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# Model study of the constituents of wall painting degradation patinas: The effect of the treatment with chelating agents on the solubility of the calcium salts



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## ABSTRACT

A model study on the application of chelating solutions on superficial calcium degradation patinas of wall paintings is presented. For this purpose the solubility of calcium sulfate, carbonate and oxalate in aqueous solutions of the  $\text{Ca}^{2+}$  chelators EDTA and citrate, was evaluated. Both the obtained solutions and their insoluble materials were analyzed by several analytical techniques. These studies revealed that the treatment of solid samples containing calcium sulfate and carbonate as the models of painting patinas resulted in higher solubilities of calcium sulfate and carbonate over that of oxalate. Moreover, our investigations confirmed the higher capacity of EDTA to chelate  $\text{Ca}^{2+}$  compared to that of citrate. All these results were interpreted and discussed on the basis of speciation models, solubility products of the salts and formation constants of the calcium complexes in solution. Finally, we report the characterization of a sodium calcium double citrate salt formed as an unexpected product in the treatment of the calcium sulfate with citrate. Overall our results suggest that the low solubility of calcium oxalate prevents its dissolution upon treatments with chelators, and that the capacity of citrate to dissolve the calcium salts is lower than that of EDTA irrespective of the duration of treatment.

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## 1. Introduction

The important aspect in the approach of conservative treatment is, as well as effectiveness, the respect of materials that constitute work of art. In fact, conservators and restorers have to choose the better way to act, often making compromises between esthetic and conservative aspect.

During the last years, the scientific research on materials, in terms of elucidating their chemical–physical properties, gave a new and more complete knowledge to restorers for making conscious choices.

Among the most useful techniques for the conservation of cultural heritage the use of chelating agents is of paramount importance, particularly in the cleaning protocols of wall paintings and inorganic materials [1,2], but often with no adequate cognizance by restorers, of the chemical aspects of the interaction with the support.

Actually, chelating agents are able to form stable complexes with metal ions and in particular with  $\text{Ca}^{2+}$ , which is present in plasters (mainly containing calcium carbonate) [3], and in many degradation products [4] arising from superficial carbonation, sulfation [5,6] and formation of oxalate patinas [7–9]. For the latter, nowadays, superintendents, conservators and art historians choose to leave it [10] for its historical value and because any treatment could be resulted to be too much invasive for the integrity of inorganic carbonate support. Also,

the efficiency and resistance of oxalate as a protection treatment on marble against chemical weathering also as an artificial conservative protection treatment is reported in the literature [11,12].

For these reasons, it is extremely important to study the interactions of chelating agents with wall brackets in order to carry out selective extractions of the materials to be removed with no deterioration of the substrate constituting the work of art [13]. In this regard, we focused our attention on ethylenediaminetetraacetic acid ( $\text{H}_4\text{EDTA}$ ) and on citric acid ( $\text{H}_3\text{Citr}$ ) as chelating agents, in the form of their salts, respectively  $\text{Na}_3\text{HEDTA} \cdot 2\text{H}_2\text{O}$  (trisodium salt dihydrate) and  $\text{Na}_3\text{Citr} \cdot 2\text{H}_2\text{O}$  (tribasic sodium citrate dihydrate), which are two of the most commonly used in the conservative practice. Here we present our investigation on the reactivity of these chelating anions with the three main compounds present in the plaster, i.e. calcium carbonate, calcium sulfate dihydrate and calcium oxalate monohydrate. Different analytical techniques, Fourier-transform infrared spectrometry in attenuated total reflectance mode (FTIR-ATR), powder X-ray diffraction (XRD) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) were used to clarify the different capacities of the two chelating agents to affect the solubility of the three calcium compounds, and the products which are formed by reacting the latter with the solution of the salts containing the chelators. The experimental observations have been compared with those expected on the basis of the speciation models calculated using the formation constants of calcium(II) complexes and the solubility products of the related salts available in the literature. Finally, we also report

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the physical–chemical characterization of a novel sodium–calcium double citrate, obtained as an unexpected by-product originated by the exposure of calcium sulfate to the citrate solution.

## 2. Experimental

### 2.1. Materials and equipments

Powders of the following compounds (>99% purity) were used:  $\text{CaCO}_3$  (calcite, Janssen Chimica),  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum, Carlo Erba) and  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (wewhellite, Carlo Erba). The salts of the chelating ligands were: ethylenediaminetetraacetic acid trisodium salt dihydrate, ( $\text{Na}_3\text{HEDTA} \cdot 2\text{H}_2\text{O}$ , Fluka, purity >98%) and trisbasic sodium citrate dihydrate ( $\text{Na}_3\text{Hcitr} \cdot 2\text{H}_2\text{O}$ , Sigma Aldrich, purity 99%).

High purity silica gel powder was purchased from Silicagel Merck, concentrated hydrochloric acid (37%) from Riedl-de Haen, and  $\text{HNO}_3$  65% from Pan Reac Quimica s.a.u.

The aqueous solutions of the salts used for the studies were prepared by dissolving the proper amount of the salts in high purity distilled water to obtain a 0.1 M aqueous solution of  $\text{Na}_3\text{HEDTA} \cdot 2\text{H}_2\text{O}$  and a 0.5 M aqueous solution of  $\text{Na}_3\text{Hcitr} \cdot 2\text{H}_2\text{O}$ . The resulting final pH values were 8.35 and 8.60 for the two solutions respectively.

The morphology of the samples was studied using an SZN-2 Optika optical microscopy. The IR spectra were collected using a Nicolet–Nexus 5PC Fourier Transform IR Attenuated Total Reflectance Spectrophotometry (FTIR-ATR), equipped with Smart Orbit Diamond Crystal (measuring range  $400\text{--}4000\text{ cm}^{-1}$ ). Powder X-ray Diffraction (XRD) was performed using a Thermo Electron–WinXRD diffractometer (range  $2\theta$ :  $5^\circ\text{--}70^\circ$ ). Elemental Microanalysis (CHN) was performed with a Carlo Erba Model EA 1108 analyzer using acetanilide as CHN standard. Thermogravimetric analysis (TGA) was performed using a Perkin–Elmer Delta Series TGA 7 apparatus from  $25^\circ\text{C}$  to  $300^\circ\text{C}$  ( $10^\circ\text{C}/\text{min}$ ) under nitrogen. Scanning Electron Microscopic analysis was performed using a Jeol 6400 Scanning Electron Microscope coupled with Microprobe (SEM-EDS) and with an energy dispersive spectrometer for the detection of X-rays (equipped with an Oxford microanalysis 15 KV, 0.28 nA). A mechanical mixture of calcium sulfate and sodium citrate (Na/Ca 1/1 molar ratio) was used as standard for chemical analysis.

The calcium(II) content in the solutions was determined using a Leeman/Philips ICP PU 7450 ICP Spectrometer and a Jobin–Yvon ULTIMA 2 ICP-AES spectrometer (Power generator 1000 Watt, Plasma Gas Flow rate 12 l/min, Nebulizer Flow rate 0.85 l/min,  $\lambda_{\text{Na}}$ : 588.995 nm,  $\lambda_{\text{Ca}}$ : 315.887 nm, 0.5–8 mg/L). The pH levels of the solutions were collected with a Crison Instruments Basic 20 pH-meter, provided with a Hamilton glass electrode calibrated daily using standard buffers. The melting point was determined by means of a Gallenkamp–OPTO-LAB s.n.c. melting point apparatus.

### 2.2. Experimental procedures

#### 2.2.1. Treatments of calcium salts with chelating agents solutions

Samples of 1.000 g of powder of each of the calcium salts were added to 1.000 g of silica to obtain six samples of 2.000 g total (two for each calcium salt). The six mixtures of calcium carbonate/silica, calcium sulfate/silica and calcium oxalate/silica were mixed thoroughly by means of a ceramic mortar and photographed using an optical microscope before and after mixing.

The obtained mixtures were subsequently heated to  $80^\circ\text{C}$  for 1 h in an oven to remove moisture, and cooled in a desiccator for 30 min, before their FTIR-ATR and XRD spectra were collected.

Three out of the six mixtures (one for each calcium salt) were treated with the trisodium EDTA solution, while the other three mixtures were treated with the sodium citrate solution. The treatment with the chelators was carried out as follows: the powdered samples were suspended under stirring in 50 ml of solution of the chelating agents,

and the mixture was allowed to react for 24 h. The pH levels of the solutions were monitored before and after treatment.

The suspensions were filtered, the solid materials were washed with 30 ml of distilled water, and the filtrate solutions were transferred into 100 ml volumetric flasks. The solutions were added with 3 drops of concentrated hydrochloric acid to eliminate any insoluble residue and diluted to 100 ml. The obtained solutions were diluted 1:2000 and analyzed by ICP to quantify the concentration of  $\text{Ca}^{2+}$  ions obtained by solubilization of the calcium salts during the reaction.

The solid recovered from the filtration of the reacting mixtures was heated in an oven at  $80^\circ\text{C}$  for 1 h and allowed to cool in a desiccator for 30 min. The solid samples were then weighed and their FTIR-ATR and XRD spectra collected.

The same experimental procedure was followed for solid samples treated with the solutions of the chelators for 7 and 30 days.

#### 2.2.2. Calculations of the speciation models in solution

The speciation for the  $\text{Ca}^{2+}/\text{EDTA}$  or  $\text{Ca}^{2+}/\text{citrate}$  systems in the presence of either oxalate, carbonate or sulfate ions was determined by calculations using the software HySS (Hyperquad Simulation and Speciation, Protonic Software, UK). The software was used to take into account the presence of the multiple formation equilibria of the  $\text{Ca}^{2+}$  and  $\text{Na}^+$  complexes and taking into account the protonation of the ligands. The stability constants of the complexes used in the calculations are those reported in the NIST–Critically Selected Stability–Constants databases [14].

The solubility product reported in the same database for calcium oxalate, calcium sulfate and calcium carbonate (calcite) was also taken into account in the calculations. The ionic strength of a 0.1 M  $\text{Na}_3\text{HEDTA}$  or  $\text{Na}_3\text{Citr}$  solution results 0.6 M and therefore the stability constants at this ionic strength and in the presence of  $\text{Na}^+$  as the background cation were used, where available. Where not available, the stability constants determined under the closest ionic strength conditions were used. The full list of stability constants of the complexes, the protonation constants of the ligands and the solubility products used in the calculations is reported as a Supporting Information.

#### 2.2.3. Characterization of $\text{NaCaC}_6\text{H}_5\text{O}_7$ (NaCaCitr)

The NaCaCitr salt was isolated using two different procedures. In the first procedure 5 ml of a 1 M sodium citrate solution in water was added to 5 ml of a 1 M calcium acetate aqueous solution. A solid appeared and the suspension was left to stir at room temperature for 24 h. The solid was recovered by filtration, washed with distilled water and dried under reduced pressure for 2 h at  $80^\circ\text{C}$ . In the second procedure, 5 ml of a 1 M sodium citrate solution in water was added to 5 ml of a 1 M calcium acetate aqueous solution. A solid appeared and the suspension was left

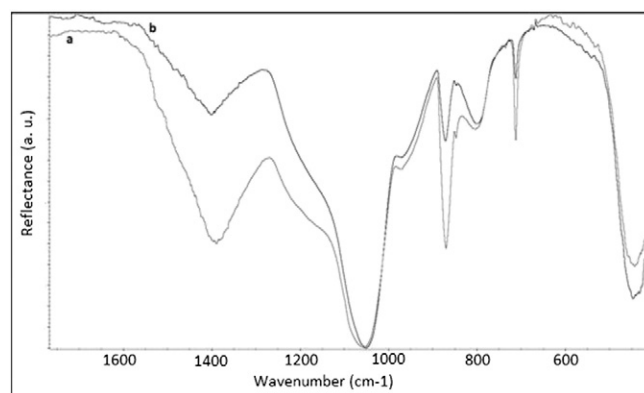


Fig. 1. FTIR-ATR spectra of the calcium carbonate/silica sample before (a) and after (b) the treatment with EDTA.

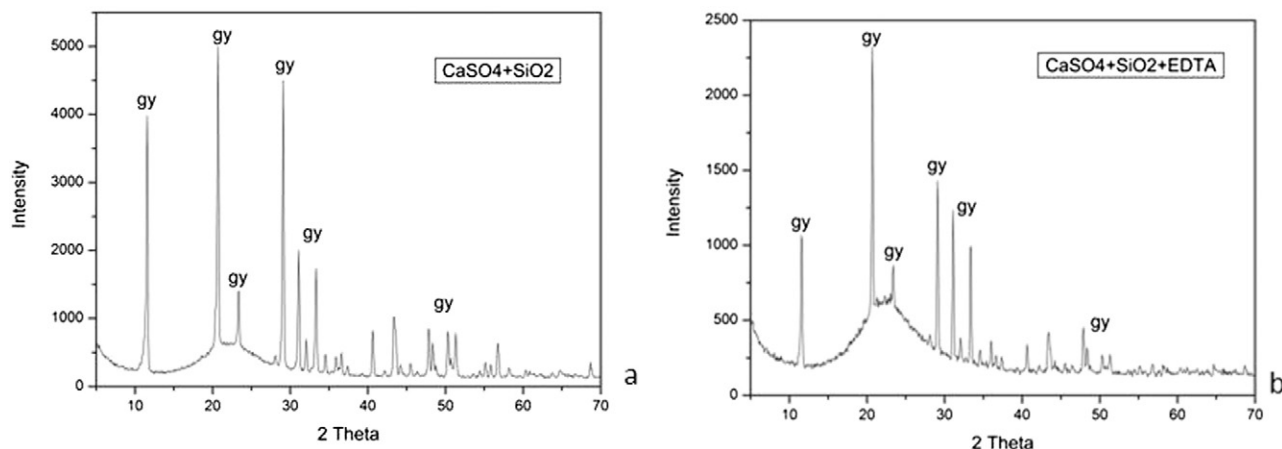


Fig. 2. Powder X ray diffraction spectra of the calcium sulfate/silica sample before (a) and after (b) the treatment with EDTA (gy = gypsum).

to stir at 40 °C for 3 h. The solid was recovered by filtration, washed with distilled water and dried under reduced pressure for 2 h at 80 °C.

The dried powder was characterized by FTIR-ATR. Hemihydrate salt 1 ( $\text{cm}^{-1}$ ): 1603s, 1576ms, 1540vs, 1467msh, 1428s, 1388s, 1272m, 1084mw, 846w, 657mw, 598m and 538m. Bihydrate salt 2 ( $\text{cm}^{-1}$ ): 1616ms, 1563s, 1540vs, 1467msh, 1428s, 1388s, 1266m, 1077mw, 839w 671w, 601m and 535m  $\text{cm}^{-1}$ . XRD characterization of hemihydrate salt 1 (deg): 11.4(100), 17.38(25), 19.8(50), 22.76(60), 28.84(30), 34.44(60), 38.28(30), 44.60(30), 46.04(40), 52.04(20). XRD characterization of bihydrate salt 2 (deg): 5.98(100), 11.56(45), 17.32(45), 22.76(35), 29.08(30), 30.21(20), 34.84(30), 37.64(20), 44.52(25), 46.66(20). CHN elemental analysis of hemihydrate salt 1: calc. C% 27.5, H% 2.3; found C% 27.0, H% 2.4. Bihydrate salt 2: calc. C% 24.9, H% 3.1; found C% 25.3, H% 3.1. TGA, hemihydrate salt 1: experimental weight loss % 4.8, theoretical hemihydrates (PM 262) weight loss % 3.4, bihydrate salt 2: experimental weight loss % 12.5, theoretical bihydrate (PM 289) weight loss % 12.5 and SEM-EDS.

The Na/Ca ratio in the NaCaCitr salt was determined as follows: 0.02 g of compound was placed in a 100 ml volumetric flask and added with six drops of concentrated nitric acid. The mixture was heated to 83 °C (boiling point). The sample was diluted to 100 ml with distilled water to yield a clear solution. A 10 ml portion was transferred into a 100 ml volumetric flask, diluted to 100 ml and analyzed by ICP-AES to determine the  $\text{Ca}^{2+}$  and  $\text{Na}^{+}$  concentrations.

The solubility of the salt was determined by stirring 0.2 g of salt in 10 ml of distilled water in a reacting flask for 7 days. An aliquot of the supernatant was transferred into a volumetric flask diluted 1:1000.

The resulting solution was analyzed by ICP-AES to determine the  $\text{Ca}^{2+}$  concentration.

### 3. Results and discussion

#### 3.1. Treatments with chelating ligands

##### 3.1.1. Characterization of solid materials containing the calcium salts

The three solid materials containing respectively calcium oxalate, calcium sulfate and calcium carbonate, mixed with silica (acting as internal standard), were placed in contact with sodium EDTA or sodium citrate.

The dry residues of the three samples treated with sodium EDTA, at pH 8.35 for 24 h, were characterized by IR spectroscopy and X-ray powder diffraction and compared with the corresponding materials before the treatment. Fig. 1 displays the IR spectra of the  $\text{CaCO}_3/\text{SiO}_2$  mixture before and after treatment.

Comparison of the two spectra shows that the intensities of the peaks attributable to the carbonate anion ( $1398$ ,  $869$  and  $711 \text{ cm}^{-1}$ ) undergo significant lowering after the treatment, while that of  $\text{SiO}_2$  at  $1050 \text{ cm}^{-1}$  remained the same. Similarly, in the case of the  $\text{CaSO}_4/\text{SiO}_2$  and  $\text{CaC}_2\text{O}_4/\text{SiO}_2$  samples, the IR spectra show a significant decrease of the intensities of the peaks attributable to the calcium salts at  $1682$ ,  $1619$ ,  $666$   $594 \text{ cm}^{-1}$  for  $\text{CaSO}_4$  and at  $1600$  and  $780 \text{ cm}^{-1}$  for  $\text{CaC}_2\text{O}_4$ .

IR data clearly indicate significant extraction amounts of calcium salts by the EDTA solution. Comparative XRD analyses have been carried

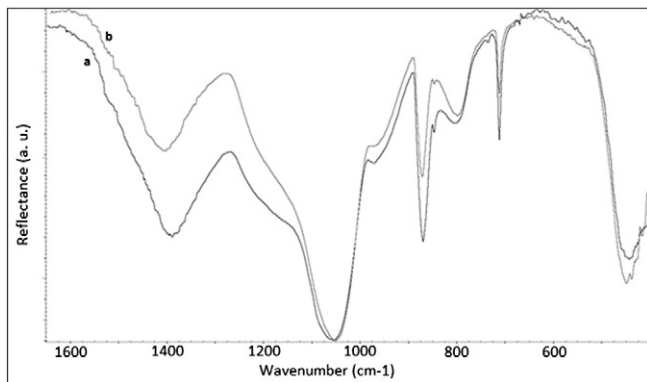


Fig. 3. FTIR-ATR spectra of the calcium carbonate/silica sample before (a) and after (b) the treatment with sodium citrate.

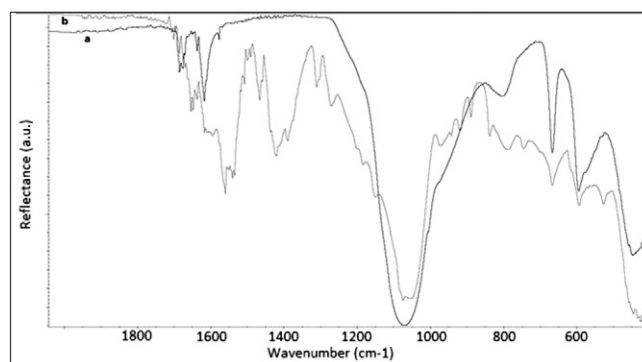


Fig. 4. FTIR-ATR spectra of the calcium sulfate/silica sample before (a) and after (b) the treatment with sodium citrate.

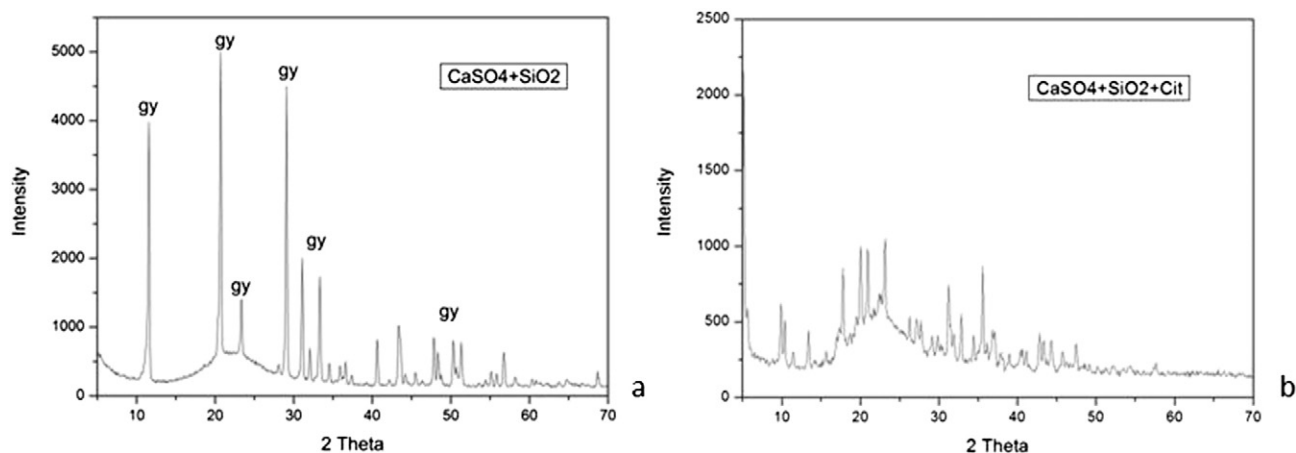


Fig. 5. Powder X ray diffraction spectra of the calcium sulfate/silica sample before (a) and after (b) treatment with sodium citrate (gy = gypsum).

out on the same salt/silica mixtures in order to confirm this evidence. In all the three cases, a significant decrease of the diffraction peaks of the calcium salts was observed, while the background profile due to amorphous silica remained unchanged. This evidence is reported in Fig. 2, which shows the diffraction profiles relevant to  $\text{CaSO}_4/\text{SiO}_2$  before (A) and after (B) contact with EDTA.

The three samples treated with citrate at pH 8.64 for 24 h were analyzed by IR and XRD, in a similar way to that described for the treatment with EDTA. As for the previous chelator, the two  $\text{CaCO}_3/\text{SiO}_2$  and  $\text{CaC}_2\text{O}_4/\text{SiO}_2$  samples exhibit significant decrease of both of the IR bands and the XRD peaks relevant to the calcium salts. Fig. 3 shows the IR spectra of the  $\text{CaCO}_3/\text{SiO}_2$  sample before and after treatment.

However, in the case of the system  $\text{CaSO}_4/\text{SiO}_2$ , both the IR spectra and the XRD patterns (before and after) indicate the unexpected appearance of a chemical species different from calcium sulfate. The IR spectrum after the treatment with citrate appears deeply changed with respect to that of the original material, exhibiting novel bands attributable to the citrate anion as shown in Fig. 4. This suggests that a novel insoluble calcium or calcium/sodium citrate compound could be formed from the reaction of calcium sulfate with sodium citrate (1618mw, 1560s, 1542ms, 1466w, 1420m, 1390mw, 666m, 593m and 526m  $\text{cm}^{-1}$ ).

A deep change occurs also in the diffraction pattern, on which the treatment produces the appearance of novel diffraction peaks. At the same time, those due to  $\text{CaSO}_4$  (gypsum) resulted undetectable after treatment (Fig. 5).

IR spectroscopy and XR diffraction data suggest that both EDTA and citrate exhibit significant solubility power towards  $\text{CaSO}_4$ ,  $\text{CaCO}_3$  and  $\text{CaC}_2\text{O}_4$ , under the conditions examined. In addition, it appears that by treating calcium sulfate with sodium citrate a novel insoluble citrate salt is formed.

### 3.1.2. Determination of calcium in the extracted solutions

ICP-AES analyses have been carried out on solutions obtained by treating the salts with the ligands in order to investigate the solubilization capacity the two chelating agents on the three calcium salts.

The well-known sensitivity of lime to acidic substances has necessarily led to the use of solutions at high pH. The results (calcium concentration and percentage of solubilization) are reported in Table 1 for the treatment with EDTA and Table 2 for the treatment with citrate.

The values reported in both Tables 1 and 2 are in substantial agreement with the solubility products of the three salts ( $9.55 \cdot 10^{-4}$  for calcium sulfate,  $9.33 \cdot 10^{-8}$  for calcium carbonate and  $1.38 \cdot 10^{-8}$  for calcium oxalate) [14].

Calcium sulfate exhibits the highest solubility in the presence of both EDTA and citrate, followed by carbonate and oxalate, the last one being the least prone to the attack of both chelating ligands. Citrate appears less effective than EDTA and in particular towards carbonate and oxalate (the calcium concentration is one order of magnitude lower). Moreover, EDTA is able to solubilize the three salts to a higher extent although in a less selective way than citrate.

Table 1 shows that, under the adopted conditions, the equilibrium concentration for EDTA is reached after 24 h for the three samples, whereas in the case of citrate it appears that prolonged exposures to the chelating agent cause poorer extraction efficacy, mainly for carbonate and oxalate. This anomalous behavior can be explained for  $\text{CaSO}_4$  taking into account the lowering of calcium concentration in solution after the first 24 h due to the subsequent formation of a novel, insoluble calcium–sodium double citrate (vide infra). Kinetic phenomena could be responsible for the lower solubility of  $\text{CaCO}_3$  and  $\text{CaC}_2\text{O}_4$  after longer treatment time, as no novel insoluble compounds have been detected anywhere. It is possible that the observed concentration decrease after the first 24 h of exposure is due to the aggregation of fine colloidal

Table 1

$\text{Ca}^{2+}$  concentration in solution obtained by treating samples of the calcium salts with 50 ml of a 0.1 M solution of  $\text{Na}_3\text{HEDTA} \cdot 2\text{H}_2\text{O}$ , pH 8.35, for 24 h, 7 days and 30 days respectively.

	24 h		7 d		30 d		calcd. [Ca] (mol/L) <sup>a</sup>	Final pH	% Salt dissolved
	Ca (mg/L)	[Ca] (mol/L)	Ca (mg/L)	[Ca] (mol/L)	Ca (mg/L)	[Ca] (mol/L)			
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1.54 ± 0.02	0.08	1.48 ± 0.06	0.07	1.60 ± 0.06	0.08	0.12	4.17	62
$\text{CaCO}_3$	1.91 ± 0.04	0.09	1.84 ± 0.07	0.09	1.57 ± 0.08	0.08	0.10	9.37	40
$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	0.59 ± 0.01	0.03	0.53 ± 0.04	0.03	0.82 ± 0.04	0.04	0.08	5.85	29

Data obtained by ICP-AES on samples diluted 1:2000 prior to analysis.

<sup>a</sup> Calculated by HYSS.

**Table 2**  
Ca<sup>2+</sup> concentration in solution obtained by treating samples of the calcium salts with 50 ml of a 0.5 M solution of Na<sub>3</sub>Citr · 2H<sub>2</sub>O, pH 8.64, for 24 h, 7 days and 30 days respectively.

	24 h		7 d		30 d		Calcd. [Ca] (mol/L) <sup>a</sup>	Final pH	% Salt dissolved
	Ca (mg/L)	[Ca] (mol/L)	Ca (mg/L)	[Ca] (mol/L)	Ca (mg/L)	[Ca] (mol/L)			
CaSO <sub>4</sub> · 2H <sub>2</sub> O	1.25 ± 0.02	0.06	0.82 ± 0.06	0.04	0.83 ± 0.08	0.04	0.11	8.21	31
CaCO <sub>3</sub>	0.63 ± 0.06	0.03	0.10 ± 0.01	0.005	0.11 ± 0.01	0.006	0.005	10.80	3
CaC <sub>2</sub> O <sub>4</sub> · H <sub>2</sub> O	0.21 ± 0.01	0.01	0.020 ± 0.002	0.001	0.09 ± 0.01	0.005	0.001	8.34	4

Data obtained by ICP-AES on samples diluted 1:2000 prior to analysis.

<sup>a</sup> Calculated by HYSS.

particles formed at the beginning of the treatment or just present in the solid samples.

### 3.2. Thermodynamic models by Hyperquad-simulation and speciation (HYSS)

In the attempt to rationalize the observed solubilities of the salts and the concentration of Ca<sup>2+</sup> reported in Tables 1 and 2, we calculated the species distribution at the equilibrium for the suspensions of the calcium salts in the chelators solutions under the same conditions (concentration of the chelating ligands, amount of calcium salts and pH). The logarithms of the protonation and complex-formation constants of the ligands and the anions present in the systems and of the solubility products of the calcium salts are those of the NIST Critically Selected Stability Constants database. These values are reported as supporting information in Table S1.

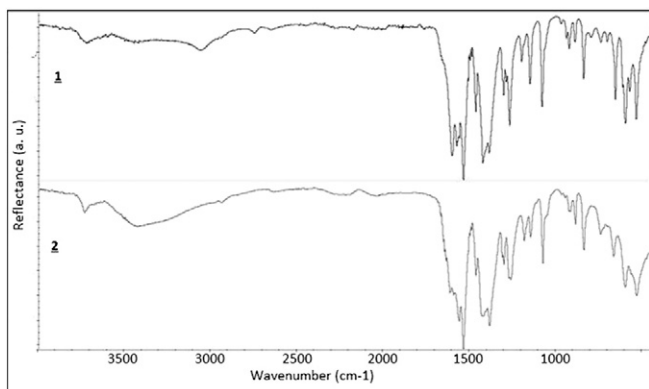
The calculated total Ca<sup>2+</sup> concentrations ([Ca<sup>2+</sup>], soluble calcium) are reported in Tables 1 and 2 and correspond to the sum of the concentration of all soluble calcium species obtained in the calculations. The distribution of calcium in the different soluble complex species and insoluble salts is reported in the supporting information (Fig. S1).

The predominant species in the EDTA solution at pH 8.35 is HEDTA<sup>3-</sup>. For the calcium salts treated with this solution, the calculated total [Ca<sup>2+</sup>] is slightly higher than that observed experimentally. However, they correspond to the same order of magnitude and underline how calcium oxalate is more insoluble when treated with the chelator than the other two salts as expected on the basis of the *K*<sub>sp</sub>. The trend of the calculated total [Ca<sup>2+</sup>] values is particularly interesting if we consider the solubility products: calcium oxalate has a *K*<sub>sp</sub> less than one order of magnitude lower than that of calcium carbonate, while in turn the *K*<sub>sp</sub> of the carbonate salt is more than three orders of magnitude lower than that of calcium sulfate. On the basis of these *K*<sub>sp</sub> values one expects that the [Ca<sup>2+</sup>] concentrations follow the same trend sulfate >> carbonate > oxalate. Instead, both the experimental evidence and the calculated total [Ca<sup>2+</sup>] show

that the trend is rather sulfate ≥ carbonate > oxalate, apparently irrespective of the *K*<sub>sp</sub> values. An interpretation of this behavior is given here below.

By treating the sample of calcium sulfate and calcium oxalate with EDTA the pH decreased significantly from 8.35 to 4.17 and 5.85, respectively. This is a quite expected behavior, as the reaction of calcium with HEDTA<sup>3-</sup> releases one proton *per* metal bound (Ca<sup>2+</sup> + HEDTA<sup>3-</sup> = [Ca(EDTA)]<sup>2-</sup> + H<sup>+</sup>). This proton is not buffered neither by sulfate nor by oxalate, resulting in a moderate acidic solution. In this respect, the higher calcium concentration observed in the sample of calcium sulfate simply reflects directly the values of the solubility products: by treating of the most soluble salt, the highest calcium concentration is obtained. On the contrary, the treatment of calcium carbonate produces the complexation of the metal ion with release of protons from HEDTA<sup>3-</sup>, but more importantly also produces a release of an equimolar amount of carbonate anions. These anions act as a strong base, which buffer the protons released from HEDTA<sup>3-</sup> upon complexation and also produce a final alkaline solution (pH = 9.37). Therefore, the deprotonation of HEDTA<sup>3-</sup> into EDTA<sup>4-</sup> produces a species more prone to bind calcium and the presence of these simultaneous complexation–protonation equilibria results in the observed sulfate ≥ carbonate > oxalate solubility. Finally, the species distribution reveals that for oxalate and carbonate the Ca<sup>2+</sup> ion is distributed between only two species: the [Ca(EDTA)]<sup>2-</sup> complex, and the solid salt. For these systems the contribution to the total [Ca<sup>2+</sup>] comes solely from the soluble [Ca(EDTA)]<sup>2-</sup> species. On the contrary, calcium sulfate is significantly more soluble than the other two salts, and a significant contribution to the total [Ca<sup>2+</sup>] comes from the inherent soluble fraction of CaSO<sub>4(aq)</sub>, and from the [Ca(HEDTA)]<sup>-</sup> species present at pH *ca* 4.

For the salts treated with citrate, the calculated total [Ca<sup>2+</sup>] matches quite well with the experimental ones (only slightly lower) with the exception of the sulfate system where the calculated total [Ca<sup>2+</sup>] is remarkably higher than the experimental one. This observation is quite well rationalized taking into account the formation and precipitation of the mixed calcium sodium citrate, which is more significant in the case of sodium sulfate (see below) by virtue of the higher Ca<sup>2+</sup> concentration present in solution for the most soluble salt. Because the *K*<sub>sp</sub> of this mixed salt is still undetermined and it was not taken into account in the calculation, the calculated total [Ca<sup>2+</sup>] for this system resulted higher than experimental one. For the salts treated with citrate, therefore, the trend for the total [Ca<sup>2+</sup>] is sulfate >> carbonate > oxalate which quite well reflects the trend in the *K*<sub>sp</sub> values and the formation of the mixed citrate salt, as described. For these systems, the lower complexing capacity of citrate for calcium compared to that of EDTA (log β<sub>CaL</sub> = 3.48 and 10.47 for L = citrate and EDTA, respectively) results in the limited capacity of this chelator to dissolve the calcium salts. Moreover, because citrate contains only carboxylato groups, the calcium binding equilibria does not displace protons and the pH of the suspensions resulted therefore higher than 8 for the systems containing sulfate and oxalate. The higher pH value of the carbonate system on the other hand is due to carbonate ions released in solution upon dissolution of the salt, as observed for the treatment with EDTA. The species distribution for these systems (see supporting information) reveals how they are dominated by the presence of the insoluble salts for the



**Fig. 6.** FTIR-ATR spectra of the mixed calcium/sodium citrate salt. Spectra of the hemihydrate species 1, and dihydrate species 2.

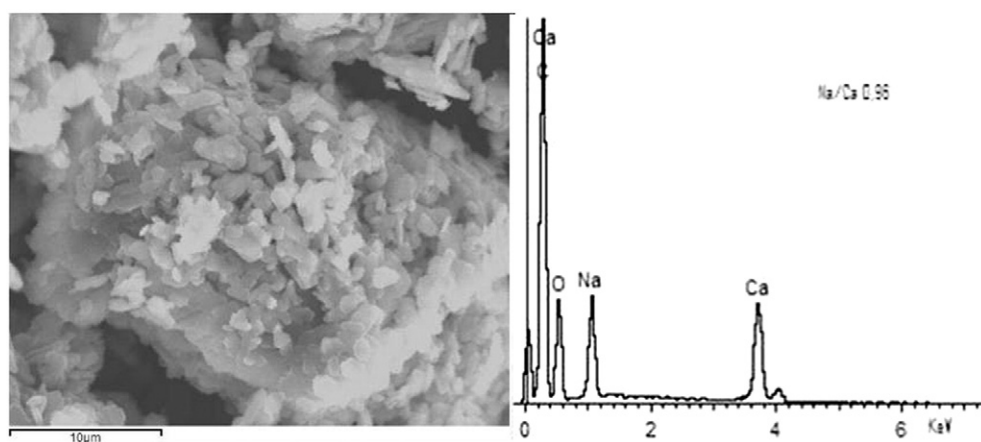


Fig. 7. SEM-SE image (a) (3700X) and EDS spectra (b) of the mixed calcium/sodium citrate salt (hemihydrate species 1).

more insoluble carbonate and oxalate calcium salts. On the other hand, the species distribution of the sulfate system is dominated by the Ca–citrate complex present as the insoluble mixed Na–Ca citrate salt was not taken into account into calculations.

From these results we conclude that the lowest solubility of calcium oxalate in the presence of the chelating agents reflects the lowest  $K_{sp}$  value for this salt. Calcium sulfate is very soluble in the presence EDTA, both by virtue of the high stability of the  $[\text{Ca}(\text{EDTA})]^{2-}$  complex and by virtue of the inherent solubility of calcium sulfate. On the other hand, this behavior was not observed experimentally in the presence of citrate, as the mixed Na–Ca salt precipitates out. Concerning calcium carbonate, its solubility is significantly higher in the presence of EDTA than expected from a simple comparison of the  $K_{sp}$  values. This behavior originates from the basicity of the released carbonate ions which influences the  $[\text{Ca}(\text{EDTA})]^{2-}$  formation equilibrium. Finally citrate, which forms a less stable complex with calcium compared to  $[\text{Ca}(\text{EDTA})]^{2-}$ , produces a remarkable lower solubilization of calcium carbonate compared to that obtained using EDTA.

### 3.3. Characterization of sodium–calcium double citrate

As reported above, it has been found that the reaction between sodium citrate and calcium sulfate leads to the formation of a novel, sparingly soluble citrate salt containing calcium and sodium. In medical literature [15–17] the existence of a calcium sodium double citrate of formula  $\text{C}_6\text{H}_5\text{O}_7\text{CaNa}$  [18] is summarily reported. We report here the preparation and characterization of the mixed citrate salt. The reaction between sodium citrate and calcium acetate led to the precipitation of a calcium sodium (1:1) double salt both in the hemihydrate and in the dihydrate form, respectively of formula  $\text{C}_6\text{H}_5\text{O}_7\text{CaNa} \cdot 1/2\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_5\text{O}_7\text{CaNa} \cdot 2\text{H}_2\text{O}$ . Both compounds decompose at ca 300 °C without melting. Their IR spectra, reported in Fig. 6, are similar and not significantly different from those of the species formed from calcium sulfate/silica treated with the citrate solution (as shown in Fig. 4).

The SEM image in Fig. 7a shows the micrometric sized of precipitated crystallites. EDS microanalysis (Fig. 7b) carried out on the hemihydrate salt confirmed the Ca/Na atomic ratio of ca. 1:1 (0.96:1).

The hemihydrate salt 1 has been subjected to solubility investigations in water and aqueous  $\text{HNO}_3$  and the obtained data are reported in Table 3.

In aqueous nitric acid the compound is completely soluble. ICP data confirmed that the solution contains Ca and Na in 1:1 molar ratio, as expected.

When suspended in water, the obtained solution contains Ca and Na in 0.33:1 molar ratio, suggesting that the double salt undergoes decomposition forming insoluble calcium citrates. This in turn results in the presence in solution of a larger amount of sodium compared to calcium. However, considering that only 37.6% of total sodium present in the solid sample is solubilized, a significant amount of the original double salt remains intact as a mixed citrate.

## 4. Conclusions

The research presented here focused the attention on a well-known method in wall painting conservative practice: the use of chelating agents for the treatment of deterioration calcium patinas.

The results presented in this work compared two chelating agents: EDTA trisodium dihydrate and tribasic sodium citrate dihydrate, and their capacity to react with calcium carbonate, sulfate and oxalate.

The ability of EDTA to chelate  $\text{Ca}^{2+}$  is higher than that of citrate, as expected on the basis of the stability constants of the obtained complexes. Actually, the solution of EDTA trisodium dihydrate at pH 8.35 was able to dissolve the calcium salts more effectively than the solution of sodium citrate tribasic dihydrate at pH 8.60. The final concentration of  $\text{Ca}^{2+}$  in solution for the different salts treated with the two chelators has been quite well explained on the basis of the stability of the complex species and the solubility products of the salts.

This study confirms what restorers usually observe in their practical work: the use of chelating agent solutions in variable percentage to remove sulfatation or carbonatation patinas does not guarantee that the action is only superficial and not dangerous for the integrity of the support. Especially in the case of the use of the strongest EDTA chelator, the control of these drawbacks has to be attained by reducing time of application.

Table 3

$\text{Ca}^{2+}$  and  $\text{Na}^+$  concentration in solution for the calcium/sodium citrate salt treated with water or  $\text{HNO}_3(\text{aq})$ .

	Sample amount (g)	Ca (ppm)	Na (ppm)	Mole fraction Ca/Na	Ca dissolved (mg)	Na dissolved (mg)
1 (water)	0.2	$0.38 \pm 0.03$	$0.66 \pm 0.05$	0.33	3.8	6.6
1 ( $\text{HNO}_3\text{aq}$ )	0.02	$3.31 \pm 0.05$	$1.78 \pm 0.03$	1.08	3.3	1.8

Data obtained by ICP-AES on samples diluted 1:1000 prior to analysis.

In the case of calcium oxalate patinas, the application of these chelators results less dangerous by virtue of the lower solubility product of this salt. For this salts, moreover, a reduced time of application should result not effective.

Finally, our results show an unexpected though important result originated by the use solutions of sodium citrate to treat materials containing calcium sulfate. The reaction between the solution of sodium citrate and calcium sulfate, caused the formation of an unexpected sparingly soluble sodium calcium double citrate ( $\text{NaCaC}_6\text{H}_5\text{O}_7$ ), which has been characterized by physical–chemical analyses.

This result has important impact in conservation practice: the treatment of plaster surfaces with sodium citrate in the presence of calcium sulfate (either derived from degradation of plaster via sulfation or as constituent material) can lead to the formation of this sparingly soluble salt resulting in a permanent compositional and morphological modification of the substrate.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.microc.2014.08.001>.

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