ELSEVIER

Thermochimica Acta 320 (1998) 127–133

thermochimica acta

Thermal and infrared spectroscopic characterization of historical mortars

Lilli Paama[a,*], Ilkka Pitkänen[b], Hannu Rönkkömäki[c], Paavo Perämäki[c]

[a] *University of Tartu, Institute of Chemical Physics, 2 Jakobi Street, EE2400 Tartu, Estonia*
[b] *University of Jyväskylä, Department of Chemistry, P.O. BOX 35, FIN-40351 Jyväskylä, Finland*
[c] *University of Oulu, Department of Chemistry, P.O. BOX 333 FIN-90571, Oulu, Finland*

Received 26 September 1997; accepted 6 June 1998

Abstract

The characterization of historical mortars was performed by thermal analysis (TG-DTG), simultaneous infrared spectroscopy (TG-FTIR) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The samples were taken from St. John Church (Tartu, Estonia), built in the 13th–14th centuries. The analyses are important for the restoration of the church.

In reality, mortar is a very difficult system, the lime is accompanied with different hydraulic components. TG-DTG analysis and FTIR methods can be used to identify various components of mortar and to observe the reactions associated with the controlled heating at 25–900°C in dynamic air and nitrogen atmosphere. The elemental composition of the acid-soluble components (ASC) was determined by using the ICP-AES techniques. © 1998 Elsevier Science B.V.

Keywords: Acid-soluble components; Historical mortars; ICP-AES; Infrared spectroscopy; TG-DTG analysis

1. Introduction

The interpretation of the thermal decomposition of mortars is generally difficult because of a great variety of components used, which depends on country, source of binding and inert materials and on the age of buildings. Using different techniques (TG-DTG, XRD and chemical analysis), a comparative investigation of calcitic and dolomitic mortars, from different Italian buildings of the 11th and 14th centuries has been performed by Vecchio et al. [1]. Calcium and magnesium contents were determined by complexometric titration and derived from TG curves and a good agreement was obtained.

Thermoanalytical research of traditional mortars in Venice is presented by Bakolas et al. [2]. A basic approach is offered by granulometric analysis, allowing separation of the mortar into its components, in which the finer fraction is richer for binder. The same analyses on this fraction (~63 μm) were performed to define the nature and quantity of the binder in the mortar. The samples were taken from various sites in Venice and examined by calcimetry, TG-DTG and FTIR analysis.

A spectrum of thermal and XRD analyses results from ancient, Byzantine, post-Byzantine and later historic mortars from Greece is presented by Moropoulou et al. [3]. Generally, the CO_2, being bound to carbonates, and the water, being bound to hydraulic components (in weight loss %), discern

*Corresponding author.

PII S0040-6031(98)00421-3

two groups of mortars, the typical lime and the hydraulic, respectively. The specific classification of mortars into groups with the characteristic transformations indicated by weight loss against temperature enables the discrimination between the different mortars: typical lime, cements, with crushed brick, with portlandite, with gypsum and with modern cement mortars. The results of analysis report the hydraulic water percentage, calculated in the 200–600°C range, the ratio CO_2/H_2O bound to hydraulic components and the temperature of CO_2 decomposition. X-Ray diffraction analysis of pulverised samples was used to identify the crystalline substances, when their concentration is not very low, usually ca. 5%.

The thermal analytical investigation of ancient mortars from English cathedrals is explained by Adams et al. [4]. Analysis of ancient mortars show that though recarbonated, they remain soft, yielding to structural deformations. The presence of gypsum in historic masonry is widely attributed to atmospheric pollution accompanied by the chemical reaction between lime mortar and sulphur dioxide. The present study supports the hypothesis that medieval masons made wide use of gypsum in transitional architecture (Romanesque to Gothic).

For the characterization of lumps in the mortars, the various samples were taken from historic Venetian masonry and were examined by TG-DTG and FTIR analyses [5]. Scanning electron microscopy (SEM) and fibre optical microscopy observations were performed. The results mainly indicate the presence of completely carbonated lime and lead to assume that the lumps arise from technologies based on the non-seasoning of lime.

In the present work, TG-DTG, infrared spectroscopy (FTIR) and inductively coupled plasma atomic emission spectrometry (ICP-AES) have been used for the analyses of historical mortars from St. John Church, Tartu (Estonia).

The St. John Church, located in Tartu, Estonia, was built in 13th–14th centuries and was destroyed during World War II. For the restoration of St. John Church, the composition of different materials has been studied in order to find out whether it is possible to reproduce the materials with composition very close to the original [6,7]. The last restoration of the church was carried out in the year 1900.

2. Experimental

2.1. Instrumentation

The TG-DTG curves were obtained using a Perkin–Elmer PC series TGA-7 thermogravimetric analyser in the temperature range 25–900°C. The sample mass was varied between 20 and 25 mg and the samples were weighed in platinum pans. The dynamic experiments were carried out in air and nitrogen atmosphere with a flow rate 80 ml min^{-1} and a heating rate 10°C min^{-1}.

The infrared evolved gas analysis was performed on a Fourier transformed infrared spectrometer (FTIR) Perkin–Elmer Syst. 2000 TG-IR with KBr optics, in a dynamic nitrogen atmosphere (80 ml min^{-1}).

For the determination of acid-soluble components (ASC) a sequential PU 7000 Philips ICP-AES was used. The spectrometer is equipped with a Gilson 221 Autosampler and Philips P3230 computer. The ICP operation parameters, measuring wavelengths and optimal conditions of analysis are summarized in the earlier publications of the present authors [7,8].

2.2. Sample preparation

The analysed mortars were manufactured in the 13th–14th centuries (Mort. 9 and Mort. 10), in the 15th century (Mort.1) and in 1900 (Mort. 2). The mortars samples were dried at room temperature for at least one week. The samples were pulverized and sieved, the most granulometric fraction was <120 μm [9].

3. Results and discussion

3.1. ICP-AES analysis

Pulverized mortar samples 0.3±0.0002 g were weighed in a conical flask. The dissolution of samples was obtained by shaking them with 10 ml of 15% HCl, v/v, Suprapure, Merck. The dissolved samples were filtrated on the fritted-glass crucible, heated at 105°C for 60 min and accurately weighed. The percent of acid-soluble components (ASC) was calculated as follows:

$$\%\mathrm{ASC} = 100(W_m - W_a)/W_m,$$

Table 1
Results of ICP-AES analysis of acid-soluble components (ASC) of mortars (four replicates)

	Mortar 1 [a] ASC 36.75 %, m/m $\bar{c}$±S.D.	Mortar 2 [b] ASC 41.30 %, m/m $\bar{c}$±S.D.	Mortar 9 [c] ASC 35.81%, m/m $\bar{c}$±S.D.	Mortar 10 [d] ASC 38.63%, m/m $\bar{c}$±S.D.
Ca	12.96±0.12	14.86±0.11	11.82±0.10	12.48±0.12
Mg	3.25±0.04	2.77±0.03	2.65±0.03	4.32±0.05
Si	0.33±0.002	0.72±0.01	0.18±0.01	0.70±0.01
Al	0.25±0.004	0.95±0.008	0.46±0.02	0.81±0.01
Fe	0.32±0.003	0.48±0.005	0.23±0.005	0.33±0.006
Mn	0.020 ±0.001	0.046±0.002	0.016±0.001	0.042±0.002
Pb	0.027±0.001	0.030±0.001	0.020±0.001	0.026±0.001
Na	0.025±0.001	0.034±0.001	0.019±0.003	0.016±0.002
K	0.43±0.006	0.58±0.005	0.45±0.006	0.35±0.005

[a] JK-1, from window frame (∼1900).
[b] JK-166, from Lübeck Chapel (15th century).
[c] JK-9, from frieze of sacristy (13th–14th centuries).
[d] JK-116, (13th–14th centuries).

where W_m is the weight of the dry mortar sample and W_a the weight of residue after acid attack.

The contents of Ca, Mg, Si, Al, Mn and Pb were determined in the acid soluble part of mortar and the results obtained are shown in Table 1. The ASC of different samples varies between 35.81–41.30%. The content of the insoluble residue was 64.20–58.57%. The molar ratio Ca/Mg is greater in samples Mort. 9 and Mort. 2 (2.68 and 2.78) than in samples Mort. 1 and Mort. 10 (1.93 and 1.73). This makes it possible to presume that the amount of Ca-based compounds is higher in samples Mort. 9 and Mort. 2. In case lime is used in building, it is important that MgO should be hydrated to hydromagnesite [4($MgCO_3$.Mg

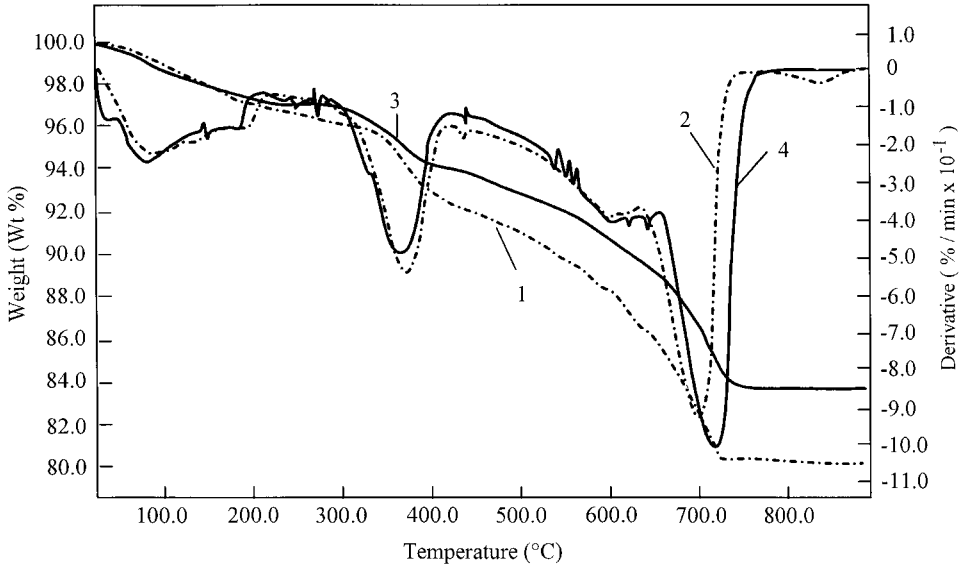

Fig. 1. TG-DTG analysis of Mortar 10 in the dynamic air and nitrogen atmosphere. 1, TG curve in air; 2, DTG curve in air; 3, TG curve in nitrogen; and 4, DTG curve in nitrogen.

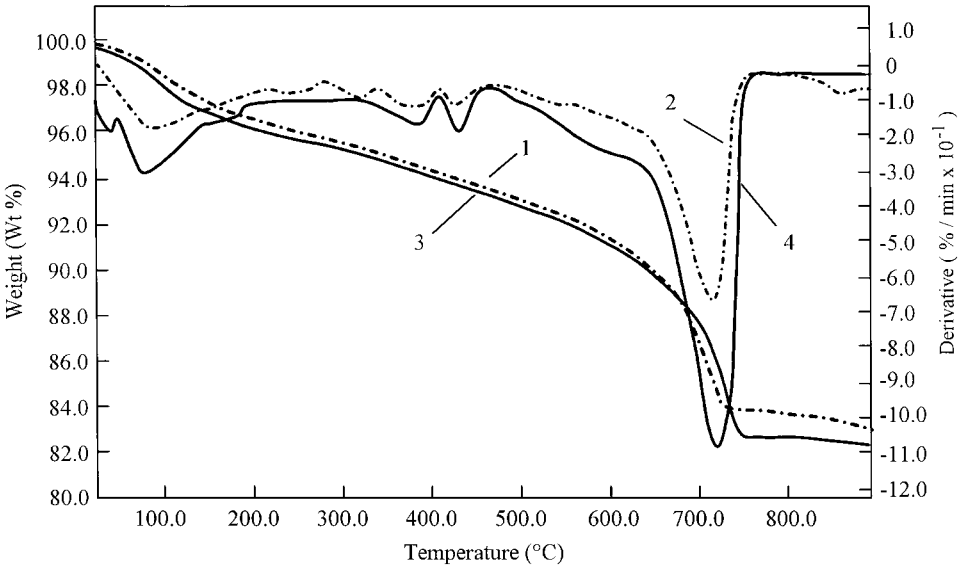

Fig. 2. TG-DTG analysis of Mortar 1 in dynamic air and nitrogen atmosphere. 1, TG curve in air; 2, DTG curve in air; 3, TG curve in nitrogen; and 4, DTG curve in nitrogen.

$(OH)_2 \cdot 4H_2O$] and magnesium hydroxide. Ca contents obtained by complexometric titration in Italian calcitic and dolomitic mortars were rather high: 18.9–22.1% and 17.9–21.6%, respectively [1]. In the mortars from St. John Church analysed by ICP-AES, the calcium contents were between 11.8 and 14.8% and magnesium contents were 2.6–4.3%. The results of spectrochemical analysis were used for the interpretation of components and the results of thermal decomposition of mortars.

3.2. TG-TDG and FTIR analysis

The TG and DTG curves were recorded in the 25–900°C range in air and nitrogen atmosphere and are shown on the Figs. 1 and 2. The weight loss peak around 100°C is induced by hygroscopic water (i.e. physically absorbed water), whereas those, appearing at 200–250°C are attributed to bound water. $Ca(OH)_2$ dehydration is detected between 400 and 520°C. Carbonates show distinctive endothermic peaks at

Table 2
TG-DTG analysis of mortars

Sample	Atmosphere	Weight loss (%)/°C					
		25–125	125–225	225–425	425–625	625–875	25–875
Mortar 9	air	0.67	0.56	1.27	1.70	12.42	16.21
	N_2	1.16	0.47	1.15	1.56	11.75	16.10
Mortar 10	air	1.66	1.46	4.58	5.28	7.34	20.32
	N_2	1.30	1.24	3.62	4.51	5.63	16.30
Mortar 1	air	2.01	1.49	2.40	3.22	7.96	17.08
	N_2	2.52	1.38	2.26	3.20	8.36	17.72
Mortar 2	air	1.36	0.75	1.87	4.26	13.97	22.21
	N_2	0.98	0.80	1.62	3.98	14.58	21.96

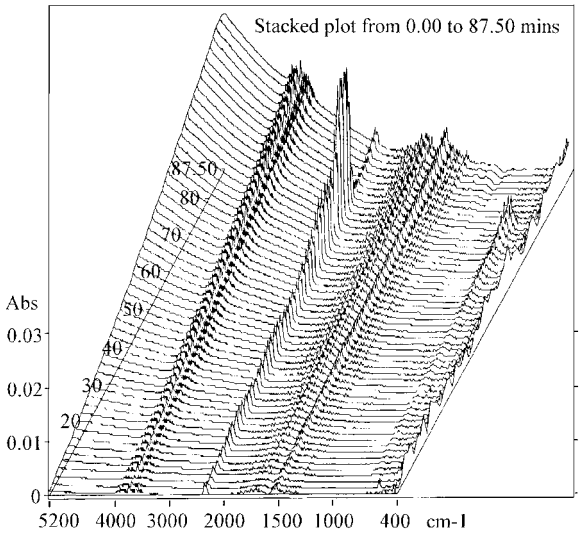

Fig. 3. T-jump/FT-IR gas spectrum of Mortar 10.

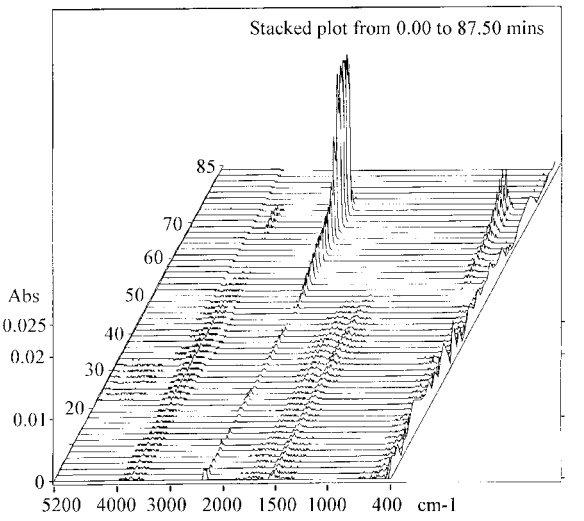

Fig. 4. T-jump/FT-IR gas spectrum of Mortar 1.

ca. 840°C (calcite) and doublets at ca. 780°C and at 860°C (dolomite), whose position may vary depending on grain size and atmosphere [9].

In the lime used in buildings, it is important that the magnesium and calcium should be hydrated. The dehydration of hydromagnesite can be identified at 250–280°C and $Mg(OH)_2$ at 350–420°C. Magnesium carbonate decomposes in the 450–520°C range and calcium carbonate, associated with it in the 700–900°C range [9].

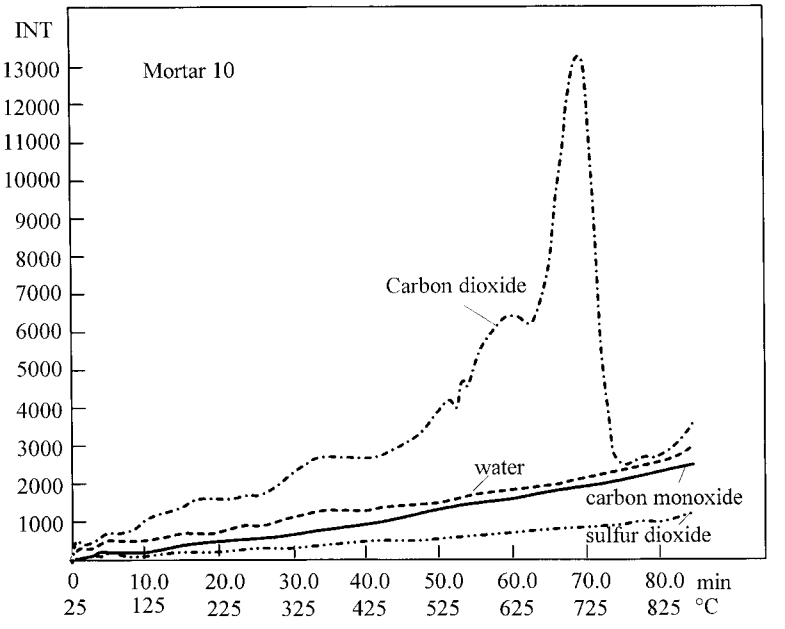

Fig. 5. TG-IR thermograms of thermal decompostion of Mortar 10.

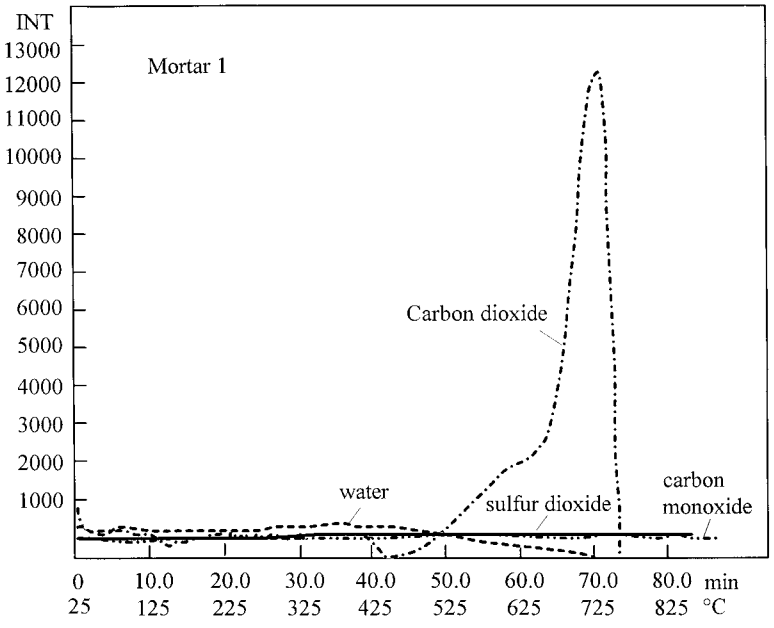

Fig. 6. TG-IR thermograms of thermal decompostion of Mortar 1.

The weight losses at the reaction temperature near 750°C, indicated the loss of CO_2 not from pure $CaCO_3$, but from recarbonated lime which includes some clay minerals. The weight loss (%) estimated from the TG and DTG curves of analysed mortars in the different temperature range selected is presented in Table 2.

The infrared spectra of mortars show hydraulic water peaks at 1520, 3746 cm^{-1} and CO_2 peaks in 670 and 2358 cm^{-1}. T-jump/FT-IR gas spectra of mortars is presented in Figs. 3 and 4. The TG-IR thermograms of thermal decomposition of Mort. 10 and Mort. 1 show the water and carbon dioxide, the concentration of carbon monoxide and sulphur dioxide was on the blank level (Figs. 5 and 6).

The analysed mortars are typical lime mortars, containing only a few of hydraulic compounds. The percent of hydraulic and bound water, calculated in the 125–425°C range was between 1.8 and 6.0%.

The temperature of CO_2 decomposition of historical mortars is different (see Figs. 5 and 6). The weight losses estimated from the H_2O and CO_2 between 425–625°C confirmed the decomposition of hydromagnesite, brucite $Mg(OH)_2$ and $MgCO_3$ (Mort. 10 and Mort. 9 and Mort. 1). The high CO_2 peaks in the temperature range 625–875°C are due to the decomposition of $CaCO_3$. The content of $CaCO_3$ calculated by the TG curves and weight losses (Table 2, air) were: 28.2% (Mort. 9), 16.6% (Mort. 10), 18.1% (Mort.1), and 31.7% (Mort. 2). The samples of Mort. 10 and Mort. 1 can contain the calcium hydroxide.

The weight losses of the TG curves, TG-IR thermograms under air and nitrogen atmosphere and ICP-AES analysis make possible to evaluate the components of Ca-based and Mg-based compounds. By XRD study the inert materials of mortars are containing quartz 56–59% and feldspar 4–6%.

References

[1] S. Vecchio, A. La Ginestra, A. Freza, C. Ferragina, Thermochim. Acta 227 (1993) 215.
[2] A. Bakolas, G. Biscontin, V. Contardi, E. Franceschi, A. Moropoulou, D. Palazzi, E. Zendry, Thermochim. Acta, 269/270 (1995) 817.
[3] A. Moropoulou, A. Bakolas, K. Bisbikou, Thermochim. Acta, 269/270(1995) 779.
[4] J. Adams, D. Dollimore, D.L. Griffiths, J. Therm. Anal. 40 (1993) 275.

[5] A. Bakolas, G. Biscontin, A. Moropoulou, E. Zendri, Thermochim. Acta, 269/270 (1995) 809.
[6] H. Helves, L. Piiri, K. Utsal, K. Kõrge, T. Ilomets, Proc. Estonian Acad. Sci. Chem. 45 (1996) 176.
[7] L. Paama, P. Perämäki, L.H.J. Lajunen, L. Piiri, Atom. Spectrom. 16 (1995) 248.
[8] L. Paama, P. Perämäki, Atom. Spectrom. 18 (1997) 75.
[9] G. Liptay (Ed.), Atlas of Thermoanalytical Curves, Heyden and Son Ltd., Budapest, 1973, pp. 21–173.