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The scientific support of a preservation work: the frescoes in the aosta cathedral upper nave, from the diagnostic research to the completed restoration ☆

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Abstract

In the field of preservation the opinion has been spreading that is necessary to promote more and more contact between humanistic and scientific sectors. After all, this kind of intervention concerns the study of materials and, therefore, it requires a rich store of knowledge that must get rid of the "trade secrets" empirism, which is typical inside the handicraft environment.

An example of benefit resulting from synergy between humanistic and scientific fields is given by the intervention in the restoration and rediscovery of the loft frescoes in the Cathedral of Aosta, which belong to the Ottonian period (XI century).

The planning of recovery intervention has required scientific understanding which was able to fill the gaps in our knowledge, regarding both historical–artistic and preservation interests.

Analytical applications have availed themselves of various technologies aimed at the characterisation of the materials. The study has been led with the help of X-ray diffraction, ion chromatography, infrared spectrophotometry and optical microscopy. The use of histochemical and immunological techniques has enabled the quantitative characterisation of binding materials/alloying elements.

Keywords: Architecture preservation; Frescoes; Histochemical techniques; Immunochemical techiniques; Ion chromatography; IR spectroscopy; Microanalysis; Microscopy; Restoration; X-ray diffraction

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1. Introduction

The concept that there should be more contact between the humanistic sector and the scientific one is becoming widespread in the preservation and restoration sector. The fact that restoration involves acting directly upon matter can make us perceive the importance of the interpenetration of the two sciences. It is for this reason that the humanistic sector should stop the univocal cooperation with workers trained in the workshop of some good craftsman and that the techno-scientific sector should step out of the austere seclusion of its university halls and understand the applied value of its presence. The techniques and methods used for the scientific support given by the test laboratory (specialised in preservation problems) to the appointed restorer are reported below. The use of basic testing techniques i.e. with a diffractometer or with ion chromatography and infrared spectroscopy together with instruments suitable for microanalysis and histochemical and immunochemical techniques enabled us to obtain information which proved to be important in carrying out the restoration of several 11th century murals found in the upper nave of Aosta Cathedral.

2. Historical notes

The paintings in the Aosta Cathedral upper nave were discovered in 1979 by Hans Peter Autenrieth, a German researcher. Their temporary loss was because in ancient times the church had undergone such a transformation owing to the liturgical service that the polychromatic part had to be covered by a layer of white which kept the paintings hidden until 1979. It was important to restore the colours and the iconographic scenes because there was another pictorial sequence in the second (in order of importance) church in the city. Moreover the presence, in this case, of a pictorial sequence of that period in a Cathedral marked a unique international event.

3. Sampling [1]

The initial difficulty in sampling was due to the "scialbatura" (a plastering coat) present, which hid the underneath part unevenly and limited the possibility of working well without causing any damage.

The first problem to be solved by analysis was the make up of the scialbo. Knowing which materials and techniques had been used in applying it was the first step to choosing the cleaning method to be used. With this aim in mind, about a hundred samples were taken from the whole painted surface in order to achieve reproducibility and check on the homogeneity of the materials used. The sampling concerned both the part with the scialbo and the areas where the colour was more easily identified and also the areas where efflorescence could be found simply because of fallen material. The colour and scialbo samples were taken by using sharp scalpels whereas a brush was used to study the salts and superficial deposits. In some cases fragments of plaster which had already fallen were collected, thus enabling destructive study of these fragments.

After the first cleaning phase, taking of other samples was possible. These were specifically aimed at studying the painting techniques.

4. Experimental

The testing included various complementary techniques.

4.1. *Diffraction*

Using a Rigaku rd/max diffractometer with a copper rotating anode and PSPC microdiffraction system. The working conditions for the tests using the wide angle were 40 kV and 30 mA, result time 2″, scanning speed $1^\circ\,min^{-1}$. 40 kV and 40 mA were maintained for the microdiffraction system, the collimator was 100μ; the operating pressure of the argon/methane (9:1) gas mixture in the detector was 0.9 mBar.

4.2. *Ion chromatography*

Using a Dionex 2000 i/SP chromatograph. Calibration was performed for the cations calcium, ammonium, sodium, potassium and magnesium, and the anions chloride, nitrite, nitrate, sulphate and phosphate [2].

4.3. *Infrared spectroscopy*

Using a Fourier transformed infrared (FTIR) spectrophotometer made by Bruker, Spectrospin model IFS 25 with CsI optics, which enables the widening of the spectrum analysis area to $200\,cm^{-1}$, and equipped with photoacoustic testing system to test the fragments without altering them.

4.4. *Histochemical tests [3]*

These are colouring techniques used in biology which enable identification of protein or oil by specific stain reactions.

4.5. *Immunochemical test [4]*

These are also biological techniques which take advantage of the formation of antibodies owing to specific serum reactions for each type of animal protein.

4.6. *Cross-sections [5]*

These enable us to study samples taken at depth. The fragment is encased in a catalysed polyester resin and when this has hardened the whole is cut transversally. Spot tests for pigment recognition and histochemical tests to determine the presence of protein can be carried out on the sections as well as simply studying the stratification under a microscope (a Reichert–Jung model Polyvar Pol). The sections can also be studied by X-ray diffraction thus obtaining a diffractogram of parts of material measuring 100 μm.

4.7. Thin sections

These enable mineralogical petrographic study of fragments; they were used during the characterisation of the mortars and aggregates used for the plaster; the sections were studied under a microscope whose light could be polarised.

5. Results

From the tests as a whole carried out by using the various techniques listed above we were able to obtain quite a complete picture sufficient to define the methods and work procedure to be adopted for the recovery of the hidden painted part.

The first important data was obtained by identifying the composition of the scialbo covering the painting. The diffractometric tests checked that it was made up of gypsum and calcite. Some doubts had been raised by the type of diffraction presented by the gypsum. Several peaks were not proportional to the intensity ratios given by the JCPDS card n. 6-46 [6]. This could lead us to assume the presence of unidentified composites that added their intensity to the gypsum's. The variableness of these variations and comparison with the non-oriented gypsum card n. 21-816, led us to believe that we had come across a case where the preparation of the sample had been carried out in such a way that the classic gypseous orientation of the powder compounds was impeded.

From the next test results it was obvious that the presence of a proteic binder was preventing the specific orientation by englobing the gypsum crystals thus determining the presence of the non-oriented diffractometric peaks.

Using the microdiffraction method enabled us to discover that the gypsum content in the scialbo layer was higher in the external part of the layer. This could mean that the scialbatura was covered with lime-water and then with the white colour made up of gypsum powder bound with lime and casein. Using the gypsum as colour and not as binder can be explained because of its concealing ability.

The diffuse presence of weddellite (bi-hydrated calcium oxalate) evident from the diffractometric analysis, gave rise to various explanations on its formation [7]. The FTIR analysis, with the help of the photoacoustic system, confirmed the diffractometer data. The possibility of carrying out infrared spectroscopy on both sides of scialbo fragment confirmed the higher gypsum content in the external surface compared with that which had faced the painting. As the microdiffraction system is more sensitive, it helped us understand the oxalate's distribution, which tended to decrease in the part of scialbo nearest to the painted surface (Fig. 1).

In this case the value of photoacoustic analysis is apparent as this type of analysis enabled us to directly test the samples which could later be treated and tested using other techniques. Considering the peculiarity of carrying out tests in the arts sector

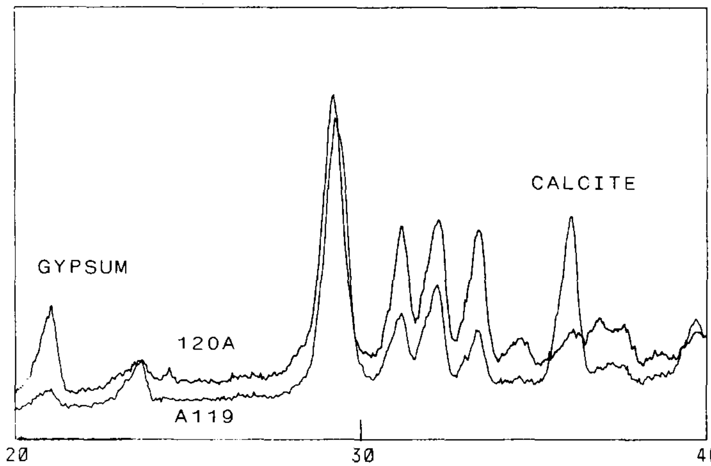

Fig. 1. Example of microdiffractometric analysis of sample M086 carried out both on the part facing the environment (120A) and on that adhering to the paintaing (A119).

where the quantity and size of the samples are always rather small, being able to carry out various tests on the same sample acquires enormous value (Fig. 2).

Among the tests carried out during the first phase was the determination of soluble salts, whose function was to highlight possible situations at risk; this was more closely

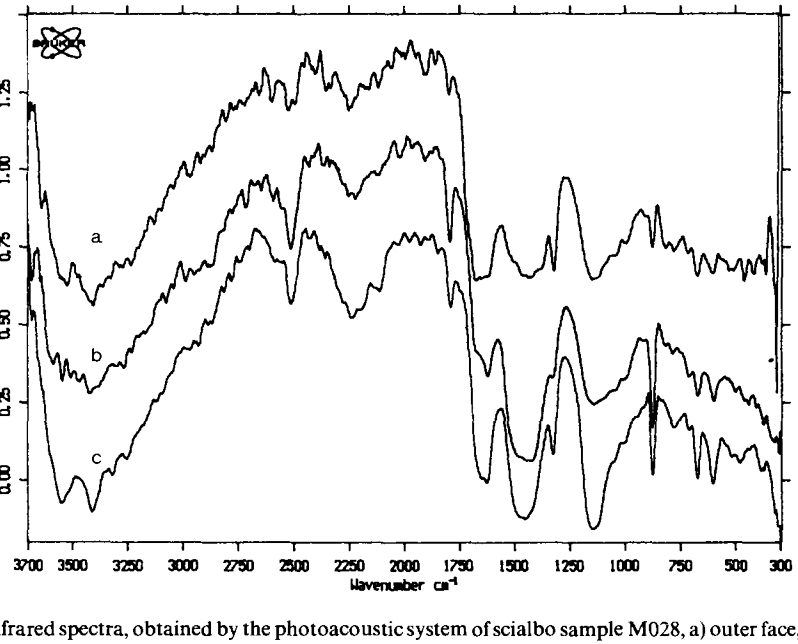

Fig. 2. Infrared spectra, obtained by the photoacoustic system of scialbo sample M028, a) outer face, b) inner face; and c) M011 powder.

linked to planning the restoration work. The results connected the presence of salts, which had caused the paint film to fall, to incidental conditions owing to direct seepage from the walls caused by accidental situations and the lack of roof maintainence in the past. The presence of large quantities of gypsum was obvious from the results, but having seen the condition of the tested area as a whole, it was supposed that this was due to the gypsum-rich surface and the walls interacting (Table 1).

Tests on the scialbo layers were also carried out with the help of cross-sections; this confirmed the presence of proteic material with the use of histochemical tests. The immunochemical tests identified this protein as casein.

After having completed the first analytical planning part, the main interest of the scientific study moved on to identifying the painting technique. Individualising the type of pigment, application technique and binders was very important for the historical study of the murals, above all for the comparison of these paintings with contemporary ones in the same church and in St. Orso's church in Aosta.

The tests carried out by microscopic techniques highlighted the poor quality of the pigments used; this had not, however, prevented the production of a diversified, varied palette mainly made by mixing the various pigments wisely and in different ways. The

Table 1
Quantity and typology of the salts/(% *w/w*)

Sample	NO_3^-	SO_4^{2-}	PO_4^{2-}	NH_4^+	Ca^{2+}	Mg^{2+}
M001	0.21	28.9	–	–	13.7	1.36
M010	0.70	9.79	–	0.38	4.56	0.76
M011	0.21	20.0	–	0.02	10.2	0.25
M019	–	12.5	2.69	0.26	5.80	0.58
M020	0.43	22.8	–	–	16.6	0.58
M031	0.12	22.2	–	–	11.7	1.11
M046	0.22	12.5	–	0.04	7.50	0.47
M053	0.50	9.41	–	0.08	5.11	0.46
M054	0.85	22.8	–	–	12.2	1.34
M061	0.98	9.40	0.04	0.15	4.38	0.53
M067	0.94	25.3	–	–	14.0	0.64
M070	0.62	7.03	0.05	0.10	3.18	0.27
M071	–	16.7	–	–	6.36	1.68
M076	0.73	8.48	0.04	0.11	4.02	0.37
M077	0.29	12.4	–	–	6.26	0.43
M078	0.72	17.1	–	–	8.85	0.89
M085	0.99	9.35	0.03	0.14	4.41	0.48
M087	0.77	10.2	–	0.07	6.14	0.51
M095	0.59	10.6	0.03	0.03	4.10	0.52
M096	2.46	12.4	0.01	0.10	7.09	1.31
M097	0.48	8.89	–	0.02	5.08	0.81
M098	1.80	13.6	–	–	7.27	3.77
M102	0.46	6.90	0.21	–	3.17	0.50
M103	1.39	12.8	–	–	8.28	1.15
M109	0.68	6.01	0.03	–	2.44	0.41
M110	1.35	11.6	–	–	7.38	1.19

common pigments were: earths (red ochre, yellow ochre, green earth), wood black and St. Giovanni white. An exception had been made for some iconographically important characters whose cloaks were coloured blue on a black background using natural ultramarine, more commonly known as lapis lazuli. This is a rather expensive pigment and this may be the reason for its sparing use.

Some testing problems were encountered whilst trying to identify the type of binder used in the areas painted in dry fresco. The presence of proteic material in the scialbo layer invalidated the possibility of verifying its use in the underlying painted layers as these could have been reached later by the protein through the penetration of casein from the scialbatura. Analysing the samples taken from another area in the same church, contemporary to the ones in question, proved to be simpler. In this case the absence of any scialbatura did not invalidate the results of the section tests and quite precise information about the organic binders used was obtained.

6. Discussion of the testing techniques used

Whoever has dealt with testing material concerning preservation will have realised the difficulty arising from the heterogeneity of the samples. The use of compounds whose composition varies from region to region as well as from age to age widens the testing spectrum enormously. If we also add the fact that the material is now old and has thus undergone various transformations, which in turn are often conditioned by environmental factors unlikely to be identified, we realise that the assumption of being able to carry out a complete, comprehensive study by means of one test or testing technique is pure fantasy. It is for this reason that finding several testing techniques that, together, can give the largest possible amount of information is very useful. We must also consider the size and quantity of the samples available. Taking a fragment from the surface is sometimes limited, depending on the type of object to be examined, to pieces little more than one millimetre in size. At this point one test result can be insufficient and tampering with or destroying the sample prevents other possibilities. It is for this reason that the Superintendance of Aosta laboratory has tried to boost those laboratory techniques which, even though carried out on samples taken, enable the performance of various test on one sample before it is ultimately destroyed.

Microdiffraction and photoacoustic infrared techniques are the basis for almost any analytical study. Both techniques work well even on small samples and as they are not destructive, the sample can be used again for other more classical tests. The few examples found on these pages have the capacity of showing the potential of these two techniques.

The photoacoustic tests are the first to be carried out as their results are very useful in choosing the following techniques to be adopted. The oxalate found during the diffractometric testing of large quantities of material was highlighted thanks to the sensitivity of the infrared technique and we were able to approximately determine its spatial position. The infrared system's sensitivity to organic substances also enabled us to highlight where markedly organic binders such as oils and resins had been used.

Microdiffraction is limited to the mineral or, rather, the crystal sector with some sensitivity difficulties regarding a few substances but its adaptability enables testing the sample however it has been taken, and also studying the stratified section. The testing potential should be able to increase the possibility of identifying mineral pigments, but this problem is of no importance for the answers we aim to give.

7. Conclusion

As has already been said, the importance of characterising the scialbo layer was directly connected to choosing the technique to remove its. Although use of dissolution is widespread in restoration work, it was avoided because of the high gypsum content. A dry method was chosen for the cleaning, i.e. the superficial layer was removed gradually by means of scalpels and fibreglass brushes.

Determining the type of salts present in the masonry can condition the choice of consolidation techniques. One technique, in particular, which makes use of mineral compounds such as barium hydroxide, is so sensitive to certain types of salt that its application is invalidated or should be avoided [8].

The data concerning the study of the pictorial technique used has a more humanistic aspect to it. The type of pigments and the quality of the blends are indications of the richness of the workshop and the technical skill of the artists. Moreover comparison with neighbouring paintings proved the validity of scientific techniques for identifying the technical differences between the painters. The data obtained showed that in the historical period in which these were painted the concept of fresco painting, as was later conceived during the renaissance, was still far off. The technique used seems to be a mixed one. The background was dry-frescoed, at least until the masonary was damp, and then in order to avoid any adherence problems it was likely that the pigments were bound with lime-water so that even if the masonry became too dry the binding strength was assured due to the carbonation.

The finishing touches, for example the faces and writing, were then dry-frescoed because the time needed for the various painting phases was such that it was impossible to obtain a real fresco. It is difficult to understand if a proteic binder was used for the painting as well as for the scialbo. As has already been said, this difficulty arises from the presence of proteins in the outer layer which can invalidate the results concerning the paintings. In fact we cannot ignore the possibility that the casein binding the gypsum could have penetrated into the wall. The situation is different for the contemporary painting of two angels in the same church, where the use of protein is evident but it is used in a simple blend with red ochre with the aim of obtaining layers of diverse optical penetrability and therefore different final chromatic effects. All this done to broaden the colour range of shades which would otherwise be limited because of the small number of pigment types used.

As we can deduce from the information concerning the recovery of the Aosta Cathedral upper nave paintings, the scientific contribution to restoration work can be considerable for both the choice of work procedure and for the examination and technical knowledge of the materials and methods originally used. Neither must we neglect the contribution concerning the choice of materials to be used during restoration. In fact questions concerning the protection of the restored surface often arise. Also in this case methods and materials that we could call common have been used for a long time, but their applicability should always foresee testing in order to check the compatibility of the materials and the surface to be preserved. For this reason the laboratory has set up a series of experiments with various products and specimens that have been prepared and aged appropriately. Unfortunately the biggest obstacle is posed by the type of products commercially available. The scarce amount of material that can be used for restoration is the reason that industry and scientific experimentation have taken little interest in this particular problem and the products which are normally employed were initially produced for other uses. These materials often work very well but we know, for example, very little about the interaction between modern materials and old or modified surfaces.

In conclusion, we should often ask ourselves this question: is our history worth more or less than marketing rules?

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