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Evaluation of Gypsum and Calcium Oxalates in Deteriorated Mural Paintings by Quantitative FTIR Spectroscopy[#]

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ABSTRACT

This study dealt with the development of a procedure based on quantitative FTIR spectroscopy to determine the amount of some contaminants in wall paintings, mortars, and stone micro-samples. As contaminants we selected gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and calcium oxalate monohydrate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, among the most common polluting substances present in

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architectural porous materials. Calibration curves of absorbance *versus* analyte concentration were determined by adopting both the internal and external standard methods. As internal standard we used Prussian blue, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$, that presents an unique infrared peak at 2094 cm^{-1} . The correlation coefficient for a linear fit was very good for every calibration, being in each case greater than 0.9900. Furthermore, the precision of the evaluation of gypsum and calcium oxalates varied in the range 8–15% and ca. 4% respectively. In order to verify the findings, some specimens, which came from real frescoes, were analysed both by DSC calorimetry and FTIR spectroscopy: we found a satisfactory match between the quantitative analyses performed by the two techniques. For the first time, the application of this method allowed the quantitative determination of the desulphatization power of the Ferroni-Dini method—based on the ammonium carbonate and barium hydroxide technique—in the conservation of mural paintings.

Key Words: Mural paintings; Conservation; Gypsum; Calcium oxalates; Quantitative FTIR spectroscopy.

INTRODUCTION

In the field of wall paintings and porous building materials one of the most important questions that have to be settled, when planning a conservation methodology, is the identification of the inorganic salts present as contaminants and pollutants in the painting substrate, i.e. the aerial mortar. They are known to be degradation agents that cause serious damage to frescoes, such as flaking of paint layers and powdering of the mortars.^[1] Among the most common and harmful contaminant salts we find alkaline and alkaline earth sulfates, oxalates, nitrates.^[2–4] Their removal is a crucial step in the cleaning procedure for painted surfaces, and conservators absolutely need to know not only the kind of the salt present, but also its approximate amount in weight percentage. Recently we set up a method based on thermal analysis, such as Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA), to estimate the amount of some of these salts in mortar and stone materials.^[5,6] These techniques are based on the measurement of the enthalpic change associated with a thermic event induced in the sample, such as dehydration or polymorphic transition. Some papers report interesting results obtained in the DTA/DSC and TG investigation of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$,^[5] NaNO_3 ,^[5] KNO_3 ,^[6] $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$,^[5–8] and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.^[9] However, thermal methods present some inconveniences, such as the large amount of sample needed, at least 20–30 mg of the material from the work of art/architecture. And the long measurement time of 30 to 60 minutes.



The aim of this work was to study a possible application of quantitative FTIR spectroscopy, which offers fast performance, and only requires the small amounts of sample common in the peculiar field of applied spectroscopy inherent to the conservation of works of art. One of the most problematic aspects of the research was to evaluate whether or not the usual quantitative FTIR analysis^[10] could be applied in the case of micro-samples taken from fresco surfaces. In fact, it was necessary to set up a calibration line using, as a standard, the selected salt in mixture with a material that could simulate the matrix of a mural painting. The goal was to achieve a standard procedure of calibration, and a subsequent measurement that was able to collect the spectrum directly on the micro-sample without any chemical manipulation. Therefore, the first part of this study dealt with investigating the best standard sample to do the calibration and to simulate a real sample constituted of mortar and contaminating salt. A second step in developing the procedure was to select the appropriate substance as the internal standard, and to evaluate the best peaks of the salts in the absorbance spectra to do the quantitative analysis. Finally, it was fundamental to check the procedure on real samples by comparing the results obtained with those achievable with other analytical procedures, namely the thermal ones.^[5]

The last part of the paper deals with an application of the procedure to ascertain the complete removal of gypsum—desulphatization—from a fresco surface after treatment with the Ferroni-Dini method, based on the application of ammonium carbonate followed by barium hydroxide.^[11–14]

EXPERIMENTAL SECTION

Materials

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) and CaCO_3 were supplied by Carlo Erba, Milan, Italy; $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and SiO_2 (quartz, 40–100 mesh) were supplied by Fluka, Buchs, Switzerland; KNO_3 and KBr were provided by Merck, Darmstadt, Germany. All these substances were *pro analysi* products (purity > 99.9%) and used without any further purification. $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$ (Prussian blue, PB) was supplied by Zecchi, Florence, Italy. Its purity was checked by running a FTIR spectrum and comparing it with the one performed on Prussian Blue supplied by Janssen and used as a standard for analytical purposes.^[15] The match was perfect.

Methods

We prepared seven standard specimens containing a mixture (named “batch mortar”, BM) CaCO_3 /quartz (35% CaCO_3 and 65% quartz by



weight) and gypsum in various concentrations, between 1 and 20% by weight of gypsum with respect to the BM; all the standard powders were well ground. These standard samples had to simulate the wall painting matrix where the contaminant agents are usually found. In order to achieve calibration lines for the quantitative determination of the analyte, two different series of experiments were performed. The first one, named the "external standard method", was realized by simply diluting every standard in KBr to prepare pellets. The second, an "internal standard method", was carried out by previously adding Prussian blue (PB) as an internal standard to the KBr. The concentration of PB in KBr was 0.0125% by weight. For both methods, we weighed 3 mg of sample (BM *plus* gypsum); then, depending on the method used, we added the KBr alone, the external standard method, or mixed with PB, the internal standard method, by adopting always the same weight ratio KBr/sample, fixed at 80. KBr pellets were then prepared by weighing exactly 200 mg of the mixture KBr/sample. The mixtures were prepared in random order, and the concentrations of the analyte were linearly independent on each other, otherwise independent information on each standard wouldn't be available.^[10]

On each pellet a FTIR spectrum was run by use of a BioRad FTS-40 spectrometer. The parameters used were: sensitivity 3, delay 600 s, mode absorbance, resolution 4 cm^{-1} , 32 scans, range $4000\text{--}400\text{ cm}^{-1}$. The analyte infrared peak to consider was accurately chosen: it should be sharp and not too weak, nor interfere with any other peak. The best choice for gypsum was the peak at 668 cm^{-1} . On each spectrum, the absorbance of gypsum was determined by measuring the peak height; this was attempted by considering the baseline to be the straight line passing through the two peak edges (see Figure 1).

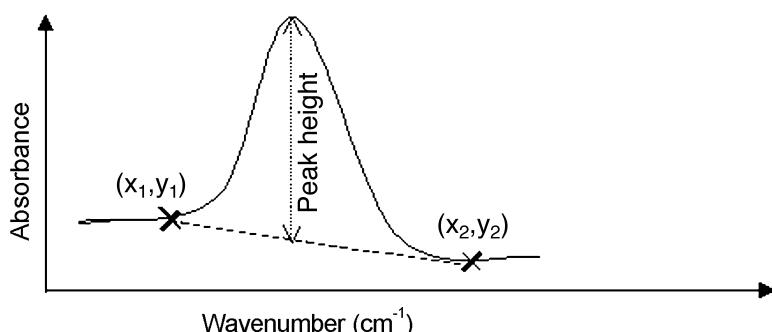


Figure 1. Determination of the peak height by considering as baseline the straight line passing through the two peak edges.

Linear calibrations of absorbance *versus* gypsum concentration (% by weight in the BM) were plotted for both the internal and external standard methods. For the internal standard method, the absorbances of the analyte and PB, which has a unique infrared peak at 2094 cm^{-1} , were ratioed and this value was plotted on the y-axis. Each point in the calibration curves was the average over six measurements, and the standard deviations calculated varied in the range of 8–15%.

In order to check the reliability of the methods, real specimens were used, while accuracy was evaluated by comparing the gypsum content measured by FTIR with the results obtained by DSC calorimetry.^[5] The method was extended to other contaminants (oxalates), by adopting the same procedure as for gypsum. In the case of $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$ the peak selected was the one at 784 cm^{-1} . The experiments on real samples were carried out with four replicates instead of six, due to the very small amount of mural painting samples. The average content of the contaminants with their standard deviation over four measurements was compared with the DSC values.

RESULTS AND DISCUSSION

The first step was to individualize which peak, typical for gypsum, could be considered for the evaluation of the absorbance. It should be sharp and strong enough to be measured even at low concentration of analyte, nor overlap with peaks of different salts present in the sample, in order to avoid multicomponent quantitative analysis.

As shown in Figure 2, gypsum has several typical peaks in its FTIR spectrum:^[16] 3545 and 3405 cm^{-1} are due to O-H stretching vibrations of the water molecules of crystallization, and could be altered by the simultaneous presence of absorbed humidity in real samples taken from frescoes, so they aren't reliable for quantitative analysis. The peaks in the region between 1690 and 1115 cm^{-1} were not considered because they overlap with the strong and broad peak of calcium carbonate (1420 cm^{-1}); the two peaks at 668 and 604 cm^{-1} were strong and sharp at high concentrations of gypsum, but when gypsum content was below 5% by weight it was shown that the peak at 604 cm^{-1} became too weak and, therefore, less suitable for quantitative purposes. Then, we selected the 668 cm^{-1} peak, since it doesn't interfere with any other peak, it's well defined, and strong enough even at low gypsum concentration. Indeed, there is linearity between peak height absorbance and concentration: in Figure 3 we show how the peak height rises as the gypsum concentration in the sample is increased in the range 1–20%.

The peak height measured for each sample was plotted as a function of the gypsum content (% by weight). Figure 4 shows this calibration test.



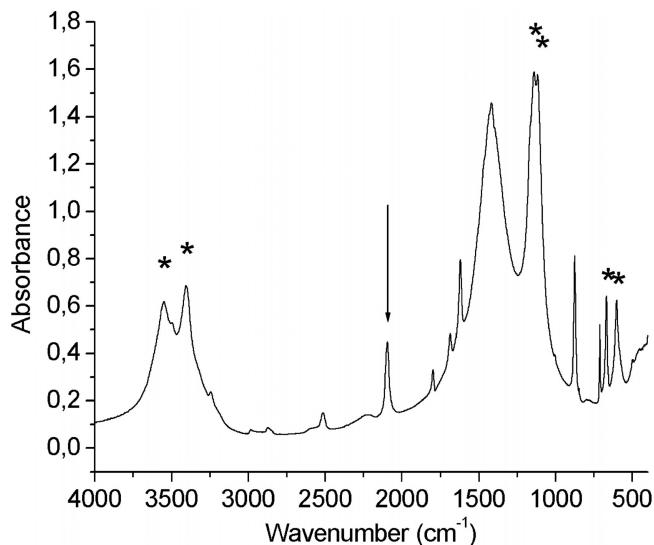


Figure 2. FTIR spectrum of calcium sulphate dihydrate (gypsum) in the batch mortar (gypsum content: 20%), with the addition of the Prussian blue. Asterisks highlight the main peaks typical of gypsum. At 2094 cm^{-1} (arrow) the peak of PB is well recognizable.

The linear behaviour was good, as checked by the value of the correlation coefficient of the least-squares fit $R^2 = 0.9905$, and this could allow the quantitative determination of gypsum in mortar samples polluted by this salt.

A second calibration test was obtained by adopting an internal standard method: this assumes that any unknown source of error will affect the internal standard and the analyte absorbances equally. By calculating the ratio of these absorbances, the effect of unknown variables will be cancelled and the analysis will be more accurate. Prussian blue ($\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$), which has a sharp, unique infrared peak at 2094 cm^{-1} , was chosen as an internal standard. Its content in the final KBr/sample pellet was 0.0123% by weight, and this was achieved by previously adding PB to the KBr.

This made the entire procedure easier and more practical. After running the FTIR spectrum of each standard, the absorbances of gypsum peak at 668 cm^{-1} and that of Prussian blue at 2094 cm^{-1} were ratioed, and this value was plotted *versus* gypsum content in the BM. The result is a linear calibration which crosses the origin and the least-squares fit has a very good correlation coefficient of $R^2 = 0.9964$ (see Figure 5).

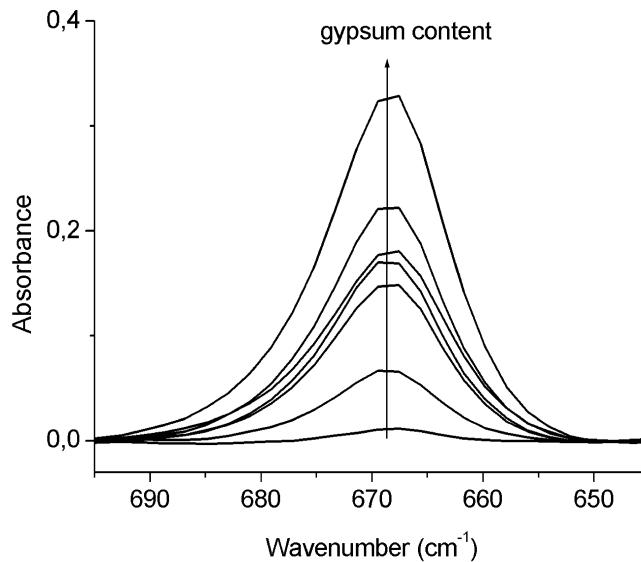


Figure 3. Behavior of the peak at 668 cm^{-1} as a function of the gypsum content.

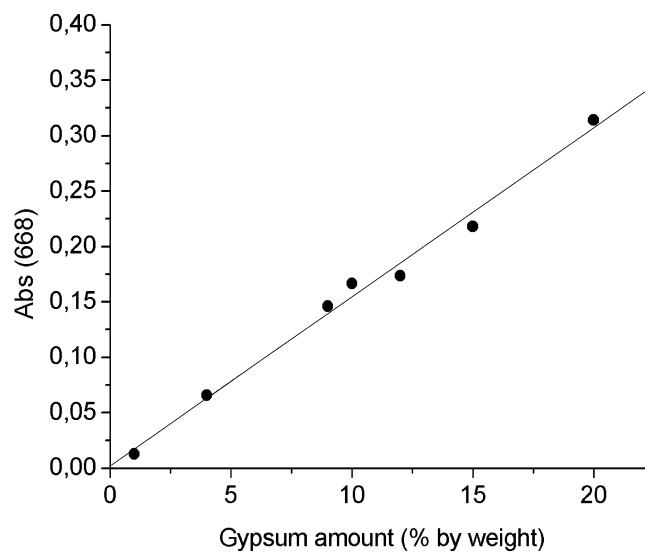


Figure 4. Linear calibration obtained by plotting the absorbances of peak at 668 cm^{-1} (typical for gypsum) measured for each standard as a function of the gypsum content.



The procedure described was set up to determine calcium sulphate dihydrate, gypsum, the most common pollutant present in carbonatic wall paintings. The infrared peak considered to evaluate the amount of gypsum was the one at 668 cm^{-1} , which is typical of gypsum and not of other less common sulphates that could contaminate the mural painting. In particular, sodium sulphate has corresponding peaks at $640\text{--}620\text{ cm}^{-1}$, potassium sulphate at $619\text{--}605\text{ cm}^{-1}$, ammonium sulphate and barium sulphate, possible secondary products in barium treatment, respectively at $621\text{--}611$ and $641\text{--}614\text{ cm}^{-1}$.^[16] Both the distance in cm^{-1} of these other sulphates' absorptions from that of the gypsum selected peak (668 cm^{-1}) and the extreme narrowness of the 668 cm^{-1} peak excluded possible interferences. Some experiments confirmed this assumption.

A calibration test for $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$ was carried out by adopting both the external and internal standard method: eight standards containing BM and calcium oxalate monohydrate in the range 1–20% by weight were prepared and analysed by FTIR in the same manner as for gypsum; the infrared peak at 784 cm^{-1} was chosen as the best one to consider for calcium oxalate.^[17] The ratio of the absorbances of the oxalate peak at 784 cm^{-1} with the PB peak at

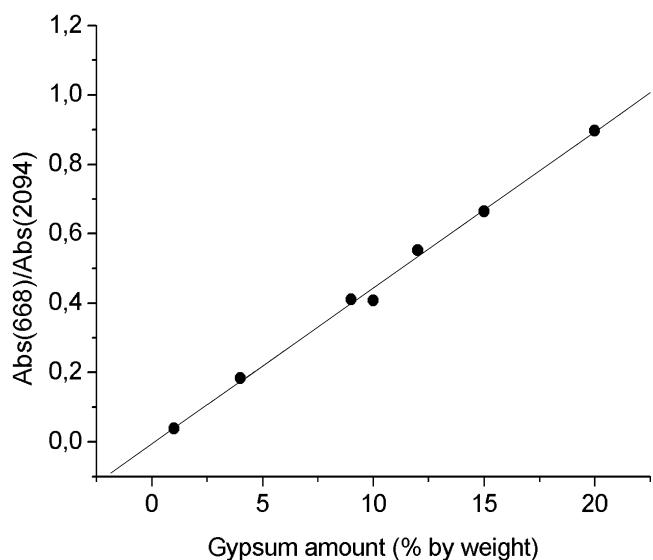


Figure 5. Linear calibration for the “internal standard method”: the ratio of the absorbances (peak height) of gypsum and Prussian blue is plotted for each standard as a function of the gypsum content.

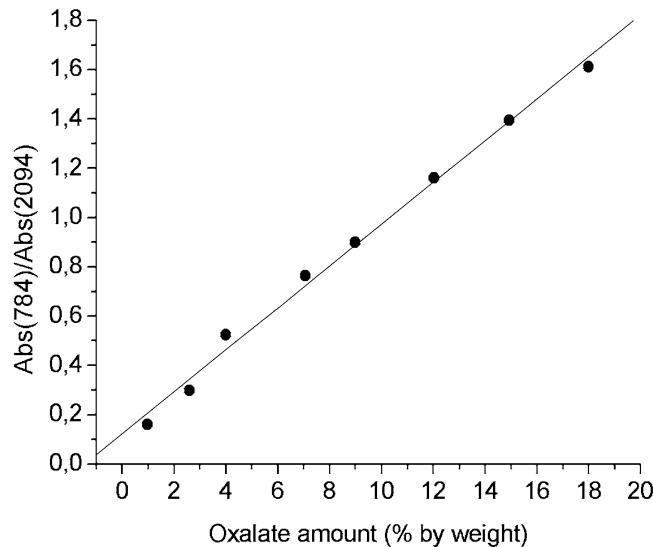


Figure 6. Linear calibration obtained by the internal standard method for calcium oxalate monohydrate.

2094 cm^{-1} gave a linear calibration, which crosses the origin, and has a satisfactory linear behaviour: $R^2 = 0.9937$ (see Figure 6).

Also the linear regression obtained by the external standard method was satisfactory ($R^2 = 0.9952$), as shown in Figure 7.

Both the external and internal standard methods were applied to determine the amount of gypsum and calcium oxalate in four real micro-samples coming from frescoes; the same samples were also analysed by DSC calorimetry, and the results are compared in Table 1.

The agreement between FTIR and DSC data is satisfactory, showing a better match when the calculated amount is obtained by the internal standard method. It was interesting to notice that the linear calibrations did not differ by very much between the internal and external standard methods, but these two approaches revealed strong differences when comparing the results achieved with real samples. In particular, as above underlined, only the internal standard method showed reliability that was sufficient to be applied to the conservation of artifacts belonging to our cultural heritage. This is probably due to the fact that the internal standard method succeeds in eliminating any source of errors deriving from the chemical and structural differences of real samples with respect to the batch mortar. Inter-



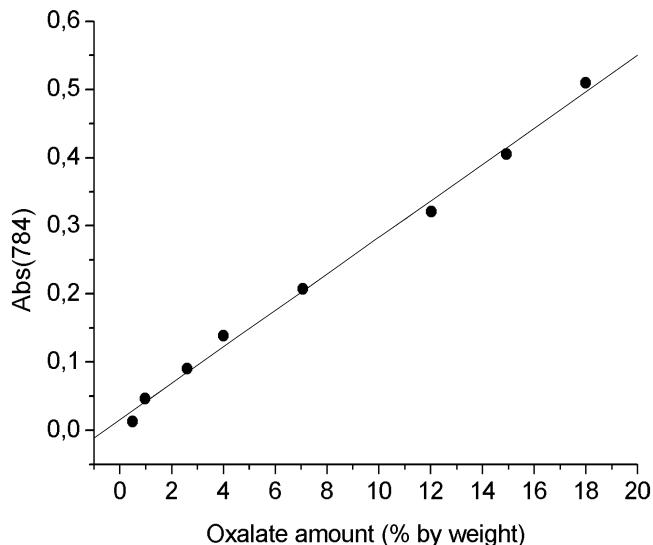


Figure 7. Linear calibration obtained by the external standard method for calcium oxalate monohydrate.

estingly, in sample C, which contains both gypsum and calcium oxalate in different weight percentages, it was possible to quantify both these salts without any problems associated to their possible mutual interference.

For sample B we repeated the measurement after the application of the Ferroni-Dini method consisting of desulphating the fresco surface by a

Table 1. Results obtained by DSC calorimetry and FTIR measurements performed on real samples coming from frescoes.

Sample	% Gypsum by			% Calcium oxalate by		
	DSC	FTIR (IS)	FTIR (ES)	DSC	FTIR (IS)	FTIR (ES)
A	3.9	3.8 ± 0.3	2.9 ± 0.3	—	—	—
B	14.9	12.8 ± 1.5	10.8 ± 1.2	—	—	—
C	7.2	6.3 ± 0.6	4.4 ± 0.4	2.4	2.3 ± 0.1	0.4 ± 0.1
D	10.3	9.4 ± 0.9	7.2 ± 0.8	—	—	—

Sample A: from the mural paintings in the Cappellone degli Spagnoli in the Church of Santa Maria Novella, Florence; sample B: from the XVII century frescoes in Palazzo Frescobaldi in Florence; sample C: from the XVI century wall paintings in Palazzo dei Priori, Volterra (Pisa); sample D: from the XVIII century frescoes in the San Gimignano Cathedral (Siena). The errors are standard deviation on four measurements.

treatment of ammonium carbonate followed by the application of barium hydroxide.^[11-14] The result was very interesting since we demonstrated that the desulphatization was complete: in fact, the peak at 668 cm⁻¹ typical for gypsum was not detectable anymore, meaning that the amount of gypsum had passed from 12.8% by weight to a concentration below 0.5% (sensitivity limit for the method).

CONCLUSIONS

This study allowed the quantitative determination, by means of FTIR spectroscopy, of gypsum and calcium oxalate in lime mortar coming from fresco micro-samples. We set up a procedure able to achieve good linear calibrations with samples simulating the mortar composition. Both external and internal standard methods were adopted, obtaining calibration curves with a very good linear correlation coefficient. In particular, the substance selected for the internal standard method was Prussian blue, (Fe₃[Fe(CN)₆]₄), that showed excellent performance due to the unique peak in a 'clean' region of the mid-IR field. In order to check the reliability of the quantitative FTIR technique, the experimental results were compared with those that can be obtained by Differential Scanning Calorimetry. This comparison showed a good match between the two techniques.

The method set up was tested with real samples coming from frescoes surfaces affected by both gypsum and calcium oxalate monohydrate. The test demonstrated that the internal standard method was more efficient and suitable, due to the ability in reducing any source of errors coming from the particular nature of the real sample. It was interesting to notice that it was possible to quantitatively determine both salts even in presence of each other.

Finally, the method was used to establish the extent of the desulphatization achieved by the Ferroni-Dini method on fresco surface. It was shown that ammonium carbonate succeeds in reducing the amount of gypsum on the fresco surface below the 0.5% by weight. The technique developed in this study appears to be a powerful tool in the field of cultural heritage conservation involving works of art that can be affected by pollutant salts, i.e. stone monuments, mural paintings, stones.

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