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UNIQUE PRE-ROMANESQUE MURALS IN KOSTOĽANY POD TRÍBEČOM, SLOVAKIA: THE PAINTING TECHNIQUE AND CAUSES OF DAMAGE*

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Pre-Romanesque murals at Kostol'any pod Tríbečom, Slovakia, have been investigated by portable X-ray fluorescence and by microanalytical methods to identify painting materials (pigments and binders), and to explain the degradation of colours. Today, missing green and blue shades have been reconstructed according to residual concentrations of Cu, which correspond to copper chlorides—products of salt corrosion of the copper carbonates azurite and/or malachite, accelerated by micro-organisms. As confirmed by powder X-ray microdiffraction, original minium (Pb_3O_4) has been transformed to brown–black plattnerite (PbO_2). In increased humidity, even insoluble pigments are washing down from the walls and the intensity of colours further diminishes.

KEYWORDS: PRE-ROMANEQUE MURALS, PAINTING MATERIALS ANALYSIS, DEGRADATION OF PIGMENTS, PORTABLE X-RAY FLUORESCENCE, X-RAY MICRODIFFRACTION

INTRODUCTION

The St George Church in Kostol'any pod Tríbečom, Slovakia, represents a simple single-aisle constructution with a rectangular presbytery. This style is a very typical for the ecclesiastical architecture of the early Middle Ages and is documented in a wide region including, for example, northern Italy, Switzerland, Austria, Germany and France (Ewald 1991; Brogiolio 2002; Terrier 2003). In Czech and Slovak countries, there are only a few other examples, such as the church in Modrá, near Velehrad (Czech Republic), or the St Marghreth Church in Kopčany (Slovakia). The last-mentioned one originally belonged to the settlement of Mikulčice—one of the centres of the first Slavic state in Central Europe, called Great Moravia (9th to early 10th century). Other churches of the same style can only be found in archaeological excavations in the Mikulčice area (Czech Republic), but they document clearly that this type of architecture was already well established in this region and period.

The church of St George in Kostol'any is the only one in the region in which a set of unique wall paintings from the early Middle Ages has been discovered beneath the modern wall paint. These murals were systematically documented for the first time in 1960s, as part of a programme of preservation works (Fodor 1967) and art-historical (Krása 1967; Bakoš 1968) investigations.

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From the viewpoint of art history, the investigation identified scenes of the central Marian cycle and dated them to the first half of the 11th century (Maříková-Kubková 2006). The research also included materials analyses which, however, failed to positively identify the painting technique and did not address in detail the causes of the chemical degradation of the colour layers.

Nowadays, it is known that copper pigments, for instance, and some lead pigments are unstable in conditions of increased humidity and alkalinity, as is typical for fresh lime plasters (e.g., Aze *et al*. 2008; Mattei *et al*. 2008). This fact limits their application in wall paintings, particularly when they are dispersed in pure or lime water and applied directly on the wet plaster—this technique has been known as true (*buon) fresco* technique since Antiquity (Vitruvius 1812 [27 BC]). Knowledge about the stability of pigments, however, developed gradually as the technological procedures responded to empirical experience. Moreover, the painting techniques kept changing—unstable pigments were mixed with organic binders and applied on a dry base into the already carbonized lime plaster, which no longer contained fresh alkaline lime (the *secco* technique rather than the true *fresco* technique). This method may also have been used only for certain parts of paintings. The use of organic binders increased the colour stability of pigments. As additives, the artists used egg, yolk or glue tempera, casein or polysacharide binders (Thompson 1956). In 1437 Cennino Cennini, in his book *Il libro del arte* (Cennini 1978 [1437]), aptly wrote about orange minium, stating that 'the paint is suitable only for work on panel paintings. Because when used on walls, it turns black and loses colour as soon as it sees air'. Still, what the level of expertise had been in this field 400 years earlier—that is, at the time when the paintings at Kostol'any were created—is hard to guess, as no literary sources are available.

A frequent (but not the only) cause of degradation of inorganic pigments in all types of wall paintings is their reaction with dissolved salts, which migrate in porous plasters and subsequently slowly crystallize just beneath the surface (subflorescence) or on the surface (efflorescence). In addition to chemical degradation, mechanical degradation also occurs due to an increased crystallization pressure (López-Acevedo *et al*. 1997). The sources of the salts may not be in the masonry itself, but they may be brought in from the soil or as a result of atmospheric humidity. Salts migrating from the subsoil are chlorides in particular (especially in close proximity to water courses or overland roads) or nitrates (in close proximity to graveyards or industrially fertilized fields). The polluted atmosphere of Central Europe contains mainly sulphate anions, which results in the development of omnipresent gypsum efflorescence (Schweigstillová and Hradil 2007).

Within our background research, we have already investigated degradation processes of lead and copper pigments interacting with salt solutions in laboratory conditions (Kotulanová *et al*. 2009; Švarcová *et al*. 2009). As shown by the results of these experiments, all copper pigments in an environment with increased humidity and chloride activity gradually transform into light green alkaline copper chlorides, most frequently rhombic atacamite and triclinic paratacamite—both $Cu_2Cl(OH)_3$. The fastest transformation occurs in acetates: verdigris $Cu(CH_3COO)_2{\cdot}H_2O$ (100% conversion as early as in 6 months), followed by carbonates; azurite $Cu_3(CO_3)_2(OH)_2$ (10% conversion in 20 months) and malachite $Cu_2(CO_3)(OH)_2$ (2% conversion in 20 months). The example of the most stable malachite makes it possible to demonstrate the accelerating effect of oxalic acid ($H_2C_2O_4$)—in its presence, almost 20% of malachite transformed in 4 weeks, mostly into atacamite. Similarly, in an environment with sulphate anions, oxalic acid accelerates the transformation of Cu pigments into brochantite $Cu_4SO_4(OH)_6$ (Švarcová *et al*. 2009).

We have also experimentally verified that the degradation of lead white (hydrocerussite $Pb_3(CO_3)_2(OH)_2$ and/or cerussite $PbCO_3$) in a suspension with different salt solutions always results in the formation of compounds containing only divalent Pb, while no significant darkening occurs. On the contrary, minium (Pb_3O_4), in a suspension with any salt solution that contains dissolved atmospheric CO_2 in the form of hydrogen carbonate anions, spontaneously disproportionates into a mixture of plattnerite (PbO_2) and cerussite ($PbCO_3$). In order to get the same products as in the transformation of minium (i.e., plattnerite + cerussite), the transformation of lead white needs to occur in the presence of a strong oxidizing agent. However, experimental comparisons of the effects of hydrogen peroxide (H_2O_2) and the mildewcide SAVO (a 5% solution of NaClO) have shown that darkening in a short period of time occurs only in the presence of sodium hypochlorite and not in the presence of peroxide. This means that relatively drastic conditions are needed for the lead white to darken in wall paintings (e.g., the application of mildewcides). If the darkening occurs, the products in the case of lead white and minium are the same—cerussite ($PbCO_3$) and plattnerite (PbO_2). Just as in the case of lead white, the darkening of yellow massicot (PbO) also requires strong oxidizing agents (e.g., NaClO); if such agents are not present, massicot carbonates gradually in a humid environment, which results in the formation of cerussite (Kotulanová *et al*. 2009).

The aim of this research is to interpret the composition of original pigments in colour layers of pre-Romanesque murals, to describe the painting technique and to reconstruct the processes that lead to the diminishing of the colour and the evident fading of paintings. For this purpose, non-invasive screening of the elemental composition by means of portable X-ray fluorescence is used to supplement a visual inspection of murals by optical methods. A detailed materials analysis of the microsamples is then carried out using a combination of microanalytical methods, particularly scanning electron microscopy and microanalysis, and powder X-ray microdiffraction.

METHODS

Portable X-ray fluorescence

The materials investigation of the paintings at Kostol'any was conducted in two stages. In the first stage, non-invasive X-ray fluorescence (XRF) measurements were completed *in situ*, using the X-MET 3000 TXR portable EDXRF spectrometer (Oxford Instruments). This method has provided information about the areal distribution of chemical elements heavier than potassium ($Z > 19$). Identification of lighter elements is not possible when measured in the air (measuring conditions: Rh anode, voltage 40 kV, detector resolution 230–250 eV, measuring time 60 s).

Microanalytical laboratory methods

We used the OLYMPUS BX-60 optical microscope, equipped with the Olympus DP 70 digital camera, to investigate polished cross-sections of microprobes of painting layers fixed in polyester resin and prepared on the Kompakt 1031 grinder. The observations in visible reflected light were complemented with observations of the luminescence of pigments and binders in incident UV light (Hg discharge lamp, light type UVA: 330–380 nm).

An analysis of the elemental composition of the cross-sections was made using the Philips XL30 CP scanning electron microscope, working under low vacuum contitions (0.5 mbar, without any need to cover the sample surface with a metallic coat) at a voltage of 25 kV, using the Robinson detector of backscattered electrons (RBS) and the EDAX X-ray detector (SEM–EDS: detection limit $Z > 4$, resolution 135 eV).

Powder X-ray microdiffraction (μXRD) was used for the direct detection of crystalline phases. Selected fragments and polished samples were measured with the Philips X'Pert PRO diffractometer, using a monocapillary to collimate the primary X-ray beam into an elliptical track with a constant width of ~140 μm and variable length, depending on the angle of the incident rays (usually 1.63–0.22 mm for the angle interval 10–80° 2θ). The measurement conditions were as follows: radiation Co–K_{α}, current 45 mA, voltage 30 kV, angle interval 4–80° 2θ, measuring step 0.0167°, reading time 2300 s per step, multichannel detector X'Celerator. The advantages of using of this method have already been reported by our team (Švarcová *et al*. 2010).

The basic identification of organic binders was performed by means of infrared microspectroscopy with Fourier transformation (micro-FTIR). Fragments and their polished cross-sections were measured at the Polymer Institute in Brno on the infrared Continuum microscope with a Nexus microspectrometer (ThermoNicolet, USA), in the reflective mode in the range 4000–650 cm^{-1} and using a resolution of 4 cm^{-1}. For more accurate distinction of the protein binders, we used MALDI-TOF (i.e., Matrix Assisted Laser Desorption Ionization Time of Flight) mass spectroscopy, performed by the Department of Biochemistry and Microbiology of the Institute of Chemical Technology (VŠCHT). Separated fragments were first enzymatically split with serine protease—trypsin—and subsequently analysed on the Bruker-Daltonics Biflex IV mass spectrometer (Kučková *et al*. 2007).

RESULTS OF PORTABLE XRF MEASUREMENTS

On the basis of visual inspection in the church, we can say that all the paintings were painted following one general concept. They may be roughly divided into three main sections: the northern wall, the southern wall and the presbytery. In the presbytery, the original paintings have been covered with probably Gothic paintings, on a new plaster layer, dating from the 13th century. There are four horizontal stripes containing individual scenes on both the southern and the northern walls. A brief iconographic determination of the best-preserved scenes is listed in Table 1. In general, the paintings are faded today; the colours are represented only by yellow, red, white, grey to grey–blue and brown–black to black.

A portable XRF was used to measure 290 points distributed all over the painted surfaces in an irregular random network in order to determine the chemical composition of the pigments used in the original paintings and to identify potential modern retouches and repaints. In the white and grey parts of the paintings, only calcium has been identified. It is not surprising, because the black

Table 1 *Descriptions of individual scenes of the central Marian cycle preserved in the middle stripe of wall paintings*

Southern wall (from left to right)			
Fragmentary (probably votive scene addressed to church donors)	*Lady Day* (Annunciation to the Virgin Mary)	*Visitation of the Virgin Mary*	*Nativity* scene (Birth of Jesus)
Northern wall (from left to right)			
Arrival of the three Magi (appearance of the Bethlehem star)	*Adoration of the three Magi*	*Escape of the Holy Family to Egypt*	Fragmentary (not definitely interpreted)
Presbytery (almost completely covered by 13th-century repaints)			
Maiestas Domini			

pigments, either on a carbon basis (e.g., wine black or charcoal black) or as calcium phosphates (e.g., ivory black), cannot be detected by portable XRF when measuring in air rather than in vacuum. The increased levels of iron in yellows and reds were again in agreement with the previous expectations—they indicated the use of iron ochres and iron red. Still, the most interesting result is the areal distribution of zinc (Zn), lead (Pb) and copper (Cu); other elements were present only sporadically. The presence of zinc (and in some cases also barium or chromium and cadmium) indicates modern repaints, retouches and fillings with zinc white (ZnO, widely used from 1834 onwards; see Eastaugh *et al*. 2004) and sometimes baryte white ($BaSO_4$, applied from *c*. 1810 in a natural form, and from 1830 also in a synthetic form; see Eastaugh *et al*. 2004), which are still evident on a fairly large area. They are present to a much greater extent on the southern wall (Fig. 1). According to literary sources (Fodor 1967), the wall paintings were renovated in the 1960s, and thus the occurrence of zinc and baryte whites is most probably connected with those restoration works.

As a heavy metal, lead can be measured with XRF even at very low concentrations. At Kostol'any, however, some places can be found where lead dominates completely: it is in all the black and brown–black colours; for example, in the framing of the scenes, the figure contours and so on (Fig. 1). One may therefore justifiably expect the utilization of a lead pigment, which has turned dark. It may have been minium and/or lead white or massicot. Considering the earlier published results of our experiments, which show that the darkening of lead white is induced only by strong oxidizing agents (Kotulanová *et al*. 2009), it is likely that the original pigment in the darkened parts was mainly orange minium. It is very logical to expect that light red colouring was original—particularly on paintings of cheeks and the contours of the Virgin Mary in the *Nativity* scene (Fig. 2). The red colour of the aureoles and also the use of minium (now turned black) are common in other Romanesque wall paintings (Knoepfli and Emmenegger 1990; Demus 1992).

Even more interesting was the finding of copper in numerous measurements, indicating the potential presence of copper pigments, despite the fact that there were practically no visible green or blue shades on the paintings. However, any other sources of copper are hard to imagine. The fact that the found copper actually comes from a copper pigment can be very clearly demonstrated by the areal distribution of copper in the individual scenes. Krása (1967) has divided each field with the scene into three horizontal zones: top blue-grey, central red and bottom ochrous. The detection of copper, however, has shown not only that the top zone was originally rather blue and represented the sky, but also that the copper pigments were used also in the bottom zone, where they—in combination with the yellow ochres that are still visible even now—created a rather green or brown–green ground instead of a yellow one (Fig. 1). On the northern wall, some residual copper pigments have survived in the clothes of the three Magi. One can retrospectively visualize that in the first scene from the left (*Arrival of the three Magi*), the figures featured the following clothing colours (from left to right): the first Magus was wearing green leggings and a light (white) coat, the second Magus was wearing light (white) leggings and an ochrous coat, and the third Magus was wearing ochrous leggings and a green or blue coat. In the second scene from the left (*Adoration of the three Magi*), the order of the Magi is different, as can be seen in Figure 3.

PLASTER

Apart from carbonates, the original lime plaster at Kostol'any contains chloride anions and Ca^{2+} and Mg^{2+} cations in particular, which are connected with the use of dolomitic (i.e., magnesium-rich) lime. The concentrations of ions found in the leachate have already been described by

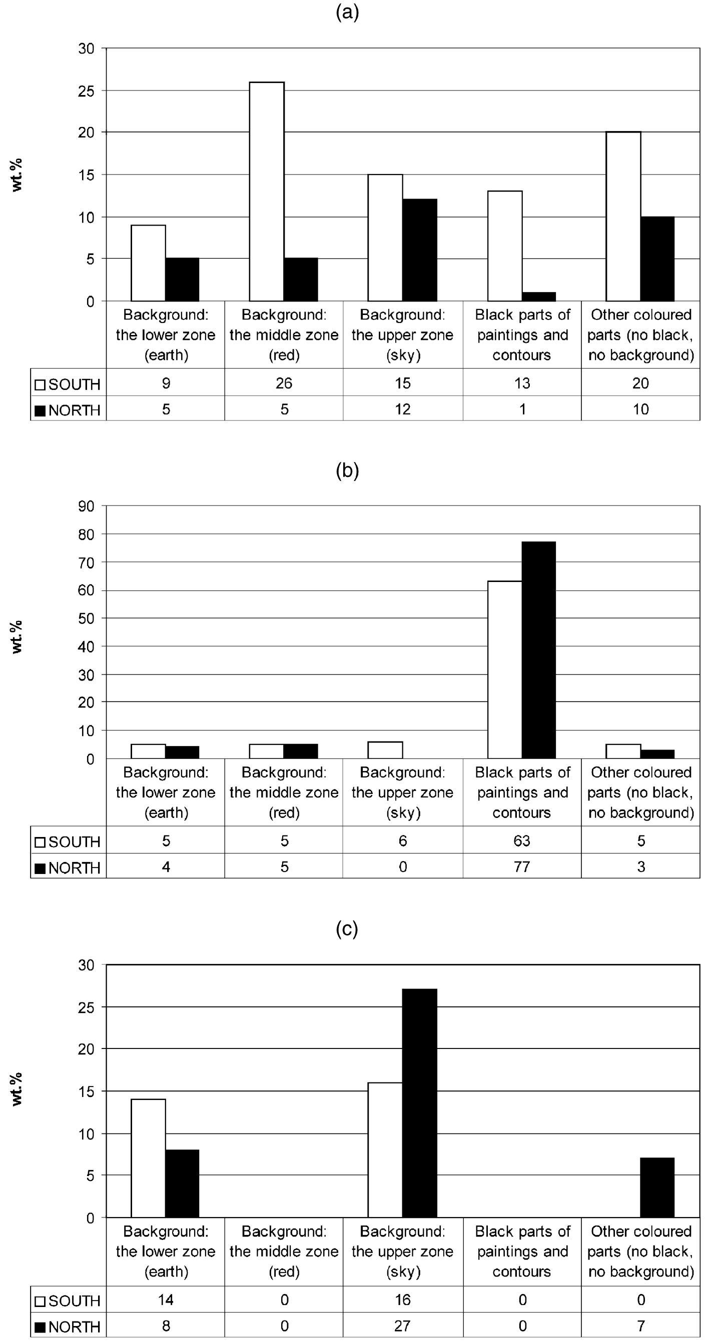

Figure 1 *The results of non-invasive measurements using the portable X-ray fluorescence method. A comparison of relative contents of (a) zinc (Zn), (b) lead (Pb) and (c) copper (Cu), related to the total content of elements heavier than calcium. Zinc is an indicator of modern repainting and retouches on the surface of the paintings, lead indicates application of lead pigments (particularly minium in the original paintings) and copper indicates the presence of copper pigments or their remnants after degradation.*

Figure 2 *The* Nativity *scene, southern wall: a detail of the head of the Virgin Mary, with nicely visible contours in the face painted in orange minium, and now transformed to brown–black plattnerite.*

Kotulanová *et al*. (2009): HCO_3^- (978 mg kg^{-1}), Cl^- (347 mg kg^{-1}), SO_4^{2-} (153 mg kg^{-1}), NO_3^- (30 mg kg^{-1}), Ca^{2+} (201 mg kg^{-1}), Mg^{2+} (145 mg kg^{-1}), Na^+ (161 mg kg^{-1}) and K^+ (56 mg kg^{-1}). Within this study, no petrographic analysis of plasters was performed. It was impossible to collect sufficiently representative samples, as the paintings were not being restored. In close proximity to the colour layers, samples of only several mm^2 were collected.

The elemental analyses via SEM–EDS have shown that the dolomite content ($CaMg(CO_3)_2$) in the raw material might have been ~20 wt%. The recrystallized binder is not homogeneous; one can find even coarse grains of calcite ($CaCO_3$) and dolomite, which may represent part of unreacted raw material (Zeman and Růžičková 1996). According to the μXRD results, the extender used in the plaster was sand, containing quartz (SiO_2) in particular, and aluminosilicates

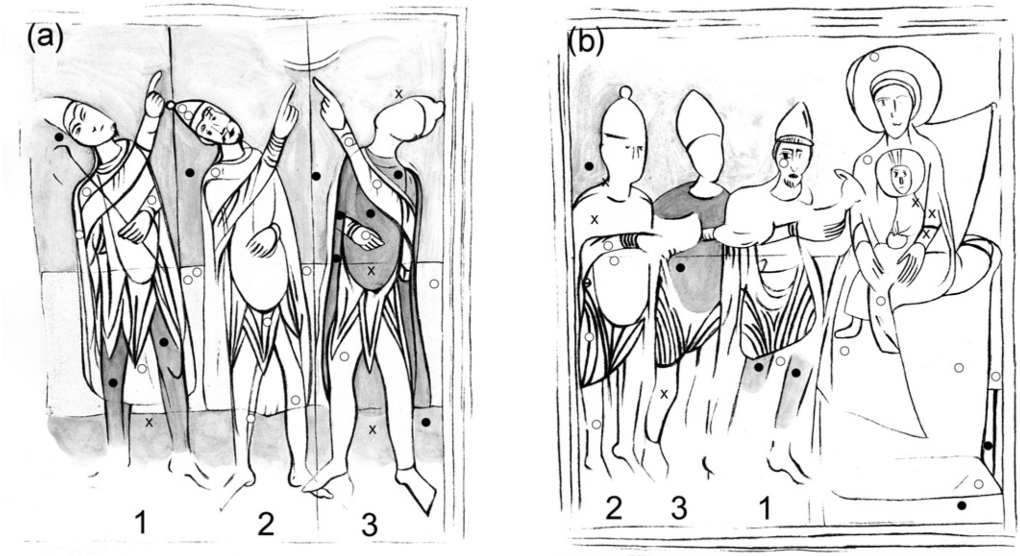

Figure 3 *The areal distribution of copper (Cu) and zinc (Zn) in the surface layers, based on spot measurements by non-invasive X-ray fluorescence and a schematic reconstruction of the original blue and/or green colouring in selected parts of the scenes depicting the* Arrival of the three Magi *(a) and the* Adoration of the three Magi *(b), both from the northern wall. Full (black) circles, Cu content >10 wt%; black crosses, Zn content >10 wt% indicating retouching, calculated as relative amounts among elements heavier than calcium (Ca). In other measurements (open circles), these elements were not identified. In all measurements, calcium (Ca) and iron (Fe) are present in addition. Originally blue and/or green parts of paintings are indicated by grey shading. The order of the Magi is indicated using numbers. Reconstruction drawing by K. Vytejčková.*

such as micas and feldspars. Furthermore, the plaster contains iron-rich heterogeneities, with a high content of free Fe oxides (particularly hematite Fe_2O_3). These admixtures are often viewed as crushed bricks in the literature, to make up the extender (Thompson 1956). In our case, the presence of bricks has not been confirmed because no calcium silicates have been found in association with Fe oxides by µXRD. Therefore, we can conclude that iron pigments (ochres and reds) were intentionally added to the plaster with the aim of modifying the colour.

The paintings on the plaster support at Kostol'any follow the roughness of the stonework. It is also clearly possible to discern horizontal lines of overlapping of the fresh plaster and earlier layers—the so-called *pontate*. The overlapping areas (seams) can be found 2 m apart and they frame a working area for a person utilizing scaffolding. They provide evidence of the scaffolding used at various stages of the work (Knoepfli and Emmenegger 1990).

PIGMENTS AND PAINTING TECHNIQUE

Preparatory lines made with tightened twisted strings outline the individual scenes horizontally and vertically into several fields. The lines were marked in the wet plaster with ferric ochre. They had been incorrectly interpreted by Fodor (1967) as brush painting. The mural paintings themselves currently mostly consist of only one or two colour layers and the colour range seems to be reduced. Optical microscopy of micro-sections of the colour layers has shown that pigments were mixed with lime water or whitewash (i.e., a mixture of lime and chalk—calcium carbonate) and painted on the uneven plaster surface. The painting was made on the wet plaster, as has already been mentioned by Fodor (1967). North of the Alps, this type of painting is called lime wall painting (Knoepfli and Emmenegger 1990), which has a similar technological meaning as most frequently used term, *fresco*.

The results of materials analyses of pigments provided by SEM–EDS and μXRD can be summarized as follows: the colouring of the original layers is mainly given by the presence of yellow ochres, iron reds, blackened lead pigments (minium), whitewash—carbonized dolomitic lime—and carbon blacks; in Incarnates, dolomitic lime with ferric ochres was used. Details of faces and figure contours, and also the framing of the individual scenes, contain minium (now blackened). We originally assumed that, taking their blue shade into consideration, the grey–blue parts of the paintings (e.g., the coat of the Virgin Mary) would contain at least some residues of copper pigments. However, no copper was found in those colour layers. A cross-section of the microsample taken from this part clearly shows only the colour layer pigmented with black. It is well known that blue coats in wall paintings with azurite or malachite were often completely or partly underlaid with a black pigment, which a technique is called *veneda* by Theophillus. The dark layer under a blue pigment enables the light dispersion on the white underlying plaster to be reduced, which increases the covering power of the blue pigment. Knoepfli and Emmenegger (1990) have reported the *veneda* technique; for example, in the case of early Christian wall paintings in Cappadocia, Turkey, and also in Egypt (beneath Egyptian blue). In Romanesque paintings in the cathedral in Norwich, United Kingdom, a layer of ground *lapis lazuli* (i.e., natural ultramarine) was applied on areas painted black (Howard and Gasol 1996). In the case of the paintings at Kostol'any, however, no blue pigment was found. The blue tint is achieved here by mixing—in the same layer—carbon black of vegetable origin with iron black (magnetite Fe_3O_4), with a metallic bluish lustre.

SEM–EDS microanalysis of polished samples has confirmed the occurrence of residual copper pigments only in those parts of paintings where they had been previously detected by making non-invasive XRF measurements. However, the copper concentrations are very low in general (mostly near the detection limit of EDS analysis: 1 at%). Only locally (in two microsamples) do they reach several atomic per cent. The highest concentration of Cu was 17 at%. Although green or blue mineral grains were not found at all, a positive correlation can clearly be observed between Cu and Cl in the EDS measurements (Fig. 4). No Cu-containing phases were found by μXRD when measuring Cu-enriched fragments taken from the bottom ochrous zone of the background on the southern wall, or from the painting of the greenish leggings of the first Magus in the *Arrival of the three Magi* scene. In these parts, only yellow ochres containing clay minerals and iron hydroxides (goethite) are dominating today (Table 2 and Fig. 5). It is not possible to indicate the provenance of these earthy pigments. The most interesting result is the presence of smectite group minerals, which are not very frequent in mid-European paints. They appear more often in Italian pigments (Hradil *et al*. 2003) and thus their presence could (speculatively) indicate the importation of materials from southern Europe. Also, the other well-known traditional source of earths in north-east Turkey (the so-called 'Armenian bole') was rich in smectites (Dehn 2005).

Sporadically, dark brown grains can also be found at Kostol'any, with high Mn contents (revealed by SEM–EDS) that indicate the use of umber. In these grains, the Cu contents are higher compared to the surrounding area. This is not surprising, because the umber from the most traditional source in Cyprus may eventually contain copper in very small quantities because of its close relation to copper deposits in ultrabasic rocks (Dill *et al*. 2007). Although Mn is accompanied by some Cu (Fig. 4), it is fairly certain that umber was not the only original pigment

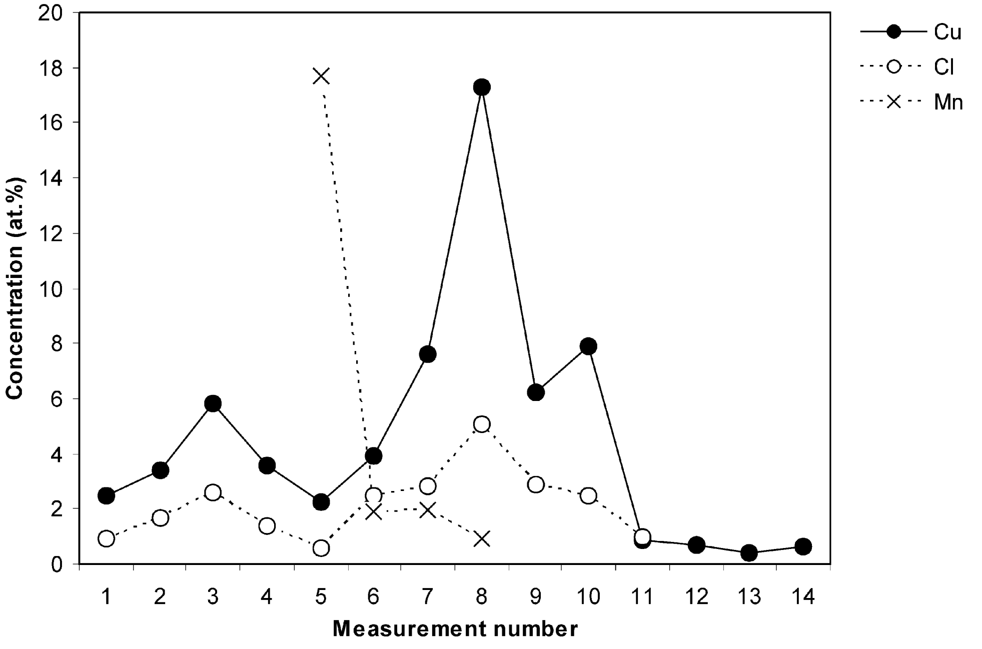

Figure 4 *Correlation of the copper (Cu), chlorine (Cl) and manganese (Mn) contents obtained by SEM–EDS in microsamples taken from the lower ochrous zone of the background.*

containing Cu at Kostol'any. The spread of residual concentrations of Cu over such a large area on the paintings needs another explanation, which is given in the following section.

DEGRADATION OF COPPER PIGMENTS

It can be assumed that in order to stabilize the Cu pigments in the alkaline environment, they had been mixed with an organic binder—as described for the *secco* technique (Thompson 1956). Then, at Kostol'any, those parts of paintings with increased Cu concentrations should also have contained some residues of the organic binders in the surface layers. The correctness of this idea was confirmed by the MALDI TOF MS method, which is highly sensitive to even very low concentrations of proteins. Four samples were taken from the original layers: two of them came from areas with increased concentrations of copper. And it is only in these samples that the remains of collagenous proteins were found; this identification was based on the detection of 11 and 21 peptidic fragments, respectively. The method frequently used for organic analysis (FTIR) was also applied, but no amidic bands and thus no proteins have been identified in any of the 12 samples of the original layers. Different results are clearly given by the differing detection limits of these two methods (Table 3). A positive identification of remains of collagenous proteins might indicate the use of glue as a binder in specific parts of murals only. This interpretation seems logical, as organic binders provided immediate protection for the pigments in the chemically aggressive environment; however, colour layers with such binders were probably mechanically less stable in the long term. It could also be a reason why these '*secco*' layers are almost completely missing.

Table 2 *A list of the results of powder X-ray microdiffraction measurements on fragments and cross-sections (the number of samples containing the corresponding phase is expessed in parentheses, if different from 1)*

Sample no.	*Description*	*Major phases*	*Minor phases*
12, 25	Original plaster	$CaCO_3$ calcite (2)	CaMg $(CO_3)_2$ dolomite (2) SiO_2 quartz K-mica; for example, muscovite
8	Heterogeneity in the plaster (red colour)	Fe_2O_3 hematite	$CaCO_3$ calcite
2, 7, 11, 12, 14, 26	Original Pb pigments (blackened)	PbO_2 plattnerite (6) $CaCO_3$ calcite (3) $PbCO_3$ cerussite $PbMg(CO_3)_2$	$PbCO_3$ cerussite (4) PbO_2 scrutinyite (4) $CaCO_3$ calcite (2) PbMg $(CO_3)_2$ (2) $Pb_3(CO_3)_2(OH)_2$ hydrocerussite (2) $CaSO_4 \cdot 2H_2O$ gypsum (2) PbO massicot $PbSO_4$ anglesite
15, 16, 21, 34	Original yellows and reds	$CaCO_3$ calcite (4) $CaC_2O_4(H_2O)$ whewellite (4) $CaSO_4 \cdot 2H_2O$ gypsum (2) $Al_2Si_2O_5(OH)_8$ kaolinite K-mica; for example, illite SiO_2 quartz	$Al_2Si_2O_5(OH)_8$ kaolinite (3) K-mica; for example, illite (3) Expandable clay structure—smectite group mineral (3) $CaSO_4 \cdot 2H_2O$ gypsum SiO_2 quartz $NaAlSi_3O_8$ Na-feldspar, albite FeO(OH) goethite
18	Original Incarnate	$CaCO_3$ calcite	$CaC_2O_4(H_2O)$ whewellite $CaSO_4 \cdot 2H_2O$ gypsum $PbCO_3$ cerussite
27	Original blue-grey colour	$CaCO_3$ calcite	$CaC_2O_4(H_2O)$ weddellite $Al_2Si_2O_5(OH)_8$ kaolinite SiO_2 quartz $CaMg(CO_3)_2$ dolomite
30	13th-century repaints (red)	$CaCO_3$ calcite SiO_2 quartz	Fe_2O_3 hematite $Al_2Si_2O_5(OH)_8$ kaolinite K-mica; for example, illite $Pb_3(CO_3)_2(OH)_2$ hydrocerussite
31	13th-century repaints (yellow)	$Ca_5(PO_4)_3(OH)$ hydroxylapatite $CaC_2O_4(H_2O)$ whewellite	$CaCO_3$ calcite
10	Baroque repaint (red)	$CaCO_3$ calcite $Al_2Si_2O_5(OH)_8$ kaolinite	SiO_2 quartz K-mica; for example, illite $Pb_3(CO_3)_2(OH)_2$ hydrocerussite FeOOH lepidocrocite
20	20th-century peck	ZnO zincite	$BaSO_4$ barite $CaCO_3$ calcite $CaSO_4 \cdot 2H_2O$ gypsum SiO_2 cristoballite $Al_2Si_2O_5(OH)_8$ kaolinite

Degradation of organic binders is accelerated particularly by the activities of micro-organisms. Their metabolic product is oxalic acid, which subsequently decomposes other substances. The most stable products of such reactions are calcium oxalates (namely whewellite $CaC_2O_4(H_2O)$ and/or weddellite $CaC_2O_4 \cdot 2H_2O$). As they tend to crystallize, they can be

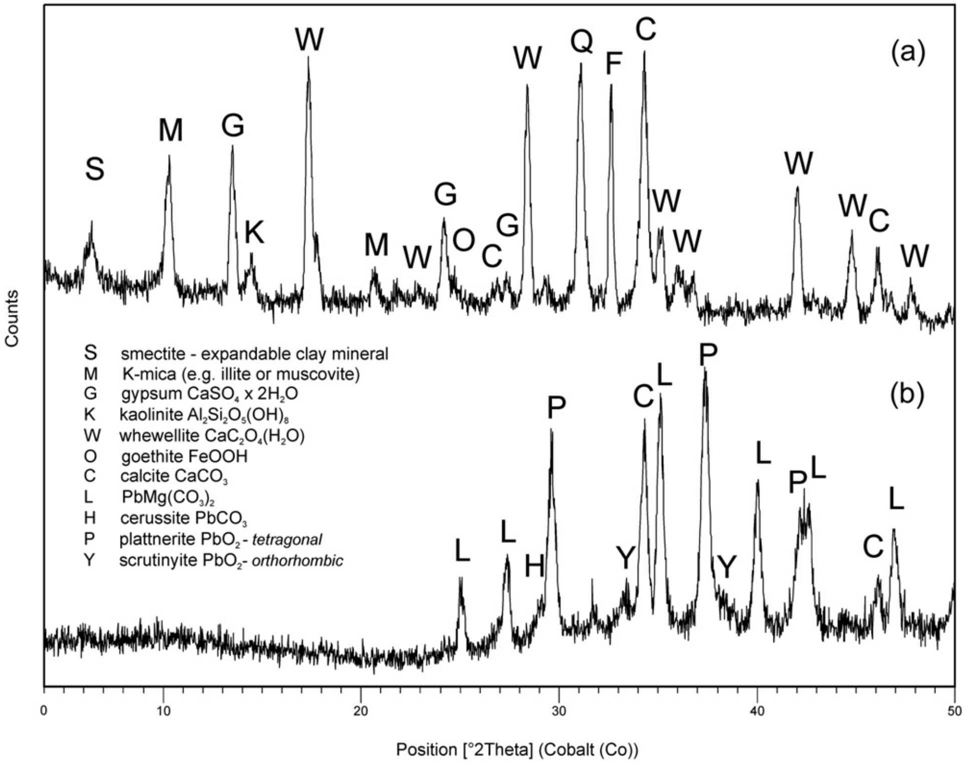

Figure 5 *X-ray microdiffraction patterns of the yellow background layer with increased copper (Cu) content (a) and the blackened layer with degraded lead (Pb) pigments (b), respectively.*

Table 3 *Organic binders and metabolic products of micro-organisms (oxalates) as identified by different analytical methods*

Parts of the paintings	*Proteins*		*Wax*	*Calcium oxalates*
	Micro-FTIR	*MALDI-TOF*	*Micro-FTIR*	*µXRD*
Pre-Romanesque (blackened minium)	0/2	n.a.	0/2	0/5
Pre-Romanesque (containing Cu)	0/4	**2/2**	0/2	**3/3**
Pre-Romanesque (other parts)	0/6	0/2	0/6	**5/5**
Gothic	**1/2**	n.a.	0/2	0/1
Modern-day interventions (20th century, pecks)	0/3	n.a.	**3/3**	0/1

Note: ratios indicate the number of positive identifications with respect to the total number of samples analysed; n.a., not analysed.

positively identified in microsamples as remnants of the above-mentioned processes, by means of µXRD. At Kostol'any, we found them in all parts of the original paintings, and to a greater extent in the areas with the increased Cu contents. They were absent only in the black colour layers, since the Pb-containing phases might have been toxic for the micro-organisms (Table 3 and Fig. 5). In this sense it is interesting that, apart from the decomposition of organic substances, micro-organisms may also accelerate decomposition of copper pigments as such, as documented by Švarcová *et al*. (2009). Copper oxalates, as unstable intermediates of the degradation processes, have been found in some wall paintings (Nevin *et al*. 2008), but unfortunately not at Kostol'any.

The high concentrations of chlorides in plasters, as found at Kostol'any, are no exception in historic buildings. These chlorides could cause the transformation of copper pigments into atacamite $Cu_2Cl(OH)_3$; atacamite and other secondary phases have also been identified in a number of other medieval wall paintings (e.g., Dei *et al*. 1998; Vandenbeele *et al*. 2005). At Kostol'any, however, the residual concentrations of Cu are very low, and even a detailed investigation did not identify original or transformed pigment grains. The only indication of the transformation process described above is the correlation of the residual Cu and Cl concentrations in colour layers at Kostol'any (Fig. 4). We can imagine that after corrosion caused by salts, probably accelerated by micro-organisms and oxalic acid produced by them, the secondary phases (e.g., copper oxalates and atacamite) were almost completely washed out from the wall by the physical action of water. Because we can exclude the possibility that this 'washing out' was intentional—that is, resulting from any documented process of cleaning or repaints removal—it is probably connected with the truly alarming climatic conditions in the church. According to measurements carried out in the winter season from October 2008 to April 2009, the relative air humidity in the interior varies in the range from 61.4 to 95.3%. The average monthly values vary from 75.7 to 88.1% near the entrance to the church, and from 74.6 to 81.1% in the presbytery. The same factor—in other words, not chemical degradation, but the physical effects of the condensed humidity on the walls—probably resulted in the washing off and thinning of the other colour layers and overall fading of the colouring.

DEGRADATION OF LEAD PIGMENTS

Another evident colour alteration at Kostol'any is the darkening of minium, as documented by the non-invasive XRF measurements and also the µXRD measurements on microsamples. The µXRD pattern in Figure 5 documents a typical mineralogical composition of a blackened colour layer found in many places—apart from brown–black plattnerite and white cerussite (both products of disproportionation of orange minium), there is also a high quantity of lead–magnesium carbonate [$PbMg(CO_3)_2$], which developed as a secondary product, and this again documents the use of dolomitic lime as a binder in the colour layer.

Mildewcides containing NaClO can also act as oxidizing agents to enhance the transformation of lead white, but there is no existing evidence of their application at Kostol'any. Former microbiological investigations of the wall paintings at Kostol'any (Šujanová and Motaj 1966) have identified several types of *Cladosporium* mildews, particularly *Cladosporium brevicompactum*. According to the authors, the mildew attacked practically the entire surface of the paintings in spring 1966, as a result of deteriorating climatic conditions. The most affected parts of the church were allegedly the northern wall of the nave and the presbytery. The mildew was only finally removed by ventilation, drying and heating of the walls with infrared lamps. Moreover, as documented by the restorer's documentation from 1960s and by samples collected at that time, the blackening of lead pigments must have occurred earlier. On the other hand, a visual comparison of the paintings after their initial exposure and their current appearance clearly indicates a significant diminishing of the colour, particularly on the northern wall. This means that the degradation of colours of this unique set of paintings continues to progress.

LATER PAINTINGS

Later (13th-century) wall paintings have been found in the eastern part of the presbytery around the pastoforium, made over the original paintings on the new plaster. The analysed samples were taken from the figure's Incarnate and from the red robe. It is very interesting that the plaster with a higher sand content, and even the paintings themselves, also contain dolomitic lime. The Incarnate and the red drapery are pigmented with iron ochres and reds, and the colour layers contain increased levels of phosphorus, related to the use of bone white (hydroxylapatite) and whitewash, which were used here. In one out of every two samples, protein binder has been identified by FTIR (Tables 2 and 3), but a definite interpretation of the painting technique was not carried out.

The ornamental decorations on the western wall of the chancel are also later. Dolomitic lime was used here in the lime plaster and in the lime coating, as well as in the paintings. In both of the above-mentioned cases, the later wall paintings have monotonous colouring and they fail to contain any specific pigments that would allow their closer historical dating. All of the later paintings were left for further research.

CONCLUSION

The cycle of the oldest wall paintings in the church of St George in Kostol'any pod Tríbečom, Slovakia, was surely created for the original church and was painted shortly after its construction in around AD 1000. According to the iconography, style and painting technique, these paintings most probably belong to the pre-Romanesque art of the 10th century.

Today, the colouring of these wall paintings is faded. The blue and/or green copper pigments were probably first altered by salt (chloride) corrosion, which was accelerated by the activities of micro-organisms that produce an oxalic acid as their metabolic product. Subsequently, they were washed out by humidity condensing on the walls. In this respect, the climatic conditions in the church deteriorated significantly in 1960s after the floor and ceiling had been covered with concrete. On the basis of the residual concentrations of copper in the colour layers, it is now at least partly possible to recall the original colouring; for example, a blue zone of the sky in the background, the colourful clothes of the three Magi and so on. Unlike the washing out of copper pigments and the related overall thinning and fading of the colour layers, the blackening of the originally orange minium is a natural process. This degradation occurred much earlier in the humid environment, where minium in the colour layer was not protected by any organic binder. The binder used in the paintings was dolomitic (magnesium-rich) lime and the paints were applied into the wet plaster (a *fresco* technique). The remains of collagenous proteins found in two samples indicate a potential use of glue exclusively in parts with copper pigments (a *secco* technique). The present colouring of the original paintings is given by the presence of yellow ochres, iron red, carbon black and blackened minium; the white is exclusively whitewash, and the use of lead white in admixture is uncertain. A special feature is the grey–blue colour shade—for example, on the coat of the Virgin Mary—which was not achieved by means of a blue pigment, but by an admixture of iron black (magnetite) with a metallic grey–blue lustre. The condition of the paintings continues to deteriorate as a result of the continuing degradation due to high and varying humidity. This degradation has become a physical process in which probably even insoluble pigment particles are washed down from the walls, and the intensity of colours diminishes very quickly.

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REFERENCES

Aze, S., Vallet, J., M., Detalle, V., Grauby, O., and Baronnet, A., 2008, Chromatic alterations of red lead pigments in artwork: a review, *Phase Transitions*, **81**, 145–54.

Bakoš, J., 1968, The origin of the wall paintings at Kostol'any pod Tríbečom, *Vlastivedný Časopis*, **17**, 178–81 (in Slovak).

Brogiolio, G. P., 2002, Oratori funerary tra VII e VIII sedilo nelle campagne transpadane, *Hortus Artium Medievalium*, **8**, 9–31.

Cennini, C., 1978 [1437], *Il libro dell' arte, the craftsman's handbook*, trans. D. V. Thompson Jr, Dover Publications, New York.

Dehn, E., 2005, *Über Armenischen Bolus*, Diploma work, Technical University Munich, Germany.

Dei, L., Ahle, A., Baglioni, P., Dini, D., and Ferroni, E., 1998, Green degradation products of azurite in wall paintings: identification and conservation treatment, *Studies in Conservation*, **43**, 80–8.

Demus, O., 1992, *Romanische Wandmalerei*, Hirmer Verlag, Munich.

Dill, H. G., Fussl, M., and Botz, R., 2007, Mineralogy and (economic) geology of zeolite–carbonate mineralization in basic igneous rocks of the Troodos Complex, Cyprus, *Neues Jahrbuch fur Mineralogie–Abhandlungen*, **183**(3), 251–68.

Eastaugh, N., Walsh, V., Chaplin, T., and Siddall, R., 2004, *Pigment compendium: a dictionary of historical pigments*, Elsevier Butterworth-Heinemann, Oxford.

Ewald, J., 1991, Kirchen und Kirchengrabungen im Baselbiet. Ein Beitrag zur Geschichte der Kirchen-Landschaft der Nordschweiz, in *Methoden und Perspektiven der Archeologie des Mittelalters* (ed. J. Tauber), 57–84, Archäologie und Museum 20.

Fodor, P., 1967, Wall paintings at Kostol'any pod Tríbečom—the painting technique. *Monumentorum Tutela*, **2**, 97–114 (in Slovak).

Howard, H., and Gasol, R., 1996, The investigation of the Romanesque paintings in the Norwich cathedral, *Technologia Artis*, 17–24.

Hradil, D., Grygar, T., Hradilová, J., and Bezdička, P., 2003, Clay and iron oxide pigments in the history of painting, *Applied Clay Science*, **22**(5), 223–36.

Knoepfli, A., and Emmenegger, O., 1990, Wandmalerei bis zum Ende des Mittelalters, in *Reclams Handbuch der kunstlerischen Technikem. Band 2—Wandmalerei Mosaik* (eds. A. Knoepfli, O. Emmenegger, M. Koller and A. Meyer), 7–212, Reclam, Philipp Reklam jun. Verlag, Stuttgart.

Kotulanová, E., Bezdička, P., Hradil, D., Hradilová, J., Švarcová, S., and Grygar, T., 2009, Degradation of lead-based pigments by salt solutions, *Journal of Cultural Heritage*, **10**, 367–78.

Krása, J., 1967, Wall paintings at Kostol'any pod Tríbečom, *Monumentorum Tutela*, **2**, 115–27 (in Czech).

Kučková, Š., Hynek, R., and Kodíček, M., 2007, Identification of proteinaceous binders used in artworks by MALDI-TOF mass spectrometry, *Analytical and Bioanalytical Chemistry*, **388**, 201–6.

López-Acevedo, V., Viedma, C., González, V., and La Iglesia, A., 1997, Salt crystallization in porous construction materials II. Mass transport and crystallization processes, *Journal of Crystal Growth*, **182**, 103–10.

Maříková-Kubková, J., 2006, Wall paintings in the church of St. George at Kostol'any pod Tríbečom, *Technologia Artis*, **5**, 85–92 (in Czech).

Mattei, E., de Vivo, G., De Santis, A., Gaetani, C., Pejosi, C., and Santamaria, U., 2008, Raman spectroscopic analysis of azurite blackening, *Journal of Raman Spectroscopy*, **39**, 302–6.

Nevin, A., Melia, R. L., Osticioli, I., Gautier, G., and Colombini, M. P., 2008, The identification of copper oxalates in a 16th century Cypriot exterior wall painting using micro FTIR, micro Raman spectroscopy and gas chromatography – mass spectrometry, *Journal of Cultural Heritage*, **9**(2), 54–161.

Terrier, J., 2003, Approche archéologique des églises rurales édifiées au voisinage de la ville de Genève, *Hortus Artium Medievalium*, **9**, 213–32.

Thompson, D. V., 1956, *The materials of medieval painting*, Dover Publications, New York.

Schweigstillová, J., and Hradil, D., 2007, Salt formation on the Cretaceous sandstones in north and northwest Bohemia, in *Sandstone landscapes* (eds. H. Hartel, V. Cílek, T. Herben, A. Jackson and R. Williams), 76–9, Academia in collaboration with Bohemian Switzerland National Park, Administration and Royal Botanic Gardens Kew, Prague.

Šujanová, O., and Motaj, S., 1966, *Kostolany pod Tribečom. Stopping-down of the fungi growth*, Unpublished report No. V-43/1, SÚPSOP Bratislava (in Slovak).

Švarcová, S., Hradil, D., Hradilová, J., Kočí, E., and Bezdička, P., 2009, Microanalytical evidence of origin and degradation of copper pigments found in Bohemian Gothic murals, *Analytical and Bioanalytical Chemistry*, **395**, 2037–50.

Švarcová, S., Kočí, E., Bezdička, P., Hradil, D., and Hradilová, J., 2010, Evaluation of laboratory powder X-ray micro-diffraction for applications in the field of cultural heritage and forensic science, *Analytical and Bioanalytical Chemistry*, **398**, 1061–76.

Vandenbeele, P., Lambert, K., Matthys, S., Schudel, W., Bergmans, A., and Moens, L., 2005, *In situ* analysis of mediaeval wall paintings: a challenge for mobile Raman spectroscopy, *Analytical and Bioanalytical Chemistry*, **383**, 707–12.

Vitruvius, 1812 [27 BC], *The civil architecture of Vitruvius*, trans. W. Wilkins, Thomson Davison, London.

Zeman, A., and Růžičková, E., 1996, Research on the materials composition of plasters, *Technologia Artis*, **4**, 93–9 (in Czech).