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Characterisation of salt efflorescences in cultural heritage conservation by thermal analysis[1,2]

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Abstract

Nitrates, oxalates and sulphates are known to be among the most harmful soluble salts in the field of wall paintings and conservation of porous materials. Under the influence of the environmental conditions these salts are subjected to cycles of crystallisation–dissolution in the porous matrix of the building material, leading to mechanical stresses and chemical alterations that can result in the flaking and powdering of both paint layer (when present) and support. Often the identification of these salts is not very easy, since the experimental techniques usually employed (FT-IR spectrometry, X-ray diffractometry, X-ray fluorescence spectrometry, etc.) are not suitable because of various problems like reciprocal interferences among the different nitrates, hygroscopicity, and low melting points. The aim of the present paper was to set up a method, based on thermal analysis, allowing the quantitative determination of sodium nitrate, calcium nitrate tetrahydrate, magnesium nitrate hexahydrate, calcium sulphate dihydrate (gypsum), and calcium oxalate monohydrate in samples of porous building materials. The idea was to analyse the thermal parameters associated to either first-order ($Ca(NO_3)_2{\cdot}4H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$), or second-order ($NaNO_3$) phase transitions, and to the dehydration ($CaSO_4{\cdot}2H_2O$ and $CaC_2O_4{\cdot}H_2O$) as a function of the salt content in a plaster matrix. The study showed that by submitting plaster samples containing different amounts of these salts to thermal analysis, it was possible to determine the type and content of the salts, even in the simultaneous presence of the degradation products mentioned above. The experimental calibration curves plot weight of the salt in the plaster versus thermal parameter of the transition were tested and the behaviour was shown to be linear in the limit of the experimental errors. The method was applied during recent restorations of a wall painting and a historical plaster in Florence.

Keywords: Thermal analysis; Salt efflorescences; Cultural heritage conservation

1. Introduction

Alkaline and alkaline earth nitrates, sulphates, and oxalates are known to be among the most harmful inorganic salts in the field of wall paintings and conservation of porous building materials [1–4]. These salts are considered as ‘degradation agents’ in cultural heritage conservation and their removal by appropriate cleaning procedures is one of the goals of the restoration techniques. In order to set up the correct conservation methodology it is crucial to know what kind of salt is present and, approximately, its weight percentage. The experimental techniques usually employed (FT-IR spectrometry, X-ray diffractometry, X-ray fluorescence spectroscopy, etc.) are not

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suitable because of various problems like reciprocal interferences among the different salts, hygroscopicity, and low melting points [3–6]. Recently [7] a method using the differential thermal analysis (DTA) to quantify the content of KNO_3 in samples of mortar was set up. This method, based on the evaluation of the enthalpic change associated to the polymorphic first-order transition α-orthorhombic⇒rhombohedral [8,9], was shown to be very successful [7]. The use of thermal analysis for this type of analytical purpose was exploited also to determine the amount of uncalcined gypsum ($CaSO_4 \cdot 2H_2O$) in plaster of Paris ($CaSO_4 \cdot 0.5H_2O$) [10,11], the setting of the two building binders plaster of Paris (that sets forming gypsum) and lime (that sets forming calcium carbonate) [12], the concentration of $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$, $CaCO_3$ and MgO in white coat plasters [13], and the content of goethite (α-FeOOH) and gibbsite [$Al(OH)_3$] in binary mixtures [14].

The aim of the present work was to extend this thermal method to the characterisation of other salt efflorescences, such as $NaNO_3$, $Ca(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $CaSO_4 \cdot 2H_2O$ and $CaC_2O_4 \cdot H_2O$, usually present on the surfaces of the porous building materials. The thermal parameters (enthalpic changes or peak heights) associated to either first-order ($Ca(NO_3)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$), or second-order ($NaNO_3$) phase transitions, and to the dehydration ($CaSO_4 \cdot 2H_2O$, $CaC_2O_4 \cdot H_2O$) as a function of the salt content present in the mixture were analysed with finely ground plaster samples. In order to check if the method was suitable for quantitative purposes, the experimental calibration curve [weight of the salt in the plaster (from ca. 150 μg up to 6 mg) versus thermal parameter of the transition] was tested for each salt. DTA curves were also performed on samples from real cases during the restoration of the historical plasters in the Cloister of the Santo Spirito Church at Florence and of the mural paintings by Andrea da Firenze (XIV century) on the eastern wall of the Spanish Big Chapel in the Green Cloister of the Santa Maria Novella Church at Florence.

2. Experimental

The Merck pro analysi $NaNO_3$, $Ca(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $CaSO_4 \cdot 2H_2O$ and $CaC_2O_4 \cdot H_2O$ products were employed to do the experiments. The plaster samples were prepared by putting an aerial mortar 2 cm thick on a 20×5×2 cm brick; the aerial mortars comprised of slaked lime and pure quartz sand in the 1:3 ratio (v/v). The mixtures of this plaster with each of the salts mentioned above were prepared 3 months after the preparation of the mortar in order to be sure of the mortar set up. Several stock mixtures salt/plaster at different content of the salt (in the range ca. 0.5%–20% of the salt by weight) were prepared by weighing the appropriate amounts of the salt and of the plaster and grinding them for some minutes in an agate mortar with an agate pestle. The samples of plaster from the wall painting and from the historical plaster were ground in the same way as above.

The thermal (DTA) curves were recorded in dynamic modes using a Mettler TA 2000 heat flux thermal analyser after calibration of the sensitivity by the 430 K melting of indium: the sensitivity was 14.68 $\mu V\,mW^{-1}$. During the experiments the oven of the apparatus was always purged by dry nitrogen flowing at 13 $ml\,min^{-1}$. The scanning rate was 1.0 or 2.0 $K.min^{-1}$ depending on the type of the experiment. The weight of the samples (mixture plaster/salt) put in the standard aluminium sample pans was in the range 25–40 mg: this meant that the mass of the salt was in the range 150 μg–8 mg. For each mixture plaster/salt five thermal curves were recorded and ΔH was evaluated from the average over these five curves. The enthalpy change was calculated according to the formula reported in the Appendix.

The sensitivity of the instrument was adjusted in relationship to both the amount of the salt, and to the entity of the thermal effect involved, ranging from 200 up to 10 (maximum value of sensitivity) μV/f.s. (full scale).

The experimental calibration curve was made by plotting the experimental ΔH/J (normalised for the mass differences) of the transition (or peak height in the case of the second-order transition) as a function of the weight of the salt in the plaster and checking the linearity.

Fourier transform infrared (FTIR) spectra were performed on KBr pellets with a Bio-Rad FTS-40 Spectrometer.

3. Results

The thermal curves of the pure $Ca(NO_3)_2\cdot 4H_2O$ (melting temperature at 316 K) and $Mg(NO_3)_2\cdot 6H_2O$ (melting temperature at 362 K) and of the mixtures of these two salts with plaster in various weight ratios were performed but are not reported here, since a reproducible linear relationship between the ΔH of the melting and the content of the salt in the mixtures was not found. This was probably due to the very high hygroscopicity of these two salts (both are deliquescent), which leads to absorption of water vapour from the atmosphere during the sample preparation. The loss of this absorbed water during heating for DTA measurements caused an enthalpic change that interferes with the ΔH of melting. Therefore, the method was not suitable for quantitative purposes in the case of these two salts, but only for qualitative analysis, as already reported [3].

Fig. 1 shows the thermal curve of the mixture plaster/$NaNO_3$ with 20% in weight of the nitrate. The second-order thermodynamic transition at 550 K of $NaNO_3$ [15] was well detectable, as shown in Fig. 1. The peak height was determined for each mixture and plotted as a function of the $NaNO_3$ content. Fig. 2 shows this calibration curve for $NaNO_3$ mixed with plaster. The linear behaviour was good, as checked by the value of the correlation coefficient of the least-squares fitting ξ=0.981, and this could allow

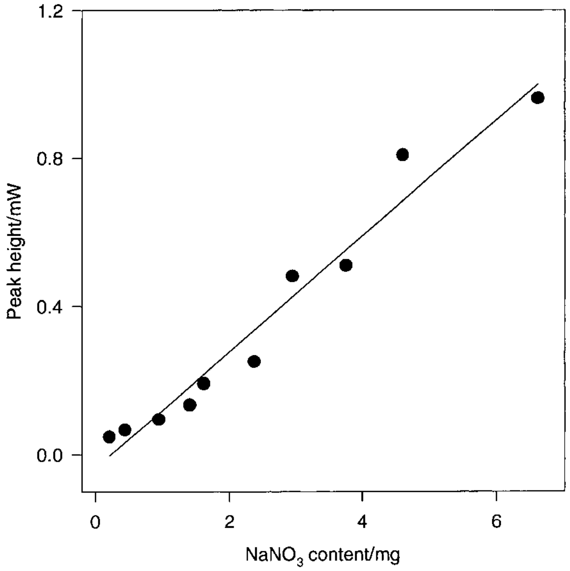

Fig. 2. Calibration curve of the peak height in mW (see Fig. 1) as a function of the salt content in mg for $NaNO_3$ mixed with plaster. The symbols are the experimental points and the full line is the linear regression.

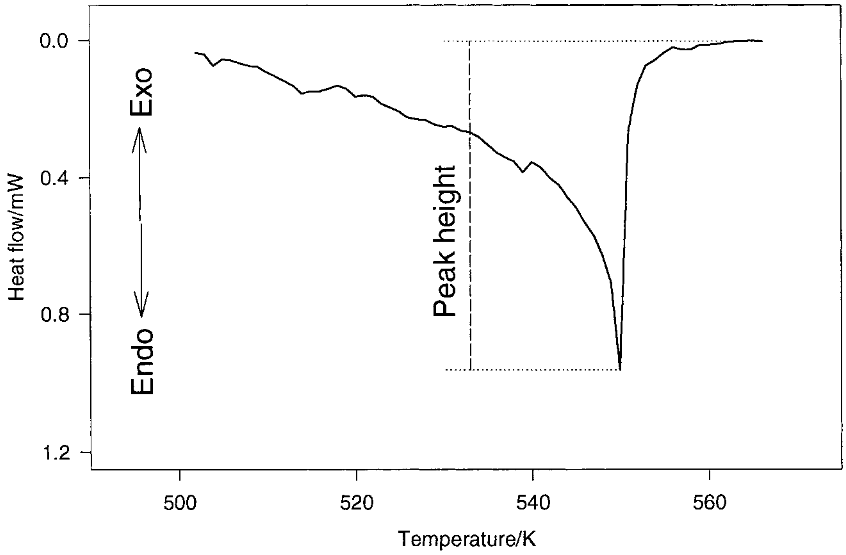

Fig. 1. DTA curve of $NaNO_3$ mixed with plaster at 20% w/w. Scan speed 2 K min^{-1}; chart velocity 0.5 cm min^{-1}; dry nitrogen flow 13 ml min^{-1}.

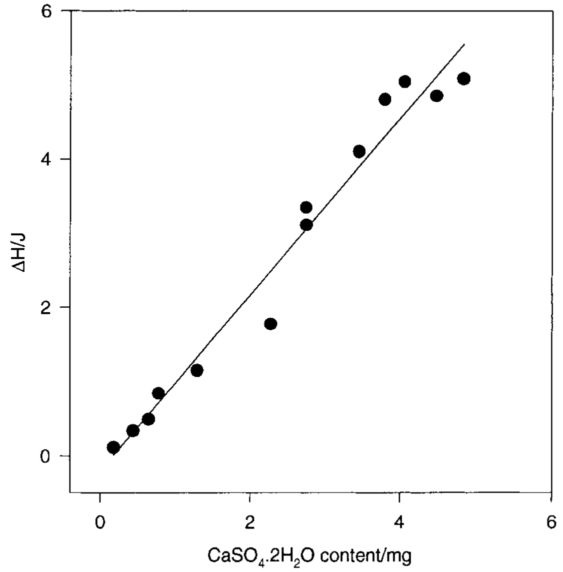

Fig. 3. Calibration curve of the enthalpy change for the dehydration in Joule as a function of the salt content in mg for $CaSO_4{\cdot}2H_2O$ mixed with plaster. The symbols are the experimental points and the full line is the linear regression.

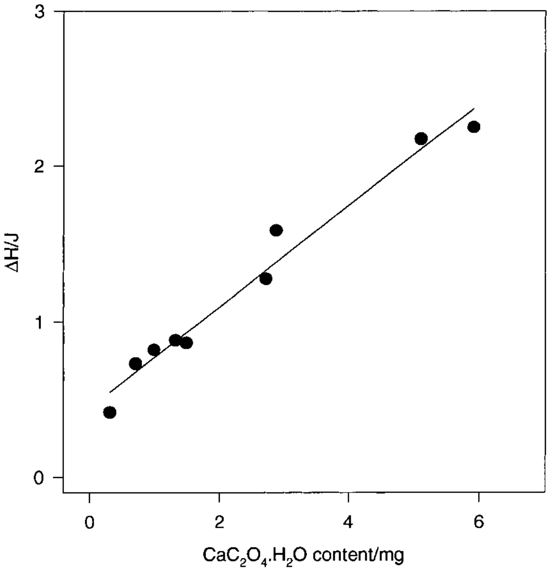

Fig. 4. Calibration curve of the enthalpy change for the dehydration in Joule as a function of the salt content in mg for $CaC_2O_4{\cdot}H_2O$ mixed with plaster. The symbols are the experimental points and the full line is the linear regression.

the quantitative determination of $NaNO_3$ in plaster samples ‘polluted’ by this salt.

For $CaSO_4{\cdot}2H_2O$ and $CaC_2O_4{\cdot}H_2O$ the thermal parameter chosen to evaluate the calibration curves was the enthalpic change ΔH(J) associated with the dehydration (two molecules for gypsum and one for calcium oxalate). The thermal curves of the pure salts were performed as standards and to evaluate the enthalpic changes that were 110 $kJ\,mol^{-1}$ for $CaSO_4{\cdot}2H_2O$ (that is 55 $kJ\,mol^{-1}$ for each water molecule) and 64 $kJ\,mol^{-1}$. Fig. 3 and Fig. 4 show the calibration curves obtained for these two salts mixed with powder of plaster. Even in these cases the linear behaviour was satisfactory (ξ for $CaSO_4{\cdot}2H_2O$ was 0.985 and ξ for $CaC_2O_4{\cdot}H_2O$ was 0.986) and this foreshadowed the use of this thermal method for the quantitative determination of these two salts in wall paintings and conservation of porous building materials.

The opportunity to test this method based on thermal analysis in real cases of conservation of cultural heritage occurred on the occasion of two restorations in Florence: the historical plasters in the Cloister of the Santo Spirito Church and the mural paintings by Andrea da Firenze (XIV century) on the eastern wall of the Spanish Big Chapel in the Green Cloister of the Santa Maria Novella Church. Fig. 5 shows the thermal curve of a fragment (about 38 mg) of wall from the historical plaster in the Cloister of Santo Spirito in Florence affected by a high degree of sulphatisation, without any other degradation product (FTIR did not show nitrates or oxalates). The broad endothermic peak, which corresponds to the complete dehydration of gypsum according to the reaction $CaSO_4{\cdot}2H_2O \Rightarrow CaSO_4 + 2H_2O$, gave an enthalpic change of 5.04 J. Considering the calibration curve reported in Fig. 3(a) content of gypsum of 11% by weight was obtained. In the case of the mural paintings by Andrea da Firenze (XIV century) on the eastern wall of the Spanish Big Chapel in the Green Cloister of the Santa Maria Novella Church the FTIR analysis reported in Fig. 6 showed the simultaneous presence of gypsum and calcium oxalate monohydrate, as indicated by the typical bands labelled in the figure. Fig. 7 shows the thermal curve of a fragment (ca. 10 mg) from this mural painting sampled in a particularly degraded region. From the two endothermic peaks related to the complete dehydration of gypsum (peak with the

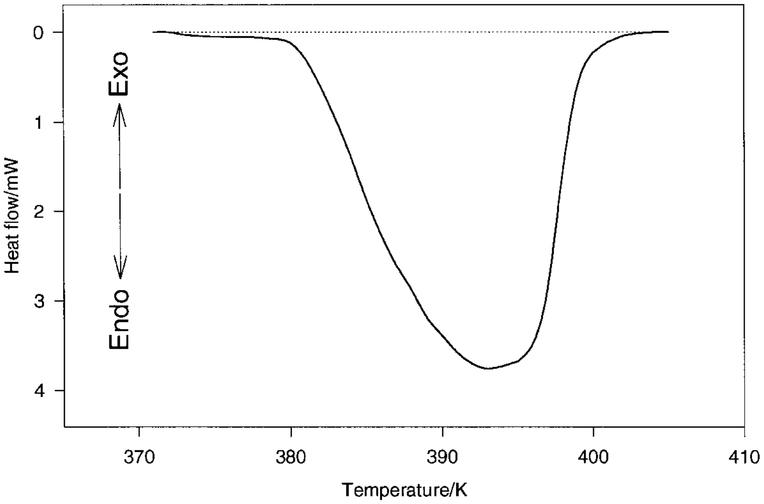

Fig. 5. DTA curve of a plaster fragment (surface of the wall) from the Cloister in the Church of Santo Spirito in Florence. Scan speed 1 K min^{-1}; chart velocity 1 cm min^{-1}; dry nitrogen flow 13 ml min^{-1}.

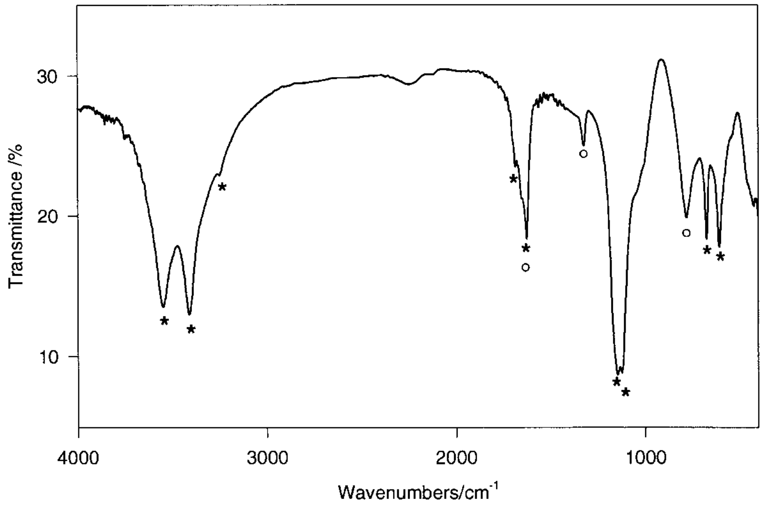

Fig. 6. FT-IR spectrum of a wall painting (Andrea da Firenze, XIV century) fragment (surface of the wall) from the eastern wall of the Spanish Big Chapel in the Green Cloister of Santa Maria Novella in Florence. KBr pellet; resolution 4 cm^{-1}; 32 scans. The typical bands of $CaSO_4 \cdot 2H_2O$ are labelled with asterisk, while those of $CaC_2O_4 \cdot H_2O$ are indicated by an open circle.

maximum at ca. 396 K) and to the dehydration of calcium oxalate monohydrate (peak with a maximum at ca. 425 K) enthalpic changes of 1.872 J (gypsum) and 0.989 J (calcium oxalate) were determined. Considering the calibration curves reported in Figs. 2 and 3 a content of 17% (gypsum) and 15% (oxalate) by weight was calculated in the fragment from the wall painting.

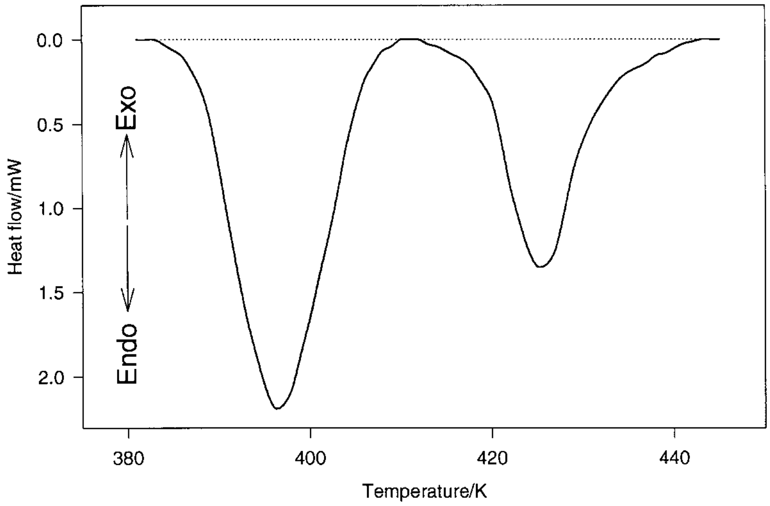

Fig. 7. DTA curve of a wall painting (Andrea da Firenze, XIV century) fragment (surface of the wall) from the eastern wall of the Spanish Big Chapel in the Green Cloister of Santa Maria Novella in Florence. Scan speed 1 K min^{-1}; chart velocity 1 cm min^{-1}; dry nitrogen flow 13 ml min^{-1}.

4. Discussion

Considering the above results presented, thermal analysis was a very suitable technique for the characterisation of salt efflorescences in the field of conservation of cultural heritage. The idea to exploit thermal parameters for the quantitative determination of inorganic salts in porous building materials, which has been successful for KNO_3, where the transition analysed was the polymorphism α-orthorhombic ⇒ rhombohedral [7–9], was shown to be valid even for the salts studied in the present paper. It was interesting to notice that in this work the method was extended both to other salts, and to other types of thermal events. In fact, with KNO_3 a first-order thermodynamic transition [7–9] was analysed, while here a second-order thermodynamic transition ($NaNO_3$) [15] and reactions of dehydration of hydrated crystals ($CaSO_4{\cdot}2H_2O$ and $CaC_2O_4{\cdot}H_2O$) are reported.

Despite the satisfactory linear fit of the experimental points for the calibration curves was in all the three cases (see Figs. 2–4), it was observed that the quality of the fits obtained, as deduced from the values of the ξ coefficient (see Section 3), was not optimum, but in any case comparable with some data in the literature for the determination of gypsum in plaster of Paris [12] and for the dehydration of gibbsite and goethite [14]. This behaviour was attributed for two different reasons. In the case of $NaNO_3$ the thermal parameter analysed was the peak height with respect to the baseline after the second-order thermodynamic transition. This parameter was chosen as the most representative for the thermal behaviour of $NaNO_3$ at the transition temperature, but it was not so reproducible as the enthalpic changes of first-order thermodynamic transitions (see, for example, the polymorphism of KNO_3 [7–9]). This could be the reason of the not perfect fit reported in Fig. 2. For the other two salts, gypsum and calcium oxalate monohydrate, the thermal parameters employed to do the calibration curves were the enthalpic changes associated to the loss of two water molecules (gypsum) and one water molecule (calcium oxalate monohydrate). In these cases the quality of the fit could be affected by the size distribution of the particles. It is well known, in fact, that the particle-size distribution and the reduction of the degree of crystallinity by grinding can influence the peak areas and therefore the enthalpic changes that are calculated from these [16–22]. Great care was taken in grinding the salts with the plaster in order to achieve a narrow particle-size distribution. It cannot be excluded that in some cases the particle-size distribution could determine effects on the enthalpic changes. Work is in progress on a detailed study of the particle-size distribution on the peak areas for these systems plaster/salts, sieving the samples before measurements [23].

Another interesting finding was that $CaSO_4{\cdot}2H_2O$ dehydrated in only one step (see Fig. 5) with a peak temperature of about 393 K giving the anhydrous $CaSO_4$. There is an apparent discrepancy between this result and some data in the literature [9,24]. In fact, in the present case the impossibility to distinguish two distinct steps, the first leading to $CaSO_4{\cdot}0.5H_2O$ and the second to $CaSO_4$ and the lower peak temperature were due to the presence of a continuous flow of dry nitrogen over the sample. This was important since otherwise it could be difficult to separate the peak due to the gypsum from that due to the calcium oxalate (see Fig. 7), which occurs at about 425 K. The same argument could be invoked to explain the dehydration temperature of calcium oxalate monohydrate, which was lower than some values in the literature [25].

Another interesting result was that the enthalpic changes associated with the loss of one water molecule were quite different for the two salts, as reported in Section 3. In particular, while the value for the gypsum matched with the one which was reported in the literature [9] and was in agreement with many other dehydration enthalpies found for other inorganic salts [26], the result obtained with calcium oxalate monohydrate was about 20% higher than the values found for most salts [26]. This supported the idea that when the salt is organic, oxalates are at the border between organic and inorganic, the dehydration mechanism is different, as found, for example, for asparagine monohydrate [27].

The application of this thermal method for the characterisation of salt efflorescences in conservation of cultural heritage was very successful, as reported in Figs. 5 and 7. In particular, the thermal analysis performed on samples from historical plasters and wall paintings allowed not only the quantification of gypsum and $CaC_2O_4{\cdot}H_2O$, but also the establishment of their presence either on the surfaces or in the inside of the wall. In fact, thermal curves on samples coming from different depths with respect to the wall surface showed that in the case of the Cloister of Santo Spirito the gypsum content decreased from the surface to the inside of the wall, up to 2 mm where no gypsum was detected. In the case of the wall painting in the Spanish Big Chapel the thermal analysis indicated the presence of gypsum of the same level of 16%–18% (w/w) from the surface up to 5 mm in depth and a sharp decrease of the $CaC_2O_4{\cdot}H_2O$ content from 14% (w/w) on the surface to zero at 0.5 mm of depth. This was of a great help for the restoration, since it allowed the restorers to set up different methodologies to remove gypsum and calcium oxalate monohydrate.

5. Conclusions

The present study pointed out that thermal analysis is a very powerful technique in the field of the conservation of cultural heritage. DTA measurements were shown to be extremely suitable for the quantitative determination of some inorganic salts usually present as ‘degradation agents’ in wall paintings and porous building materials. The advantages of the technique are that the results are not affected by reciprocal interference among the various salts and the method is very sensitive (ca. 100 μg).

The method allowed the quantitative determination of $NaNO_3$, $CaSO_4{\cdot}2H_2O$, $CaC_2O_4{\cdot}H_2O$ in samples of powdered aerial mortars exhibiting a second-order thermodynamic transition ($NaNO_3$) or dehydration processes ($CaSO_4{\cdot}2H_2O$ and $CaC_2O_4{\cdot}H_2O$). The calibration curves, thermal parameter (peak height or ΔH) vs. salt content, were linear within the experimental error meaning that the method could be applied for quantitative determinations. Furthermore, the method was tested in two real cases during the restoration of the historical plasters in the Cloister of the Santo Spirito Church and of the mural paintings by Andrea da Firenze (XIV century) on the eastern wall of the Spanish Big Chapel in the Green Cloister of the Santa Maria Novella Church, both in Florence, obtaining very positive results even in the case of mutual presence of gypsum and calcium oxalate monohydrate.

Appendix

$$\begin{aligned}\Delta\mathrm{H/J} = {} & [R(\mu V)60(\sec\cdot\min^{-1})\cdot A(\mathrm{cm}^2) \\ & E_{\mathrm{ln}}(\mu\mathrm{V}\cdot\mathrm{mW}^1)E_{\mathrm{rel}}\cdot V_{\mathrm{c}}(\mathrm{cm.min}^{-1}) \\ & \cdot L(\mathrm{cm})]/1000\end{aligned}$$

where:

$R(\mu V)$	instrument sensitivity relative to full scale;
$A(\mathrm{cm}^2)$	area of the endothermic or exothermic peak;
$E_{\mathrm{ln}}(\mu V\cdot \mathrm{mW}^{-1})$	14.68;
E_{rel}	relative calorimetric sensitivity (see below);
$V_{\mathrm{c}}(\mathrm{cm}\cdot\mathrm{min}^{-1})$	plotter chart velocity;
$L(\mathrm{cm})$	plotter chart width.
$E_{\mathrm{rel}}(-253\ \mathrm{K}\div 638\ \mathrm{K})$	$0.8535+0.2165\cdot 10^{-2}\cdot \mathrm{T}(^{\circ}\mathrm{C})-0.7927\cdot 10^{-5}\cdot \mathrm{T}^2(^{\circ}\mathrm{C})$

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