The mural paintings of the coastal area of Slovenia are of a unique style due to various stylistic tendencies that met there during the Middle Ages. Until now they have been studied only from the art-historical point of view. The present research is the first analytical approach to these monuments. The purpose was to find out if (i) these paintings are diverse also in their technique and material, and (ii) if the real fresco technique is typical of those paintings influenced by Italian tradition, while the lime technique of the central-European influenced murals. To answer these questions, several mural cycles were chosen: Zanigrad (1400-1410), Pomjan (1410-1420), Nozno (1/2 15C), Volarje (2/4 15C), Vremski Britof (1445-1450) and Famije (1450-1460). All murals were studied in situ and micro-samples of mortars and pigments were analysed in powdered form or as cross-sections using different instrumental techniques: OM, SEM-EDS, FTIR and XRD. The composition of mortars is predominantly lime and sand. The pigments applied are mostly of inorganic origin. The painting techniques are different combinations of fresco, secco and lime technique. Geographically closer paintings are technically similar. The local tradition was stronger than foreign influences.

1 Introduction

In the coastal area of Slovenia many medieval churches are preserved, the majority of which are decorated with extensive mural paintings. These are very different in style: the Italian, the central-European and the local one and have been studied from the art-historical point of view, however, practically no materials research has been carried out. The techniques and materials applied were of interest only during conservation interventions, however, reports in archives cannot be found in almost all cases. In order to understand the object holistically, technical and material aspects of artwork have to be taken into account, alongside the art-historical approach. For this reason, the present study was dedicated to the former aspects, to complement the already existing theoretical investigations.
For the study, several mural cycles were selected, covering the time span of the 15th century, the geographical area of now-a-day Slovenian coastal region and the style aspects from Italian to northern influences. The parish churches of St. Stephen in Zanigrad (1400-1410) and of Virgin’s Nativity in Pomjan (1410-1420) show artistic language of the Venetian and Paduan art of the early 15th century. In Zanigrad (Figure 1) all walls are covered with scenes from Christ’s childhood and Passion, probably carried out by three different masters.

In Pomjan only a small part of the whole cycle is conserved, showing fragments of Adoration of the Magi, St. George’s and St. Steven’s legends. The parish church of Sts. Peter and Paul in Nozno (1½ 15th century) reveals South Tyrolean artistic language of around 1400, which can be found also in mural paintings at the parish church of St. Briktius in Volarje (2/4 15th century). In both churches only a very small part of the paintings is conserved. In the first one rests of Nativity, Adoration of the Magi and some figures of saints can be recognized, while in the second one only separated fragments, showing saints, architecture or figural composition (Figure 2), are conserved. On the other hand, the paintings in the presbytery of the parish church of Virgin’s Assumption in Vremski Britof (1445-1450) reveal connections with the north of Europe, specifically with Salzburg’s painting of 2/2 15th century. The master must have known Konrad Laib’s works. The cycle, not conserved in its wholeness, shows apostles as martyrs (Figure 3), Nativity, Virgin’s coronation, Imago Pietatis and Christ as a Judge. Mural cycle in the parish church of St. Thomas in Famlje (1450-1460) is, again, connected to Venetian painting, but in this case of the second quarter of that century. The scenes, damaged in parts, cover all the walls and are mostly dedicated to different saints’ lives.

It is well known that mural paintings of the Italian Trecento and Quattrocento were carried out on fresh mortar, in a good fresco technique, with some additional secco finishing, depending on the master, on the pigments chosen and on the atmospheric conditions. This technique was spread, along with stylistic influences, through other European countries mostly by traveling artists and was enriched with domestic tendencies. On the other hand, north of the Alps, the more simple lime technique was commonly used, especially due to more humid and colder atmosphere that permitted longer drying period of the mortar or lime-wash. However, it cannot be ascertained whether the genuine fresco was an Italian re-invention only and that it did not exist by itself as well in northern countries without the Italian influence.

In areas of more intense artistic transition, such as Slovene or Austrian territories in the Middle Ages, the different artistic techniques encountered each other. Sometimes fresco technique prevailed, while in other cases the lime-technique was the predominant technique.
one. But also a combination of both techniques, together with a secco was very common. The relation between all three depended on the master and his skills, on the atmospheric environment (humidity, temperature) and on supplies. It is not known, how, if at all, the stylistic influence extended to technical execution. In most cases, it was expected that on the mural paintings showing Italian stylistic language, also the better a fresco technique was to be found. However, this is not always the case.

The purpose of this study was to find out if the mural paintings are diverse not only in the stylistically aspect, but also in their technical execution and in materials used, such as support and pigments. In other words, if the genuine a fresco technique is really characteristic for those paintings influenced by Italian Trecento and Quattrocento tradition where it was revived and cultivated, and if the lime technique is more commonly found in the murals showing the central-European artistic expression. The structure of mortars, the composition of pigments and their selection, as well as the binding media used was of interest. It was also of interest if only one technique of mural painting or possibly a combination of two or three (a fresco, a secco, lime-wash) was used.

2 Experimental

To achieve the goals of this research, first of all, the paintings were studied in situ. For this, day- and spot-light were used, applied directly and diagonally, to see the surface structure, and photographs were taken. Next, micro-samples of mortars and pigments were extracted.

Scientific investigations of the samples mainly consisted of preparation of cross-sections. This methodology allows to study the different layers of mortar as a support and of the painting itself. The sample cross-sections were studied by setting in resin and polishing, or in the ground form, depending on the laboratory procedures and instrumental techniques used, as are commonly applied in materials characterization. optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) to carry out the sample microanalysis, Fourier Transform Infra-Red spectroscopy (FTIR) and X-Ray powder diffraction (XRD).

OM was carried out by means of a conventional reflected light microscope Nikon, model 115, with fibre optic illumination fitted to a Nikon Coolpix 5000 digital camera. SEM observations were undertaken with a JEOL JSM 5400 instrument. The cross-section samples were covered with a thin layer of Au by sputtering. EDX microanalysis of these cross-section samples was performed using the SEM equipment using an Oxford Link analyser with Si(Li) detector, Be window, at 20 kV. For additional information concerning mortars, pigments and possible organic substances, FTIR spectra of selected layers in the cross-sections were obtained with a Nicolet FTIR model 510. In some cases, 1 mg powdered sample and 400 mg KBr were mixed and ground, preparing pressed pellets used for the analysis by FTIR transmission spectroscopy. For mortar analysis the best technique proved to be XRD. Selected samples were ground using an agate mortar and pestle. This very fine powder was studied by Siemens D-501 diffractometer, at 40 kV and 20 mA, with CuKα Ni-filtered radiation and speed 0.5 ° in 20 per minute.

3 Results and Discussion

3.1 Mortars

The composition of mortars of first four mural cycles, that are also temporally closer to each other, is very similar; they are made of lime and sand. The intonaco is always rich in lime and well-polished. In Zanigrad and Pomjan the yellowish colour shows the presence of clay, demonstrated also by XRD results (Figure 4). The presence of clay can be explained not only by the sand chosen, but also by the lower cleanliness of it, due to the lack of insufficient previous washing with water. On the other hand, the sand in Nozno is very clean and that is why also the mortar is whiter.
In Volarje, the workshop applied a high quality mortar, the best found among the selected monuments. It is made of lime and crushed marble or lime rock (Figure 5), which is a very suitable composition for a fresco painting. If offers a clean, white surface to paint on and it is very consistent and long-lasting. In this locality the mortar was surely put on in two layers, arricio and intonaco, which permitted the use of sinopia, preparatory drawing carried out on the mortar under-layer.

In Volarje, mortar layers are thicker, put on wall in smaller portions of one day’s work, giornata, which made it possible to always work on a fresh surface. Giornatas were discovered also in Nozno, while in Zanigrad and Pomjan these are not so clearly seen; the workers at both localities must have applied the mortar in larger portions, the layer was thinner and it dried quicker. This is why the presence of a lime wash (Figure 6) was discovered in these paintings, applied in different areas where the mortar was already too dry to paint on.

In contrast, in Vremski Britof and Famlje, two geographically close localities with younger paintings, the mortar is characterized by a high quantity of sand, seen already in the cross-sections (Figure 7). The yellowish colour of mortars reveals that the sand was not well washed, while the XRD results confirmed the presence of impurities. The sand must have been collected nearby both churches, possibly in the same locality. On the other hand, the relative amount of lime is low, what causes bad consistency of mortars which tend to pulverize. Giornatas are mostly limited to a scene. Mortar in both churches was put on walls in very thin layers that dried quite quickly and not permitted a longer work on a fresh support. However, there was no lime-wash discovered in any of those two mural cycles.

### 3.2 Pigments

In comparison with other mural paintings on the Slovene territory, the studied ones surprise with warm and vivid colours. The pigments applied are almost all of inorganic origin, which is convenient for fresco painting\(^4\,5\,14\,17\,19\) lime white, yellow and red ochres (Figure 8), green earth (Figure 9) and umbra.\(^6\,8\)

The most characteristic chemical element, as shown by SEM-EDX analyses is Ca from lime that served as the major binding medium, while Fe reveals the use of iron oxides (Figure 8). In the case of green earth also K, Mg, Al and Si were detected, since the pigment contain a lot of silicates (Figure 9). Malachite, a green pigment of mineral origin and chemically basic copper carbonate, was confirmed only in Vremski Britof. The analyses of blue pigment gave no conclusive results. However, it is assumed that azurite must have been applied. This mineral pigment, also a basic copper carbonate, can be observed in situ by some typical changes, caused by the environment – due to humidity azurite changes to green paratachamite.\(^4\,5\)

This pigment is normally painted a secco on a grey or brownish-azurite under-layer, which is way it probably fell off the tiny samples taken from the paintings and, therefore, could not be detected. In Zanigrad and Vremski Britof the presence of lead-based pig-
The present study tried to ascertain whether the Italian-influenced paintings were carried out in a genuine a fresco technique, while those with a northern-style expression in lime-technique, which was mostly in use in North-European countries. All the paintings were examined visually, and micro-samples of mortar and pigments were carefully extracted. The samples were ground or prepared as cross-sections and then studied using different instrumental techniques: OM, SEM-EDS, FTIR and XRD.

The results showed that the mortar is in almost all cases made of lime and sand, which mainly contains are mostly lost, while the a fresco parts are still in a relatively good conservation state.

The modelling of these murals shows painters of relatively high quality and good knowledge. However, the best quality mural painting was revealed in Volarje, carried out almost entirely on a fresh mortar. Colour layers are thin and adhere to the support well, which is why the colour is so well preserved. When the fresco technique was applied, no sharply defined border between the mortar and the colour layer can be seen on cross-sections (Figures 6,8,9). In Nozno, the characteristic element is a thick basic colour layer (Figure 8), while modelling was made with thin ones. This kind of painting is similar to that found on mural cycles of the Gorica-Suha-Bodešče workshop and, on the other hand, reveals a more provincial painter that could not carry out fine tonalities.

Paintings in younger Vremski Britof and Famjle show some similarities, although they show different stylistic influences. This must be due to geographical proximity. Because of thin mortar layers in both churches, a big portion of the work was finished on an already dry support, which is why a lot of modelling has been lost. The mortar dried too quickly also due to numerous incisions; these have an important role in both paintings, revealing the use of cartons for transferring compositions. The painter, after the incisions were finished, managed to only carry out pre-drawings and local colour layers on a fresh mortar, where necessary, while the rest was done a secco with pigments mixed with an organic binding medium. This is why the colour layers are quite thick and the line between the mortar and colour layer can be seen clearly (Figure 7). The later the colour was put on the wall, the thicker and less persistent it is. A more extensive a secco part is observed in Vremski Britof, where the way of modelling and the thin drapery folds represent a connection with paintings of Konrad Laib.2,3

4 Summary and Conclusions
Six different mural cycles from the 15C, spread in the coastal area of Slovenia were technically analysed: the parish churches of St. Stephan in Zanigrad (1400-1410), of Virgin’s Nativity in Pomjan (1410-1420), of Sts. Peter and Paul in Nozno (1/2 15C), of St. Briktius in Volarje (2/4 15C), of Virgin’s Assumption in Vremski Britof (1445-1450) and of St. Thomas in Famjle (1450-1460). They all reveal different stylistic influences, mostly Italian, but also North-European. The composition of mortars, the choice of pigments and binding media, the way of colour modelling and especially the painting technique were of interest.

The composition of mortars, the choice of pigments and binding media, the way of colour modelling and especially the painting technique were of interest.
a lot of impurities. Only in Nozno the sand was properly clean, while in Volarje, crushed limestone or marble was used instead of sand, providing the best quality mortar of all. Here, a two-layered mortar was also found, making it possible for sinopia to be used on an arriccio layer. Less clean sand, mixed with a low quantity of lime was found in Vremski Britof and Famlje, two geographically close localities, with the same sand source possibly having been used. The mortar was applied in relatively thin layers (especially in the latter two churches) in big portions/giornata, which in most cases resulted in quick drying of the support.

In all paintings, the work started on fresh mortar, on which pre-drawings, under-paintings and local tones were carried out, while colour modelling had to be done on a lime-wash or on a dry mortar. The portion of a fresco and a secco varies from painting to painting. In Zanigrad and Pomjan, lime-wash was also added to specific areas to freshen up the mortar. The pigments used were of inorganic origin, earths and minerals, bound with calcium hydrate or with an organic binding medium if applied a secco.

If the basic colour layers are mostly thin, except in Nozno, those a secco are thick and have in many areas fallen off. Selected monuments with paintings associated with the Italian style, better technical aspects are recognisable (Zanigrad, Pomjan, Famlje), while in other instances this is not the case (Nozno, Famlje). With respect to mortar composition, Famlje is closer to Vremski Britof, and the use of incisions, colour image and a big a secco part make it distinctly from Pomjan which is stylistically influenced by Venetian painting.

However, local tradition was of most importance in this area of Slovenia, with a fresco, a secco and lime technique associated with the masters’ skills, material supplies, pigment selection and the environment. The results of this research show that geographically closer paintings are also technically similar, and local tradition was stronger than foreign influences. Stylistic and technical influences do not always coincide.

## Acknowledgements

The authors acknowledge the financial support of Research Project MAT2002-02549, partially financed by FEDER, and the Bilateral Co-operation Project between Slovenia and Spain. The support of CSIC Thematic Network of Cultural Heritage is also acknowledged.

## References