets and the necessity for handling has led to an acceptance for this treatment for these objects. The changes brought about by firing would not interfere with the techniques which would presently be employed for provenancing studies. These are based on techniques developed for the study of pottery, which has obviously undergone firing already. The firing process is known to have adverse effects on some tablets. Firing can open existing cracks and delaminations in tablets or disrupt their surfaces. Surface disruption is particularly damaging in this instance as it can lead to loss of text and information. The aim of this project was to determine if just one firing schedule was appropriate to all tablets in the museum's collections, which, originating from 22 sites, may have been made with different clays. An assessment of the present firing schedule was important to devise a schedule or schedules that are as sympathetic to the tablets as possible and to minimise any of the types of damage described previously.

3. Experimental

Samples from standards and tablet fragments used in the initial trial were ground and the sieve fraction 200 (120 μm) to 100 (256 μm) was analysed. Samples from cuneiform tablets were taken by drilling using a 0.8 mm drill bit from an actual tablet. Sample characterisation was performed using a combination of thermal and X-ray analytica techniques. A Phillips X-ray diffractometer, and a Joel 840 scanning electron microscope with energy dispersive X-ray analyser Oxford Instrument link GEM detector with SATW windows were used as the X-ray analysis. Shimadzu DSC50, TGA50 and TMA50 analysers were used for the thermal characterisation. Samples were heated in alumina crucibles at 10°C/min in N_2 purge gas (20 cm^3/min). A separate TGA experiment was also performed to simulate the firing schedule used in the kiln (Table 1).

TMA was undertaken using two solid pieces of tablets that had become detached. Each piece was worked with a hand file to produce two flat, parallel surfaces which were placed directly under the quartz probe. The pieces, were then analysed with a Shimadzu TMA50 using a heating rate of 3 K min^{-1} between 20 and 500°C and with a 1 g applied load (10 mN) on a quartz probe (3 mm diameter) on the sample.

3.1. Initial trial by DSC and TGA

A number of tablet fragments with no text and hence of no academic value were supplied by the Department of Western Asiatic Antiquities of the British Museum for an initial trial by TGA and DSC. Typical TGA and DSC curves obtained are shown in Fig. 2. The thermal events labelled will be discussed at a later stage in this paper. Large samples could be removed from these fragments. In fact they had already been used to undertake petrographic, sedimentation, and X-ray diffraction studies to characterise the tablet material. TGA analyses were performed using a heating rate of 10 K min^{-1} from 20 to 800°C. A Shimadzu DSC50 was also used with

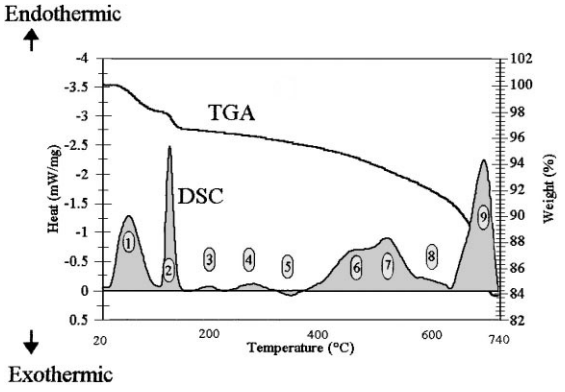

Fig. 2. Typical TGA and DSC curves of cuneiform tablets (Group A).

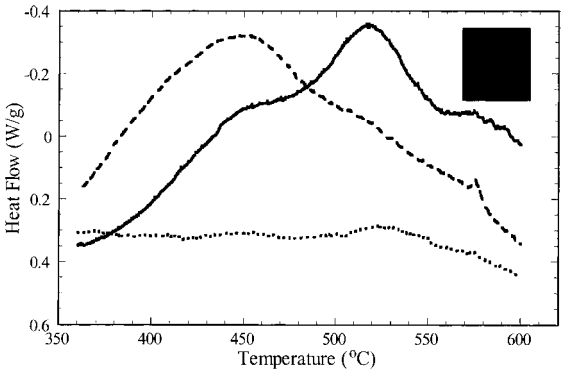

Fig. 3. 360–600°C region of DSC showing three groups identified in cuneiform tablets.

the same experimental parameters, except that the maximum temperature used was 700°C. The initial trial optimised experimental parameters and enabled the sample size to be reduced to 3 mg. The larger fragment size enabled repeat analyses to be performed which gave reproducible data. This sample size was removed using a 0.8 mm drill bit from an actual tablet without causing unacceptable disruption to the tablet's surface.

3.2. DSC of provenanced tablets

The museum's tablet collections were purchased and not excavated and hence have no reliable documentary provenance information. However, the text on some tablets identifies that they were produced at a particular site. A number of such tablets were sampled by drilling into broken surfaces and the samples analysed with DSC as before. Multiple tablets from two sites, Sippar and Ur were analysed to determine the variation within sites. The analyses showed the same set of major transitions, but the sites could be placed into three groups separated by the relative intensities of transitions in the 360–600°C temperature range, shown in Fig. 3. The sites analysed and their groupings are shown in Fig. 4.

Group A had an exotherm at 350°C (labelled 5, Fig. 2), a medium intensity endotherm at 450°C (labelled 6, Fig. 2) and a stronger endotherm at 520°C (labelled 7, Fig. 2) and comprised of tablets from the southern sites (Fig. 4). This group contained both Sippar and Ur. The endotherms are shown in an enlarged version in Fig. 3. One of the tablets from Ur did not show a 350°C exotherm. The presence and intensity of this transition was found to be dependent on the concentration of iron present (as iron oxide) in the tablets. Fig. 5 shows a strong correlation between the iron oxide concentration, (determined as wt% FeO by X-ray analysis) and the enthalpy values of this exotherm.

Group B showed a strong endotherm at 450°C with a weaker 520°C endotherm appearing as a shoulder (Fig. 3). This group was composed of tablets from the northern site of Nineveh and the trading centre of Kanesh in Anatolia (Fig. 4).

Group C showed only a very weak endotherm at 520°C (Fig. 3). This material had undergone previous strong heating which had effectively destroyed the majority of the thermoanalytically accessible information present. Such heating could have been the result of a fire in antiquity and several tablets do appear to have been subject to burning. The archive at Nineveh was reported to have burnt in 600 BC. It was also common practice to 'fire' tablets on site after excavation in purpose built kilns. The majority of the museum's collections was purchased before 1940 and it is impossible to know whether firing has occurred as they have little or no associated documentation. Such firings were likely to have been poorly controlled and would only rarely have produced the robust properties that can be achieved with the present conservation method.

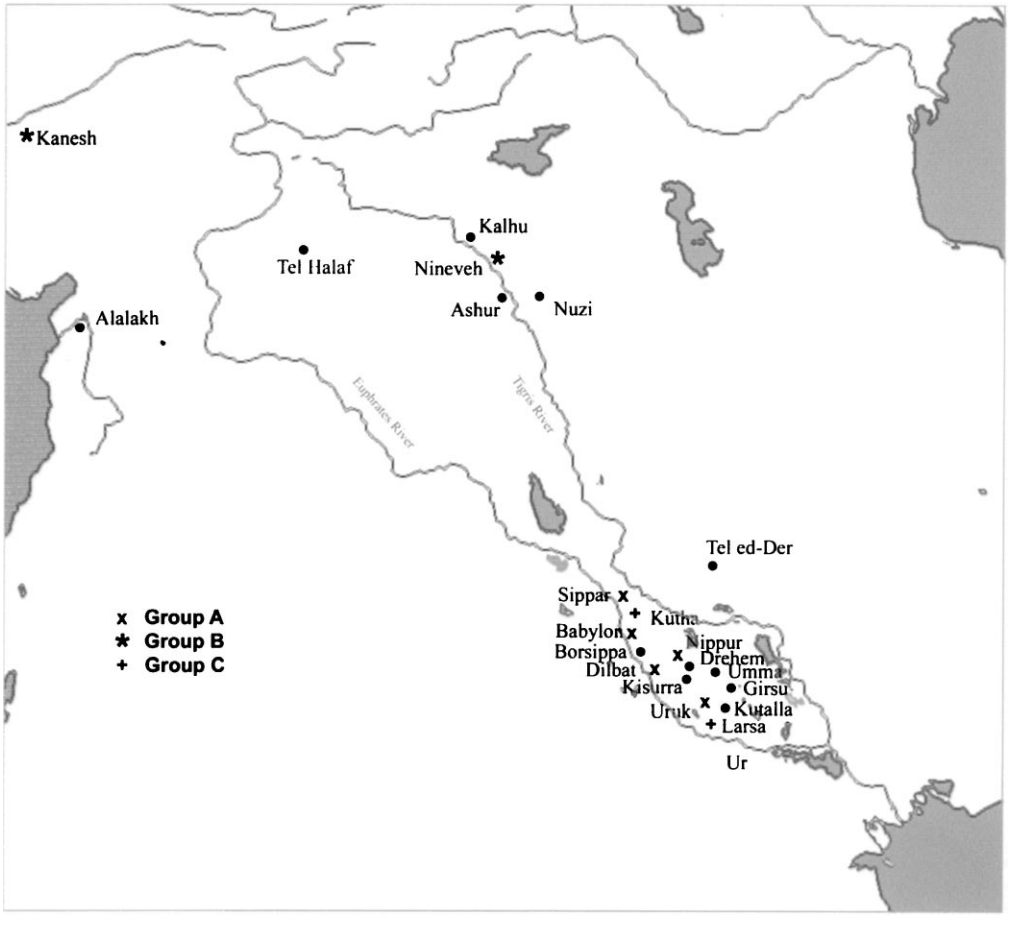

Fig. 4. Map showing provenance sites for The British Museum's collections of cuneiform tablets and their thermal groupings.

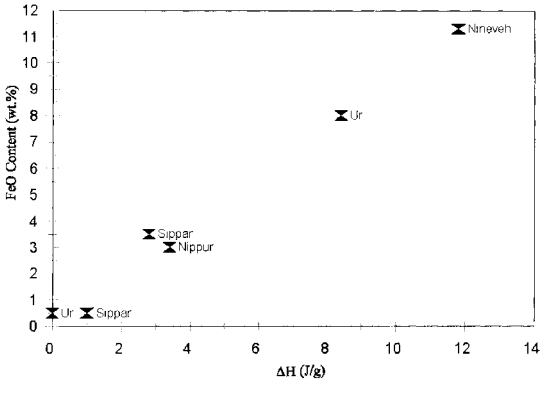

Fig. 5. Graph of iron concentration analysed in tablets against area of endotherm at 350°C.

3.3. Assignment of thermal transitions observed in the cuneiform tablets and assessment of their damage potential

The previous section described the observed transitions in the cuneiform tablets. In order to assess or modify the firing schedule some degree of knowledge about the reactions occurring is required. The materials present in the tablets have been previously reported in another paper [3], Characterisation was made on the basis of data collected on available standard samples. Table 2 shows the standard materials investigated. Three samples of palygorskite, obtained as clay minerals, were investigated. These will show variation in their chemical composition, with substitution and ion

Table 2
Standard minerals analysed[a]

Mineral	Source	Supplier	Additional minerals Detected	Elemental analysis (weight% as oxides)						
				Na_2O	K_2O	MgO	Al_2O_3	SiO_2	FeO	CaO
Palygorskite	Seaton, UK	Mikon GMBH	Calcite	2.0	1.6	7.2	15.9	51.5	2.1	18.9
Palygorskite	Kank, Croatia	Mikon GMBH	Calcite	2.0	3.2	7.8	14.4	50.0	11.1	9.4
Palygorskite	Poldolk, Russia	Mikon GMBH	Calcite	1.4	4.4	8.3	15.9	52.9	8.1	7.4
Albite	Unknown	University College, London	None	11.6	0.0	ND[b]	20.4	67.1	ND	0.3
Orthoclasse	Unknown	Unviersity College, London	None	3.7	11.4	ND	19.9	64.3	ND	0.2
Amphibole 1	Unknown	University College, London	None	12.3	0.3	20.2	13.0	53.0	ND	1.0
Amphibole 2	Unknown	University College, London	None	6.7	ND	0.4	21.6	47.3	16.5	6.9
Tablet 1	Sippar	–	Various, see text	2.8	2.5	8.6	16.9	54.1	3.5	10.2
Tablet 2	Nippur	–	Various, see text	3.1	1.7	9.1	14.6	47.1	3.0	16.6
Tablet 3	Ur	–	Various, see text	1.4	2.8	14.2	10.9	46.8	8.0	7.3

[a] Analysis errors: $< 1 \pm 10\%$ value; $1-5 \pm 5\%$ value; $> 5 \pm 2\%$ value.
[b] Not detected.

exchange, which will also influence their thermal behaviour. The identity of the standards was verified using a Phillips X-ray diffractometer, XRD, and Joel 840 scanning electron microscope with energy dispersive X-ray analyser, SEM–EDX. TGA and DSC curves of the Seaton palygorskite samples showed two endothermic peaks at 120 and 180°C, respectively. In TGA this corresponded to a small weight loss of about 0.5%. The two endothermic peaks have been previously reported at higher temperatures (180 and 280°C, respectively) with higher mass losses [4] and peaks being assigned to loss of water in the channels of the structure and of some bound water. Variation in the composition of the clays may result in the lower values observed here. A further endothermic peak in the range 350–600°C was also observed, as previously reported, and this has been assigned to the loss of the remaining bound water together with water the hydroxyl groups. These features with the supporting data from the other techniques confirmed that the clay mineral present was palygorskite and this was dominating the thermal behaviour of the tablets. Calcite was also shown to be present in all three of the standard samples of palygorsite by DSC and TGA (endothermic peak after 600°C together with weight loss ca. 30% measured between 600 and 710°C). High calcium concentrations were also recorded (see Table 2).

The changes occurring during the heating of palygorskites and sepiolites may in general be classified as follows [4]:

1. loss of water molecules (endothermic);
2. dehydroxylation of the lattice (endothermic);
3. collapse or transformation of the lattice (endothermic);
4. crystallization of new phases (exothermic).

The size of the effects obtained for loss of water and dehydroxylation are not only proportional to the amount of water evolved but are dependent on the location of water molecules and hydroxyl groups in the structure. Consequently interpretation of the DSC curve must be supported by information obtained from other techniques, e.g. TGA and TMA.

Representative tablet DSC and TGA curves marked with the assigned transitions previously shown in Fig. 2 will now be further discussed.

(a) The endothermic transition at around 60°C (labelled 1) has not been reported explicitly in the literature. Bradley has stated that water molecules in the channel-like interstices of the structure of palygorskites are lost below 100°C, but the exact temperature of this is not clear [5]. The 60°C transition was shown by one of the standard palygorskite samples. A small, accurately weighed sample of clay was placed in a well-sealed enclosure with a relative humidity probe. This was then placed in an oven at 60°C. The relative humidity rose from 10 to 65%, which is equivalent

to 0.19 mg of water expelled as vapour, or 1.87% of the original sample weight. This compares reasonably well with the 2% weight loss measured by TGA for this transition observed in both samples from cuneiform tablets and in some of the palygorskite samples.

(b) The transition at around 130°C (labelled 2) could be due to several possible reactions. The peak was quite sharp, unlike the broader peaks expected from physically adsorbed water. Likely reactions for this material would be dehydration of gypsum or calcium oxalate. The presence of calcium oxalate in the tablets was ruled out by the lack of oxalate peaks in ion chromatograms (Dionex DX100 with AS12 column and 18 mM Na_2CO_3 and 22 mM $NaHCO_3$ eluent) in either water or dilute acid extracts of tablet samples. Up to 2% sulphate was detected by SEM-EDX in some tablets and an association with calcium was also observed in some, but not in all of these samples.

(c) The transitions at 185 and 280°C are reported to be due to loss of bound water from palygorskite and that at 280°C due to loss water in the channels [4].

(d) The transition at 350°C is due to an iron species, as already shown. No obvious endotherm could be discerned just prior to the exotherm which would have indicated that the iron was present as the γ-hydroxide lepidocrite FeO(OH). The exothermic effect was caused by the transition of γ-Fe_2O_3 into α-Fe_2O_3 [6,7].

(e) The endotherms at 450 and 520°C are due to the dehydroxylation of palygorskite [5,8,9]. Above 400°C the crystal lattice contracts and the structure will no longer rehydrate after heating above 450°C [8].

(f) Weak, sharp endotherms were observed in several of the samples at 573°C as can be seen in Fig. 3 (sample B). Petrological examination and SEM-EDX had identified a sparse amount of fine grained quartz in some of the samples. Despite the volume % increase associated with this transition, it would not pose a significant risk of damage during firing because of the low concentration, small size and highly dispersed nature of the quartz present.

(g) The endotherm at the highest temperature was due to calcite decomposition. This was the most variable transition in terms of temperature and began between 635 and 680°C. It was the strongest endotherm and greatest weight loss observed, up to 12.3%, which is equivalent to 31% by weight of calcite present, assuming a calcite to calcium oxide decomposition. XRD analysis of a sample fired to 630 and 700°C verified the loss of calcite and production of calcium oxide. The calcite decomposition will generate large volumes of carbon dioxide gas in some tablets, which can cause high internal pressures and hence damage. Lime blowing, the reconversion of calcium oxide to calcium carbonate via calcium hydroxide by reaction with atmospheric moisture and carbon dioxide has not been observed as a damage mechanism on cuneiform tablets. Whilst such damage may be expected from the amount and large particle size of calcite in some tablets, it should be borne in mind that the regenerated calcite has only the same volume of the original (although this is 20% greater than that for the calcium oxide). The tablets are not fired to a great deal higher temperature than that of the calcite decomposition and do not undergo significant further shrinkage, unlike ceramics in which lime blowing is frequently reported.

3.4. TMA

As previously mentioned TMA was also undertaken with two solid pieces of tablets that had become detached. The results are shown in Fig. 6. The curve features an initial shrinkage up to 80°C, after which thermal expansion of the material was observed. Above 400°C the material began to shrink which is in keeping with the dehydroxylation effects shown in Fig. 2 (labelled 6 and 7) and this continued to the extent of the temperature range used.

3.5. Simulation of firing conditions by TGA

Since the temperatures at which reactions are observed depend strongly on experimental parameters, an experiment was undertaken to try and compare the results obtained from conditions used for the previous experiments with those used obtained in the kiln during the firing protocol used in conservation treatment. One of the samples from the tablets,

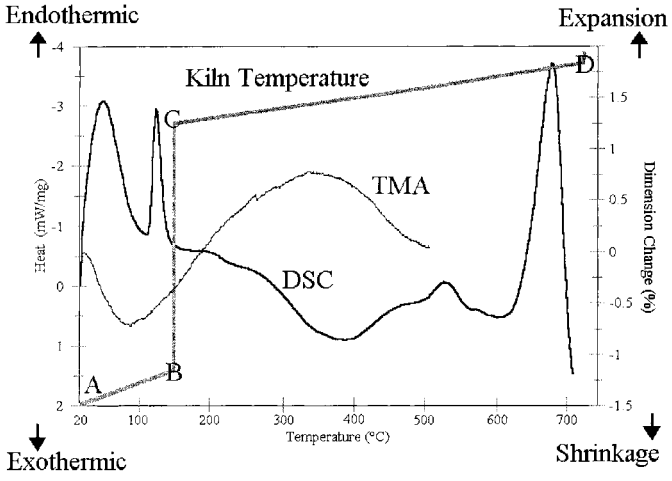

Fig. 6. DSC and TMA curves superposed over temperature programme of firing schedule.

with no text, analysed in the initial trial, was analysed using the heating schedule used in conservation treatment with no carrier gas and the ends of the furnace bunged with refractory mineral wool to mimic the closed atmosphere of the kiln. The alumina crucibles used for the experiment probably had similar heat conduction characteristics to the white ware saggars used to fire the tablets and would act in a similar manner for the tolerances of this experiment. A low heating rate (0.3°C/min) was used to simulate the firing conditions. The temperature programme used is shown in Fig. 6.

4. Ramifications for the conservation firing schedule

The differences detected between the groups of tablets are not significant and can be accommodated by a single, well designed, firing schedule. They mainly involve different intensities or the absence of peaks. Fig. 6 shows the present firing schedule superimposed with DSC and TMA data. The following points were drawn from the thermal analysis:

- The initial slow heating rate (19°C/hr) is appropriate because of the low temperature endotherm and shrinkage observed in TMA.
- The first soak temperature (marked B—C on Fig. 6) should be reduced from 150 to 140°C. The endotherm is complete by 140°C and shrinkage has stopped.
- In an average batch of tablets only approximately 0.5 l of water is removed at this temperature, hence the first soak period should be reduced from 48 to 24 h. The TGA experiment which simulated the conservation heating schedule did not show further weight loss during this soak period.
- 50°C/h heating rate is appropriate to allow the observed shrinkage and weight losses to occur gradually, thus minimising the damage. The firing temperature should be lowered to 630°C to avoid calcite decomposition reaction.
- The second soak period (marked D—E on Fig. 6) should be extended to 4 h to compensate for lowering the firing temperature.

The new firing schedule has been extensively tested using the tablet fragments without text. The physical properties of fired tablets were also determined and compared to those fired with the old schedule. A small reduction in strength and Vicker's hardness was observed. This was due to glass formation which occurred between 690 and 740°C. The 630°C firing temperature produced tablets that were considered sufficiently robust to undergo the anticipated handling without damage. No differences were observed in resistance to water immersion between tablets fired to 630°C and those fired to 740°C. Trials are underway to test the new firing schedule with actual tablets.

5. Conclusions

Thermoanalytical techniques provide an extremely useful adjunct to more widely accepted analytical techniques in the study of conservation problems encountered with inorganic materials. They are particularly and uniquely suited to the study of previous heat treatments; and development and optimisation of new firing schedules. This is illustrated by their extensive development and use by the ceramics industry. They have made a very significant contribution to advances in the conservation of cuneiform tablets, which would not have been possible without their application.

Acknowledgements

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