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THERMOANALYTICAL MEASUREMENTS IN ARCHAEOMETRY

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INTRODUCTION

A variety of analytical methods - both chemical and physical - are applied in the area of archaeological investigations on ceramincs, glass, pigments, paper and other materials [1]. They all try to find the answers to questions such as: when and by whom was the material or object made and used; which were the raw materials and the technological processes; were there any environmental effects or changes? Basically, detailed characterization of the materials is required with respect to chemical and phase composition, microstructure and various physical properties. The choice of a specific technique is usually governed by its availability and cost, by its speed and accuracy, by the degree of damage to the specimen, by the type of material and the properties and elements to be determined. Most studies require the combination of several and quite different techniques for useful conclusions. The present paper demonstrates that also thermoanalytical methods combined with x-ray and mass spectrometry may be very useful in such archaeological investigations.

EXPERIMENTAL TECHNIQUE

For experimental investigations on ancient materials destructive methods can be tolerated only if they are sensitive and therefore require very small amounts of material. This is the case for x-ray and MS but also for the special thermoanalytical instrumentation (Mettler TA3000) which was used in the present studies. This new measuring and evaluation system is composed of a basic processor unit and several measuring cells for DSC, TG and TMA. The data acquired during these thermal analysis are held in a working storage which is accessible for the subsequent evaluation.

NABATEAN POTTERY

The typically painted Nabatean ceramic was manufactured within the first century B.C. and A.D., the period in which many of the famous rock tombs and monuments were created around Petra and Hegra [2]. A variety of fragments of this thin-walled ceramic is studied with re-

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spect to the phase composition and to the thermal behavior. Two of these samples with quite different chemical composition (table 1) will be briefly discussed. The x-ray patterns of these samples are shown in fig. 1. The Fe_2O_3-rich and CaO-poor sample 25 contains only quartz as crystalline phase. The typical red-brown color of this ceramic is due to the use of iron-rich clays for its manufacture. Heating this sample for 1 hour at

Fig. 1 X-ray photographs (CuK) of Nabataen pottery samples

900° C and at 1000° C did not cause any changes of the x-ray pattern or color. After heating at 1100° C, crystallization of mullite and cristobalite was observed with a decrease of the quartz content. The DSC, TG and TMA-analysis of this sample (fig. 2, left side) proved that exothermic reactions with weight loss (carbonaceous residues?) occur at around 300° C and 500° C, followed by the endothermic quartz transformation at 573° C. Strong sintering with corresponding deformation (see TMA) starts above 900° C. A completely different behavior was found for sample 26, which has a high concentration of CaO and also MgO, but much less SiO_2 and especially Fe_2O_3 in comparison to sample 25. The x-ray pattern (fig. 1) shows the presence of the following crystalline phases: quartz, augite (pyroxene), plagioclase and gehlenite. Again there was no change in phase composition after heating to 900° C and at 1000° C. Heating this cream-colored strong ceramic material at 1100° C caused the disappearance of gehlenite and a strong increase of the plagioclase concentration, whereas the pyroxene phase did not change significantly. Formation of mullite could not be observed. The DSC and TG-curves (fig. 2, right side) are somehow similar to those of sample 25, but the TMA-curve proves that this ceramic does not show any shrinkage due to secondary sintering up to at least 1000° C. These preliminary results suggest that a $CaCO_3$-rich clay was used in the manufacture of this material and that the firing temperature was higher than for the other material (sample 25) but probably not much above 1000° C.

Nabataen Ceramic	Loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	TOTAL
NC 25	1,77	61,18	22,30	8,50	1,48	0,36	0,83	2,89	0,74	100,03%
NC 26	2,86	49,99	20,96	1,80	0,71	17,63	3,07	2,17	0,58	99,78%

Table 1

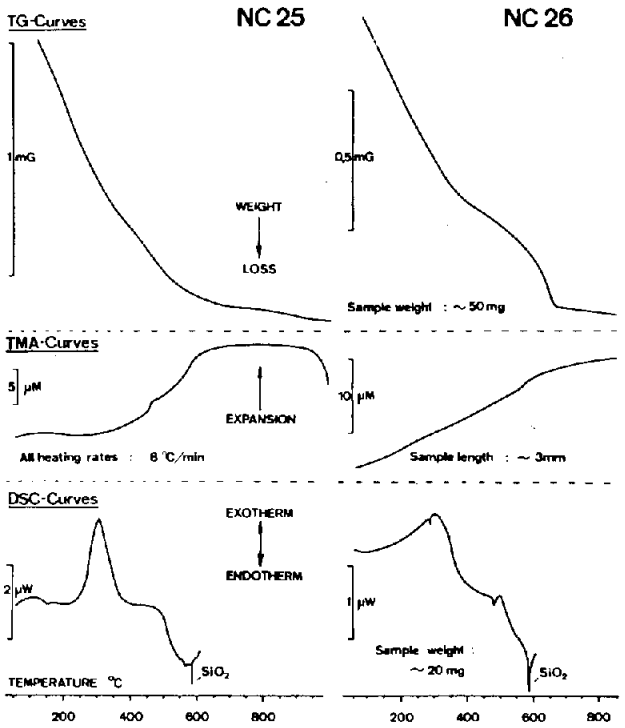

Fig. 2 DSC-, TG- and TMA-curves of Nabataen pottery

ANCIENT EGYPTIAN PIGMENTS

Many of such coloured materials were produced from natural minerals, however also a wide range of synthetic pigments was used mostly in form of glass frits. This is true especially for the blue pigments which were much in demand, since blue was the colour of the gods. During our research we studied a large number of ancient Egyptain pigments, especially blue ones, from various dynasties [3]. We also had the unique possibility to investigate the original pigments used for decoration of the bust of Nefertiti. These studies proved that the blue pigment of

the bust is indeed the crystalline compound CaCu (Si_4O_{10}) - Egyptian blue - and not a blue glassy frit as assumed by Rathgen. In further investigations we also could find out more details about the experimental conditions for synthesis of this important blue pigment and its thermal stability. Egyptian Blue was in use already during the fourth dynasty in Egypt, i.e. at about 2600 B.C., and was produced in consistent quality for more than 2000 years. For the thermal synthesis of Egyptian Blue we used calcite, malachite (or azurite) and quartz (from Egyptian localities) as the raw materials.

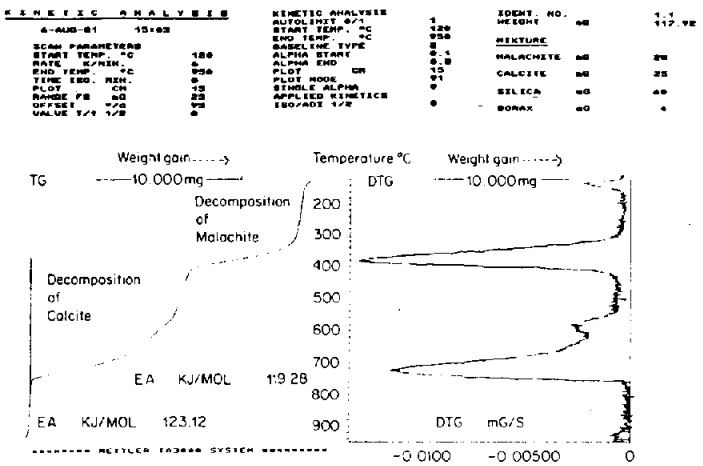

Fig. 3 Thermosynthesis of Egyptian blue, TG and DTG-curves

Four different fluxes were added to the above stoichiometric mixtures, namely borax, papyrus ash, salt or sodium sulfate. Fig. 3 shows the thermogravimetric analysis of the formation of CaCu (Si_4O_{10}) from the mixture limestone/malachite/sand/ borax as an example. The TG curve proves that the decomposition of malachite to CuO occurs at 300 - 400° C, followed by the decomposition of limestone to CaO at 550 - 740° C. The maximum of the reaction rate

Fig. 4 X-ray photographs (CuK) of Egyptian blue: A. Nefertiti (1355 B.C.), B) synthetic (1980 A.D.)

at 380° C and at 725° C respectively can be seen from the DTG. Above this temperature CaO and CuO react with SiO in the presence of the borax flux to form the compound CaCu (Si_4O_{10}). Fig. 4 shows the x-ray patterns of this synthetic Egyptian blue product and of the original blue pigment taken from the bust of Nefertiti. The agreement is obvious and unambiguous. These investigations on the thermal synthesis of Egyptian blue lead to certain conclusions with respect to the mixture ratio, the effect of fluxes, the heating temperature and atmosphere, all of which are important for the intensity of the colour and for the stability of this pigment.

WAX BINDERS IN ANCIENT PIGMENTS

Waxes like beeswax were frequently used as binding media for pigments. This is also true for the black carbon pigment which served for decorating the eyelashes of the bust of the Queen Nefertiti. A suitable method for investigating the type of wax used is DSC which allows to determine the melting point and the heat of fusion. In the previous investigation on the bust of the Queen Nefertiti F. Rathgen assumed that wax was used as a binding medium and quoted a melting range of 60 - 64° C. He did not try, however, to identify the type of wax which might have been used. Fig. 5 shows our DSC-curve of the original wax binder from the bust of Nefertiti. The melting range from 40 - 60° C is in agreement with the values given by Rathgen. The maximum of the melting peak was found at 64,4° C for the original wax binder and at 63,4° C for beeswax. The corresponding heats of fusion were 127.4 J/g and 207 J/g

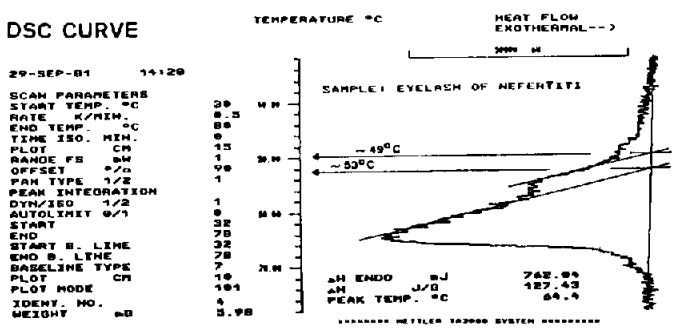

Fig. 5 DSC-curve of the ancient wax sample

respectively. This larger value for fresh beeswax is obviously caused by the high content of volatile components.

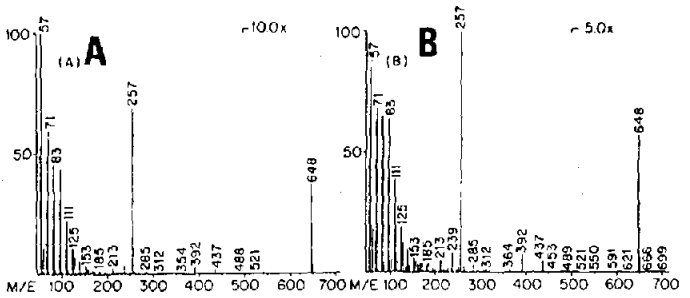

Fig. 6 MS-spectra of ancient wax (A) and of beeswax (B)

Further investigations on this sample have been carried out by means of a Finnigan 4510 quadrupol mass spectrometer equipped with a Carlo-Erba gas chromatograph. Two spectra from the same GC-fraction of the original sample (wax binder from the bus of the Queen Nefertiti) and of beeswax are shown in fig. 6. The similarity of the spectra is obvious, the mass numbers of the original sample correspond to the components typical for beeswax, e.g. higher paraffines, cerotin acid and especially esters of C16-C30 acids and C24-C36 alcohols.

ANCIENT PAPYRI

The application of thermoanalytical methods for differentiation between ancient papyri has been described previously [4]. A further problem encountered with such historic papyri is their overall state of preservation, since they are usually very fragile. Many papyri are in a bad shape mainly due to the effect of fungi. These fungi can be easily identified by means of electron microscopy but it is not possible to use DSC in such studies since there is an overlapping of the peaks of cellulose and chitine of fungi (fig. 7). In addition the swelling behavior of papyri was investi-

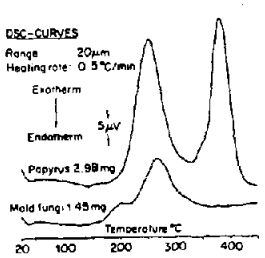

Fig. 7
DSC-curves of papyrus and of mold fungi

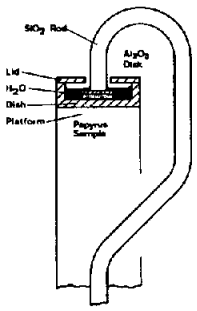

Fig. 8 TMA-cell METTLER 3000

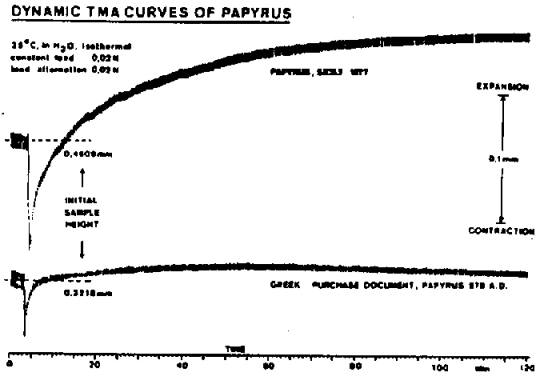

Fig. 9 Swelling behaviour of fresh and ancient papyrus

gated by dynamic TMA measurements. Fig. 8 shows the TMA-cell with the punched disk-like papyrus sample and the posistion of the water container. The sample was placed between the vitreous silica platform and movable SiO_2 rod and subjected to a variable load. After equilibration ((3 - 5 minutes) water is added into the dish. The next figure (fig. 9) shows a comparison of the swelling behaviour of a fresh and an ancient papyrus sample. At first there is a sudden contraction due to the inhibition with water, followed by a parabolic swelling curve. If we take the fresh papyrus as reference (100 %), we can derive that the ancient papyrus shows a swelling in the order of 5 - 6 %. Further experiments with ancient papyri from different periods proved that papyri around 1000 B.C. show about 2 - 3 % swelling whereas the older papyri do not show such expansion behavior at all.

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