

CHEMICAL CLEANING OF QUAGLIOS' MURAL PAINTING IN THE CATHEDRAL OF SAINT NICHOLAS IN LJUBLJANA

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ABSTRACT

Due to significant age – induced darkening it was decided to chemically clean the Quaglios' mural painting in the cathedral of Saint Nicholas in Ljubljana. Before the cleaning, the actual status of colour layers was established by means of x-ray diffraction, SEM / EDS and FTIR microscopy. The analyses showed a gradual transformation of calcium carbonate into calcium sulphate from the surface into the interior of colour layers. On some surfaces, the transformation even penetrated into the plaster beneath the colour layers. We also determined the palette of pigments in the original and later restoration procedures, and identified the casein layer on the surface of fresco. In the darkened lips and cheeks we identified the transformation of red cinnabar (α -HgS) into its black phase metacinnabar (α' -HgS).

Selecting chemical cleaning as the restoration procedure we expected to achieve two effects: to transform the calcium sulphate back into calcium carbonate and to remove the casein layer from the surface of fresco. For this purpose the best reagents were found to be $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 while the best absorbers were cellulose pulp and a combination of cellulose pulp and silicate absorber. The optimal time of application was dependent on the depth of the transformed calcium sulphate and could exceed two or more hours on the most effected areas.

KEYWORDS: chemical cleaning of mural paintings, calcium carbonate transformations, artists' pigments, casein

1. INTRODUCTION

The renovation of Giulio Quaglios' mural paintings (1705 – 1706)⁽¹⁾ on the nave vault and the west wall in the Cathedral of Saint Nicholas in Ljubljana is one of the most extensive interdisciplinary projects of the Restoration Centre. It started in the year 2002 and will last till the year 2006, and here we represent only a part, that was mostly important for the development of the chemical cleaning.

On the nave vault and the west wall there were four major restoration actions in the past (1859⁽²⁾, 1906⁽³⁾, 1944-1948 and 1961-1965). In the published records of the second renovation there are also notes about an application of a coat over the whole surface of the nave vault.

The aims of this particular research were to determine the condition of colour layers and to select the best cleaning procedure. After detecting the transformation of calcium carbonate into calcium sulphate in the surface layers of fresco, we were testing different already known reagents and absorbers to transform it back in order to select the most appropriate in this particular case.

There was a lot of work already done and published about the influence of sulphur dioxide from the air on calcareous surfaces^(4,5). General cleaning techniques were described in *Introduzione al restauro: storia, teorie, tecniche* by G. Perusini⁽⁶⁾. The re-conversion of gypsum films into calcite was studied by Skoulikidis et al.⁽⁷⁾ by using potassium carbonate. There was also much work done and published about the use of ammonium carbonate for the conversion of calcium sulphate back to the carbonate⁽⁸⁻¹⁰⁾. By M. Matteini⁽¹⁰⁾ the use of ion-exchange resin was described. The use of barium hydroxide for consolidation of colour layers after treatment with ammonium carbonate was also described by G. Botticelli^(8,9) and M. Matteini⁽¹⁰⁾.

2. EXPERIMENTAL

2.1. Samples

Micro samples were systematically collected from different areas of the mural painting before and after cleaning. For optical and SEM / EDS microscopy examination, samples of colour layers on lime plaster underneath were embedded in a polyester resin, then grinded and polished in order to get cross sections. For x – ray powder diffraction samples were ground and homogenised. For recording the FTIR spectra, samples were placed in a diamond cell.

2.2. Experimental procedures

For conversion of calcium sulphate back to calcium carbonate we were testing $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 in different absorbers: carbogel, cellulose pulp of different fibres length and silicate absorber in order to achieve the best grasp at the surface. In each case a saturated solution of $(\text{NH}_4)_2\text{CO}_3$ or NH_4HCO_3 was added. The swollen absorber with a reagent was applied over the japan paper and left on the surface of fresco for some time. The testing time of application was 15 min, 30 min, 1 or 2 hours. After that, the absorber and japan paper were removed, and the surface was washed with water- moistened sponge.

We also tested the effect of transformation of sulphate to carbonate by using anion – exchanging resin (OH form). 1p in weight of resin was mixed with 1p in weight of deionised water, applied to the surface and left there for 15 or 30 min.

To research if barium hydroxide is appropriate for stabilisation of colour layers after treatment with ammonium carbonate and bicarbonate, we tested its application on a few areas. For this procedure cellulose pulp was mixed with deionised water, left to swell up over the night, then the exes of water was squeezed out and barium hydroxide was added (in 1 kg of mixture 100 g of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$). The mixture was then applied to the surface over the japan paper and removed after 4 hours.

The areas on the surface of the mural painting that were tested in all abovementioned procedures were of a size about 10 x 10 cm. The samples were collected before and after cleaning and

analysed. After we established what procedure is the most appropriate the selected cleaning areas were about 1 m².

Manufacturer of all mentioned used commercial products is C.T.S.: Carbogel, Arbocel (cellulose pulp), Seppiolite (silicate absorber), Akeogel (anion – exchanging resin), (NH₄)₂CO₃, NH₄HCO₃ and Ba(OH)₂·8H₂O.

2.3. Instrumentation

Polished cross-sections of the samples were investigated by optical microscopy (Olympus BX60), recorded by JVC 3-CCD video camera and by scanning electron microscopy (SEM, Jeol 5500 LV, Japan), while qualitative, quantitative and mapping analyses of selected areas of the samples were performed by energy dispersive spectroscopy (EDS, Oxford Instruments, Great Britain) using the INCA software. SEM examination was done in the low-vacuum mode, in which the samples need not be coated with an additional highly conductive film of gold or graphite.

X – ray powder patterns were taken on a Huber Guinier camera 620 (Cu K_α). The patterns were compared with standard patterns in the PDF⁽¹¹⁾ using μPDSM computer program⁽¹²⁾.

To obtain the FTIR transmission spectra, the samples were put in a Specac's GS02550 Diasqueese Plus Diamond Compression Cell and analysed by a PerkinElmer's FT-IR spectrophotometer Spectrum GX with an AutoIMAGE FT-IR microscope.

RESULTS AND DISCUSSION

By x – ray powder diffraction a high content of calcium sulphate dihydrate was found in the surface layers of fresco. In the darkened lips (Figure 1) and cheeks we identified also the transformation of red cinnabar (α-HgS) into its black phase metacinnabar (α'-HgS) (Table 1).

Table 1: The comparison of diffraction lines (d) and relative intensities (I/I₀) of a sample taken from the darkened lips with lines of compounds from PDF. Mineral names and numbers of PDF cards are also presented.

Sample		HgS Cinnabar 42-1408*		Pb ₃ O ₄ Minium 41-1493*		HgS Metacinnabar 6-21		CaSO ₄ ·2H ₂ O Gypsum 6-0046D		CaCO ₃ Calcite 24-0027D	
d [Å]	I/I ₀	d [Å]	I/I ₀	d [Å]	I/I ₀	d [Å]	I/I ₀	d [Å]	I/I ₀	d [Å]	I/I ₀
7.576	40			6.23	16			7.56	96		
6.215	10										
5.541	10							4.27	48		
4.277	60										
4.130	10										
3.832	10									3.852	15
3.776	20							3.79	19		
3.614	10	3.594	10	3.659	2						
3.362	90	3.361	212	3.379	100	3.38	100				
3.289	10			3.282	8						
3.213	30										
3.159	70	3.165	49					3.163	3.8*		
3.112	30			3.116	18						
3.059	60										
3.032	60									3.030	51
2.9592	20										
2.9303	20					2.926	35				

Table 1 continues

Sample		HgS Cinnabar 42-1408*		Pb ₃ O ₄ Minium 41-1493*		HgS Metacinnabar 6-21		CaSO ₄ ·2H ₂ O Gypsum 6-0046D		CaCO ₃ Calcite 24-0027D	
d [Å]	I/I ₀	d [Å]	I/I ₀	d [Å]	I/I ₀	d [Å]	I/I ₀	d [Å]	I/I ₀	d [Å]	I/I ₀
2.8994	40			2.904	45						
2.8595	100	2.865	197					2.867	24*		
2.8019	20			2.787	37						
2.7869	10							2.786	5.8		
2.7143	10										
2.6806	30							2.679	27		
2.6304	10			2.632	27						
2.4509	30			2.445	2			2.450	3.8*		
2.3741	20	2.3757	11	2.291	3						
2.2762	10									2.284	9.2
2.2726	20										
2.2451	10										
2.2161	10							2.216	5.8		
2.1918	10			2.204	1						
2.1282	10							2.139	1.9		
2.0702	50	2.0746	45	2.078	1*	2.068	55	2.073	7.7*		
2.0219	20	2.0272	13	2.033	7						
1.9807	60	1.9815	40								
1.9091	20			1.9133	18					1.9071	8.7
1.8753	20			1.8878	1			1.879	9.6	1.8726	17
1.7613	30	1.7653	28	1.7630	2*	1.764	45				
1.7504	30			1.7556	26						
1.7331	40	1.7352	30	1.7287	1*						
1.6776	70	1.6799	34			1.689	10				
1.6390	10			1.6413	7						
1.6147	10										
1.6029	10							1.599	1*	1.6040	7.7
1.5801	10	1.5827	8	1.5879	7			1.584	1.9*	1.5821	1
1.5611	10	1.5625	6	1.5591	5						
1.4313	20	1.4328	8								
1.3721	10			1.3729	1*						
1.3412	10	1.3446	11	1.3473	2	1.342	12				
1.3043	10	1.3056	11			1.3085	10				
1.2653	10	1.2693	4	1.2695	1						
1.2544	10	1.2584	6	1.2584	2						
1.2450	10	1.2482	4	1.2462	4						

After detecting CaSO₄·2H₂O we had to answer the following question: did Quaglio already add gypsum in the original or it is a consequence of a transformation of calcium carbonate. For that purpose 20 samples from different areas of fresco were investigated by SEM / EDS mapping analyses. The analyses showed a gradual transformation of calcium carbonate into calcium sulphate from the surface into the interior of colour layers. On some areas, the transformation even penetrated into the plaster beneath the colour layers. The depth of conversion was found to be correlated with fluctuations of relative humidity and temperature on the wall. Samples taken from surfaces where the fluctuations of relative humidity and temperature over the year were the highest showed the deepest transformations. Figures 2–5 show two extreme examples.

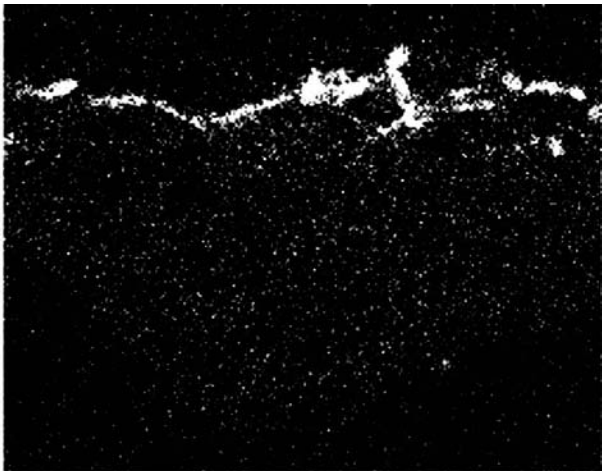


Figure 3: Distribution of sulphur by EDS mapping analysis in the sample taken from the blue sky. Compare to fig. 2.

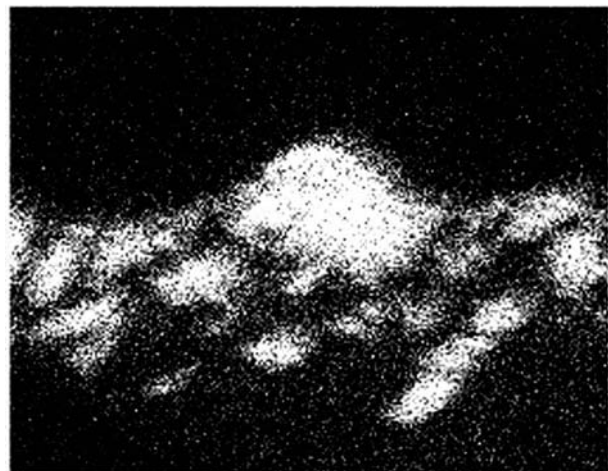


Figure 5: Distribution of sulphur by EDS mapping analysis in the sample taken from the violet sky. Compare to fig. 4.

By SEM / EDS analyses we also determined the palette of pigments in the original and later restoration procedures:

-pigments in the original: yellow ochre, red iron oxide, smalt, green earth, caput mortum, umber, red lead, cinnabar, carbon black

-pigments in restoration actions: Prussian blue, barium sulphate, zinc white, red iron oxide, red organic pigment, ultramarine, red or white lead pigment 1)

For investigation of the coat, which was applied to the whole surface of fresco at the second restoration procedure in the beginning of the 20th century, the FTIR microscopy was used for determination of the organic components. Because there was no visible border between the coat and original colour layers underneath and the coats' penetration was very deep, it was not possible to mechanically separate it. So, from the FTIR spectrum of an untreated sample we could only say that there are proteins present, because in the range where little differences can be noticed between glue and casein the strong carbonate and sulphate modes⁽¹³⁾ disturb the identification. For separation of the coat from the inorganic components the sample was treated with sodium hydroxide solution (pH 9). The dry extracted sample of the coat treated with sodium hydroxide was placed in the diamond cell of the FTIR microscope. The FTIR spectrum (figure 6) corresponds to the spectrum of the artificially aged casein⁽¹⁴⁾. In the isolated sample of the coat there was also found 0,5 weight percent of phosphorus and it is known that there can be up to 0,8 weight percent of phosphorus in a pure casein⁽¹⁵⁾.

We were also researching what binder Quaglio used for his secco technique. Till now, we've found no other organic compound except the casein inside the colour layers, but it penetrated deep into the layers while the coat was applied. We do not exclude the possibility that also Quaglio used casein, but we were not able to make a difference. The research of a possible organic binder in his secco technique is still going on.

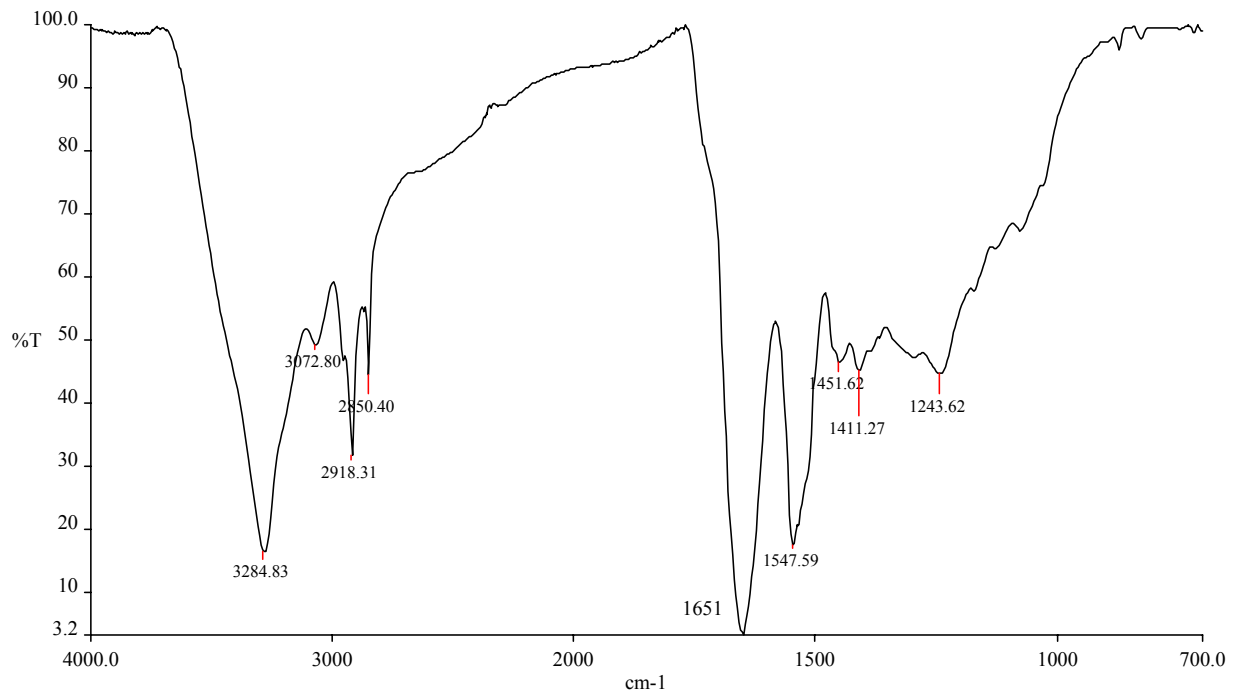


Figure 6: The FTIR spectrum of the extracted sample of casein from the coat.

For determination of the most appropriate chemical cleaning procedure 25 different areas were tested and samples were analysed before and after cleaning using SEM/EDS mapping analyses. Examples of the efficiency of the tested procedures are listed below:

1.) Application of ammonium bicarbonate in carbogel, the time of application: 1 hour (comparing Fig. 7 and 8)

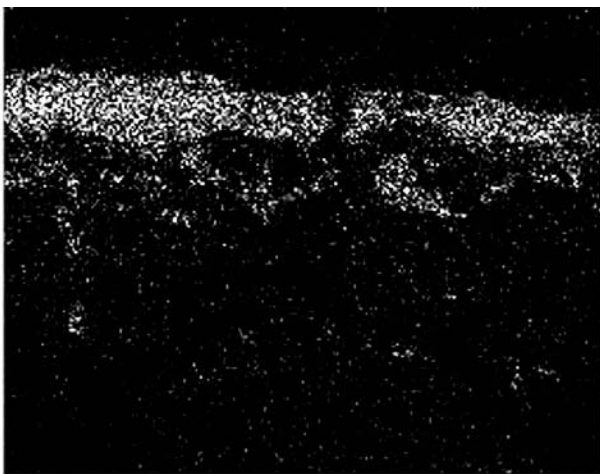


Figure 7: Distribution of sulphur by EDS mapping analysis in the sample before cleaning. ($w_s = 2,62\%$)

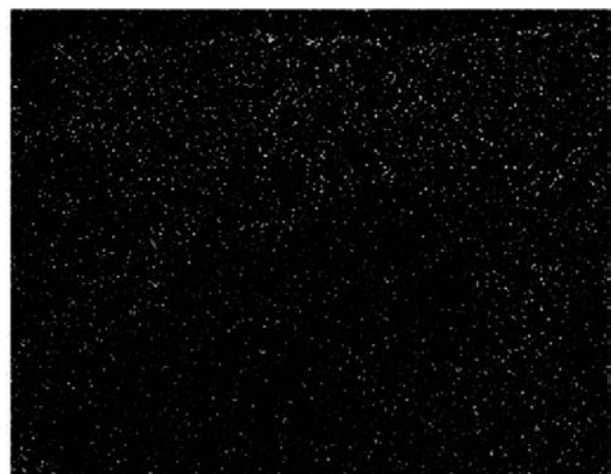


Figure 8: Distribution of sulphur by EDS mapping analysis in the sample after 1h of application of ammonium carbonate in carbogel. ($w_s = 0,32\%$)

After treatment the weight percent of sulphur in the samples fell from 2,62% to 0,32%.

2.) Application of barium hydroxide after the application of ammonium bicarbonate in carbogel; for 1 hour (comparing fig. 9 and 10)



Figure 9: Distribution of sulphur by EDS mapping analysis in the sample after 1 hour of application of ammonium carbonate in carbogel. ($w_S = 0,28\%$)

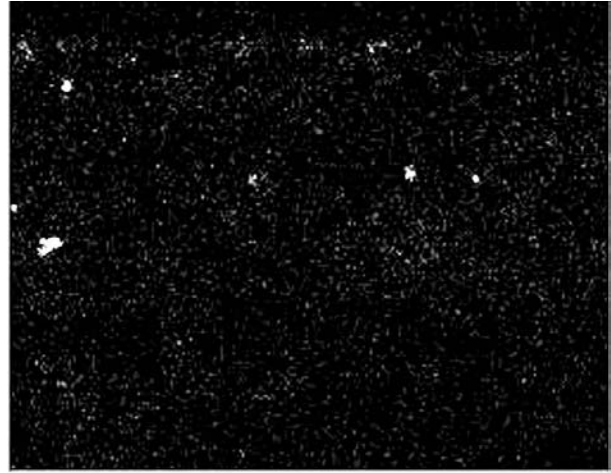


Figure 10: Distribution of barium by EDS mapping analysis in the sample after treatment with barium hydroxide. ($w_{Ba} = 0,71\%$)

By comparing the distribution of barium (Figure 10) with the distribution of sulphur (Figure 9), it can be seen, that positions don't match. A very low content of sulphur ($w = 0,28\%$) that was left in the sample after cleaning is evenly distributed while barium is concentrated in certain areas. After this result we decided not to use barium hydroxide for stabilisation of colour layers.

3.) Application of ion-exchange resin; for 1/2 hour (Fig. 11)

As it can be seen from figure 11, the ion-exchange resin should be left on the surface for more than a half of hour. We did not go on with researching its time of application, because the effect of cleaning was much worse then after the use of ammonium carbonate and bicarbonate after a half of hour of application.

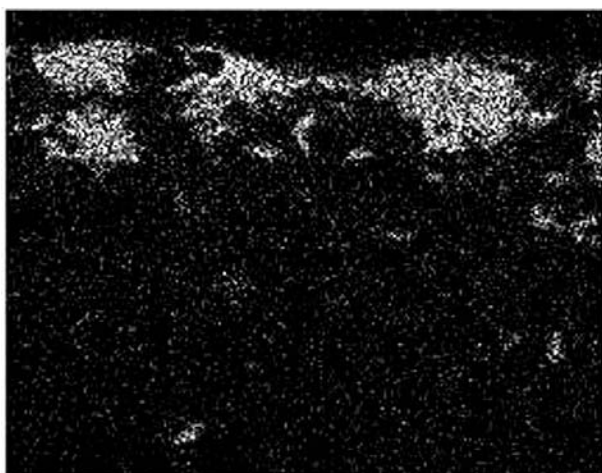


Figure 11: Distribution of sulphur by EDS mapping analysis in the sample after the use of anion-exchange resin Arboceel; for 30 minutes ($w_S = 2,03\%$)

4.) Application of ammonium carbonate in a cellulose pulp; for 2hours (comparing fig.12 and 13)

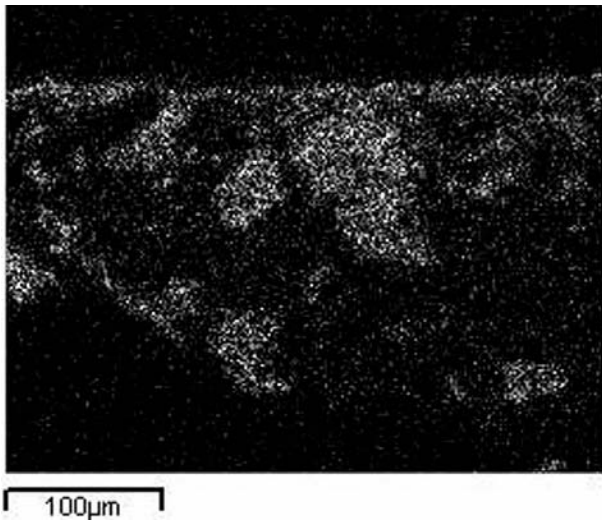


Figure 12: Distribution of sulphur by EDS mapping analysis in the sample before cleaning ($w_s = 2,87\%$).

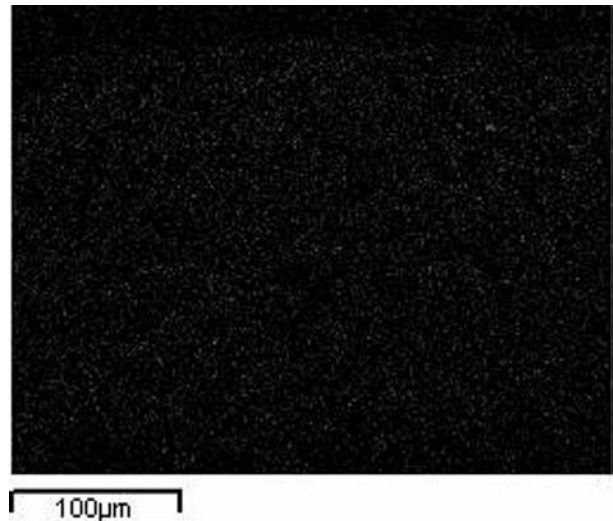


Figure 13: Distribution of sulphur by EDS mapping analysis in the sample after 2 hours of application of ammonium carbonate in a cellulose pulp ($w_s = 0,21\%$).

As it can be seen from figure 12, the transformation of calcium carbonate to sulphate in the area where the sample was taken was very severe as it spreads deep into the plaster under the colour layers. After cleaning the weight percent of sulphur fell from 2,87 % to 0,21% (figure 13).

By comparing the results of all tested procedures on 25 different areas, we were able to choose ammonium carbonate and bicarbonate in cellulose pulp or in a combination of cellulose pulp and silicate absorber as a basic cleaning procedure.

We contacted the Environmental Agency of the Republic of Slovenia, to check the concentration of sulphur dioxide in Ljubljana. In the last years its concentration fell to a negligible level, since the heating station has been using a coal imported from Indonesia, which has a very low content of sulphur. So, we decided not to place special filters in the Cathedral.

CONCLUSIONS

The palette of pigments that were found in the original colour layers of the Quaglios' mural painting: yellow ochre, red iron oxide, smalt, green earth, caput mortum, umber, red lead, cinnabar, carbon black. In the darkened lips and cheeks we identified the transformation of red cinnabar (α -HgS) into its black phase metacinnabar (α' -HgS).

The palette of pigments that were found in the colour layers of later restoration actions: Prussian blue, barium sulphate, zinc white, red iron oxide, red organic pigment, ultramarine, red or white lead pigment 1)

In the surface colour layers we identified casein, which was applied to the whole surface of fresco at the restoration procedure in the beginning of the 20th century.

For the chemical cleaning procedure the best reagents were found to be $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 while the best absorbers were cellulose pulp and a combination of cellulose pulp and the silicate absorber. The optimal time of application was dependent on the depth of the transformed calcium sulphate and could exceed two or more hours on the most effected areas.

The research of a possible organic binder in Quaglios' secco technique is still going on.

We were also researching what binder to use for the retouch by using accelerated ageing tests, and this is going to be represented on The 10th Euroseminar on Microscopy Applied to Building Materials⁽¹⁴⁾ this year in Scotland.

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NOTES:

1) Out of elemental analysis in this case, it was only possible to say that it is a lead pigment, for certain identification x-ray powder diffraction would make it possible to identify, but a bigger sample would have to be taken. Because it is not original it was decided not to go on with the identification.

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