

LABORATORY POWDER X-RAY MICRODIFFRACTION – THE USE FOR PIGMENTS AND SECONDARY SALTS IDENTIFICATION IN FRESCOES

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ABSTRACT

Laboratory X-ray powder microdiffraction (micro-pXRD) is a very effective non-destructive method for direct phase analysis of samples smaller than 1 mm containing crystal constituents with no need of their pre-treatment. It is suitable for identification of pigments in fragments of colour layers of artworks, or their cross-sections, as well as for examination of secondary degradation products. X-ray powder diffraction is indispensable in the identification of pigments that are variable in mineralogical composition and similar in elemental composition, such as copper-based or earthy pigments. The micro-pXRD with a conventional X-ray tube, monocrapillary with an exit diameter of 0.1 mm and position sensitive detector permits us to deal with samples routinely prepared for microscopy. Contrarily to the microdiffraction using synchrotron beams the presented technique is suitable for routine laboratory analysis. In the case of wall paintings, compared to easel paintings, inorganic components are predominating. Lower amounts or even absence of organic stuff facilitate the measurements using XRD.

We used micro-pXRD for distinguishing of different copper-based compounds, basic copper chlorides, carbonates, sulphates and copper acetates, used as green pigments, e.g. atacamite, malachite, verdigris, in fresco-secco paintings from the 15th century found in monasteries and churches in the Czech Republic. We found that chlorides are much more frequent in frescoes than in easel paintings from the same period, probably because of the conversion of azurite to atacamite. Micro-pXRD was also successfully used to distinguish the structural type of the lead tin yellow usually present in Gothic wall paintings and for the identification of secondary salt efflorescences on their surface. To decide how much the colour layers are affected by secondary alterations laboratory experiments focused on copper- and lead-based pigments stability were carried out.

INTRODUCTION

Materials investigation of artworks by modern methods should be integrated into their restoration or artistic evaluation. It is based on the identification of materials and painting techniques. The success of that identification depends on the nature of materials sampled and the correct choice of analytical methods. In the case of easel and wall paintings, analytical methods used routinely in laboratories associated with galleries and restorations ateliers are optical microscopy and scanning electron microscopy supplemented with X-ray microanalysis (SEM/EDX) ⁵. Microscopic methods provide the information about the stratigraphy of painting layers that are distinguished according to their different colour, luminescence and chemical contrast by observing the cross sectioned samples in white and UV light and in backscattered electrons, respectively. On base of chemical composition determined by EDX analysis, the pigments present in the painting layer can be estimated. However, in many cases the mentioned traditional techniques are insufficient for proper pigments identification and thus an additional method has to be employed. Very effective tool for indisputable determination of mineral, thus practically all inorganic crystalline pigments and materials, is powder X-ray diffraction (XRD) ^{1,9,12}. The essential problems for XRD phase analysis are the cases when some substances having the same or similar chemical composition occur in more crystal modifications, e.g. aluminosilicates in earthy pigments or copper-based pigments.

In this paper we describe an application of X-ray powder microdiffraction as a non-destructive analytical technique for identification of mineral components in colour layers of paintings. The first systematic reports on X-ray microdiffraction materials analysis, especially using synchrotron microbeams, appeared in the late 1990s, e.g. Wang *et al.*¹⁴. Synchrotron radiation sources are noted for high intensity of x-ray beam allowing collection of diffraction data from small areas (typically in order of 0.001 – 0.1 mm) in reasonable time^{4,8,11}, however, a synchrotron is not commonly available for the routine research. A much more convenient setup for routine work is a point focus laboratory X-ray source combined with collimating capillaries and position sensitive solid state detector. Šímová *et al.*¹² showed that laboratory X-ray microdiffraction equipped with moncapillary with an exit diameter of 0.1 mm and position-sensitive detector allows analysis of fragments as well as polished cross sections of samples routinely prepared for optical and electron microscopy. We used micro-pXRD for examination of secondary degradation products¹², for distinguishing of lead-tin yellows⁶ and for detection of minor phases indicating provenance of pigments⁷. Benedetti *et al.*² reported the use of laboratory X-ray microdiffraction for separate phase identification of binder and filler particles in ancient mortar, Aze *et al.*¹ involved this technique in study of red lead pigment fading. Here we used it for identification of copper-based pigments present in Gothic wall paintings found in monasteries and churches in the Czech Republic.

EXPERIMENTAL

In the laboratory microdiffraction the diverging X-ray beam is collimated in glass moncapillary into narrow quasiparallel beam¹⁵. Because of slight divergence of primary beam in the Bragg-Brentano experimental setup the irradiated area corresponds to an ellipsoidal spot with a constant width of 142 μm (perpendicular to beam) and variable length. The length of ellipse varies with the incident beam angle from 4.01 mm at $4^\circ 2\theta$ down to 0.22 mm at $80^\circ 2\theta$. Correct adjustment of a sample is an important factor affecting the quality of collected data. In the microdiffraction experiment the sample is fixed to the x-y-z sample stage. The detector is replaced with a light microscope (Huber, magnification 50x) to align the sample at the proper high and tilt and to select the area for analysis (Figure 1).

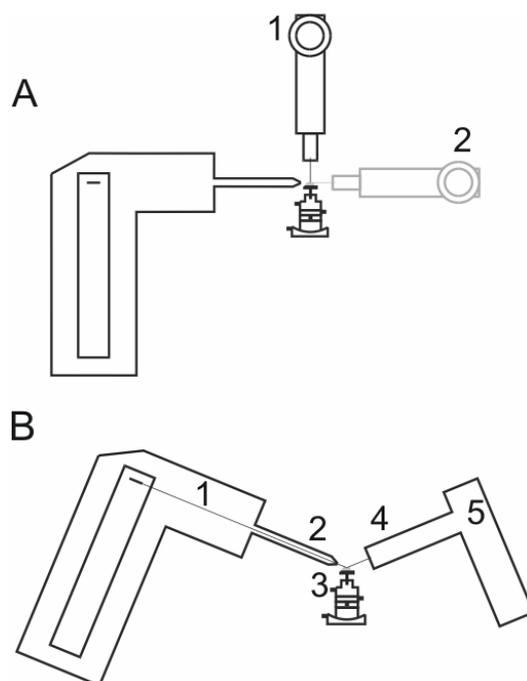


Figure 1. Setup with a microscope (A) to sample adjustment along the x, y (position 1) and z axis (position 2). Microdiffraction experiment (B): primary beam (1), moncapillary (2), sample stage (3), antiscatter shield (4), detector (5).

The documentation of analyzed point on the sample surface is allowed using a video camera accommodated in the position of the microscope eyepiece³. The measurements of fragments can be complicated by irregularity of their surface and it demands certain skills to adjust sample precisely and to find a proper area for analysis. On the other hand it is sometimes possible to rotate the sample and thus enhance output signal. It is almost always possible to select a 0.1 mm large flat area on the sample surface even it is irregular. The sample adjustment to the plane of diffraction is much easier with the polished cross sections, however, when the colour layers are porous or cracked the moulding resin penetrates them during embedding, which results in background worsening of output signal as it is shown in Figure 5 (sample 4).

The main limitations of microdiffraction analysis are size of irradiated area, size of crystals present in the studied material and detection limit of given diffracting substance. The size of crystals or their number in the irradiated volume relates to the basic condition of powder diffraction namely to the sufficient statistical representation of diffracting crystal planes. We carried out experiments with diamond crystals of various size fractions to examine the influence of the crystal size on the quality of powder diffraction record in the microdiffraction measurement. We found that diamond crystals up to 20 μm behaved as powder, the intensity ratio was kept and thus the condition for powder diffraction was satisfied. In the case of crystals of size 20 – 50 μm , the insufficient number of particles in the irradiated volume was obvious and the intensity ratio changed. In the case of crystals bigger than 50 μm it was impossible to determine crystal phases reliably using microdiffraction because some diffraction lines missed (Figure 2). The detection limit of some phase is individual for each material. In the presence we investigate the detection limits of malachite and azurite in the model samples measured using micro-pXRD.

Size fraction of diamond crystals (μm)	Intensity of diffraction lines (counts and %)		
	111	220	311
63-80	22754 (100%)	0 (0%)	0 (0%)
40-50	5433 (100%)	183 (3%)	273 (5%)
1-2	451 (100%)	87 (19%)	58 (13%)
PDF 6-675	100%	25%	16%

Table 1. Intensities of diffraction lines (111), (220) and (311) for three size fractions of diamond crystals and for diamond phase reported in PDF for comparison.

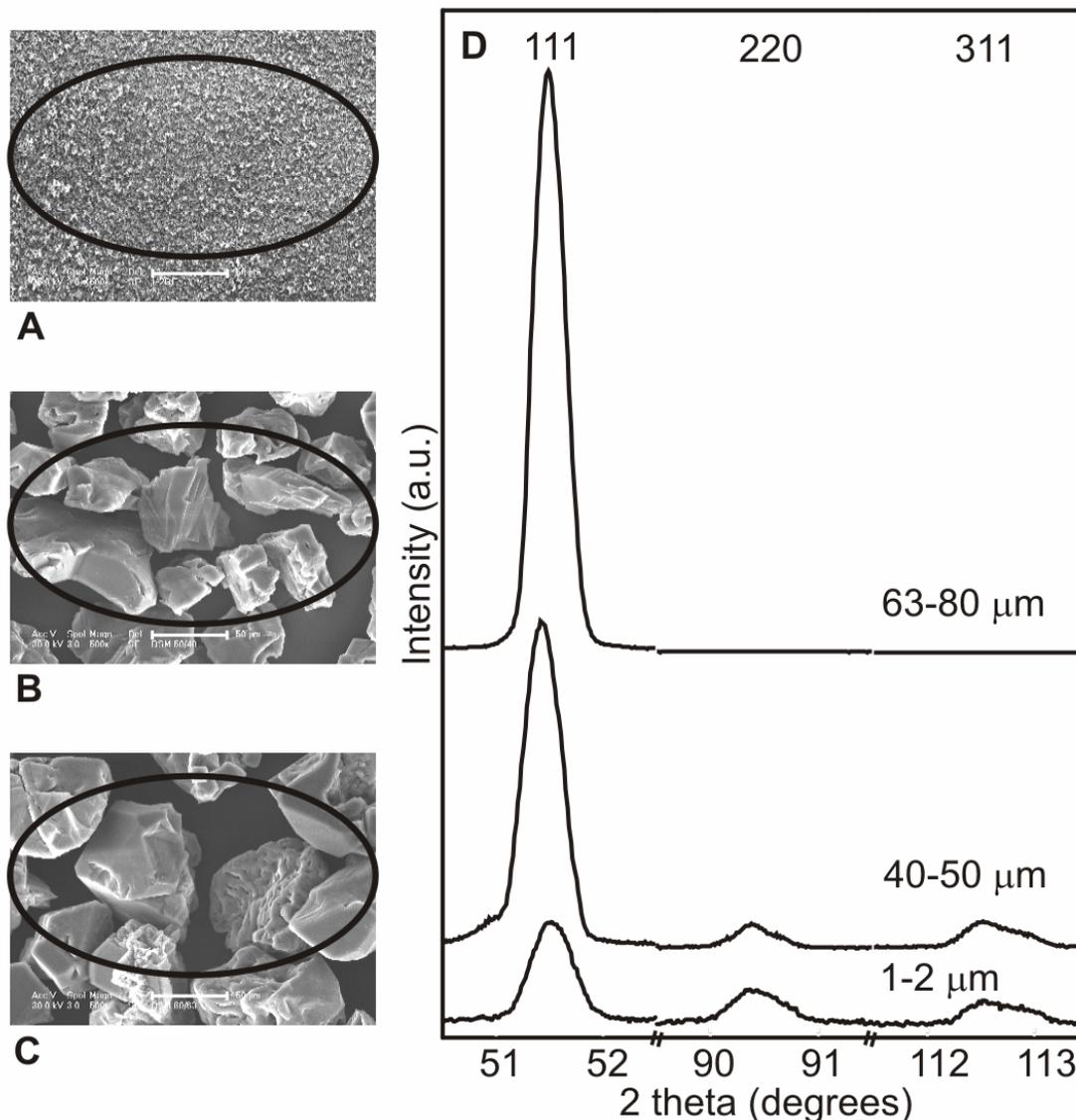


Figure 2. Irradiated area vs. number of particles. SEM images of diamond crystals of size fractions of 63-80 μm (A), 40-50 μm (B), 1-2 μm (C), ellipse marks off the irradiated area at 51.4° 2θ corresponding to the diffraction on plane (111), length of area is 330 μm and width is 142 μm . Selected diffraction lines (D) of diamond crystals measured using micro-pXRD.

Diffraction data were obtained with a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube (Co $K\alpha$ radiation, 40 kV, 30 mA, point focus), monochapillary with an exit diameter of 0.1 mm, and a multichannel position sensitive detector (X'Celerator) with an antiscatter shield. Diffraction patterns were recorded in the 2θ interval from 4° to 80° with a step of 0.0167° and counting time 2300 s per step, the total measurement time per pattern was about 22 hours.

The samples were analyzed either as fragments of colour layers or as their cross sections embedded in polyester resin. All samples were first examined by optical microscopy (Olympus BX60) in reflected white and UV light and by scanning electron microscopy supplemented with energy dispersive spectroscopy (SEM/EDX; Phillips XL30CP, EDAX).

Sample label	Description of sample	Provenance of sample, estimated date of origin
1, fragment	Wall painting	St. Benedict Church, Krnov-Kostelec, Czech Republic; 15 th century
2, fragment	Wall painting	Franciscan Monastery, Kadaň, Czech republic; 15-16 th century
3, fragment	Wall painting	Franciscan Monastery, Kadaň, Czech republic; 15-16 th century
4, cross section	Wall painting	Sazava Monastery, Czech Republic,

Table 2. Description of samples.

RESULTS AND DISCUSSION

In the following case studies we show the possibility of identification of the copper based substances used as green pigments in 15th century wall paintings found in monasteries and churches in the Czech Republic.

In the sample 1 (Figure 3) we found that green layer contains paratacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), calcite (CaCO_3), quartz (SiO_2) and whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$). Paratacamite is one of crystal forms of basic copper chloride and is sometimes considered to be a secondary corrosion product of another copper pigment, e.g. malachite^{10, 13}. Calcite and quartz originated from plaster and ground layer. Presence of calcium oxalate, whewellite, can indicate either original use of organic binders or metabolic products of micro-organisms living on walls.

The micro-pXRD analysis of green layers of sample 2 and 3 provided different diffraction patterns although both samples originated from the same wall painting. According to the first pattern (Figure 4) we found in the green layer of sample 2 malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), calcite (CaCO_3), cerussite (PbCO_3) and lead tin oxide (Pb_2SnO_4). Malachite was used as a green pigment mixed together with lead white (cerussite) and lead-tin yellow I (Pb_2SnO_4), calcite originated from ground layer. In the sample 3 (Figure 5) we found following phases: calcite, lead tin yellow I, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and posnjakite ($\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$). The absence of malachite in this fragment could be caused either by its amorphous character or by its degradation caused by salt attack. The present basic copper sulphate, posnjakite, could be a corrosion product of malachite formed as a result of sulphate action that could be also indicated by formation of gypsum. However, we can not exclude the posnjakite is an attendant mineral of natural malachite that can sometimes occur in amorphous form.

Two diffuse maxima relatively high intensity in the diffraction pattern of sample 4 (Figure 6) that can worsen the analysis are caused by penetration of moulding polymeric resin into colour layer. Despite this the interpretation was made on base of results from EDX analysis. We found atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), barium sulphate (BaSO_4), quartz and calcite. Atacamite is another modification of basic copper chloride mentioned above, barium sulphate is used as filler in colour, quartz and calcite are components of ground layer. In present state we can not decide if basic copper chlorides, atacamite in sample 4 and paratacamite in sample 5, are originally used green pigments or are consequence of corrosive activity of chlorides to another copper pigment.

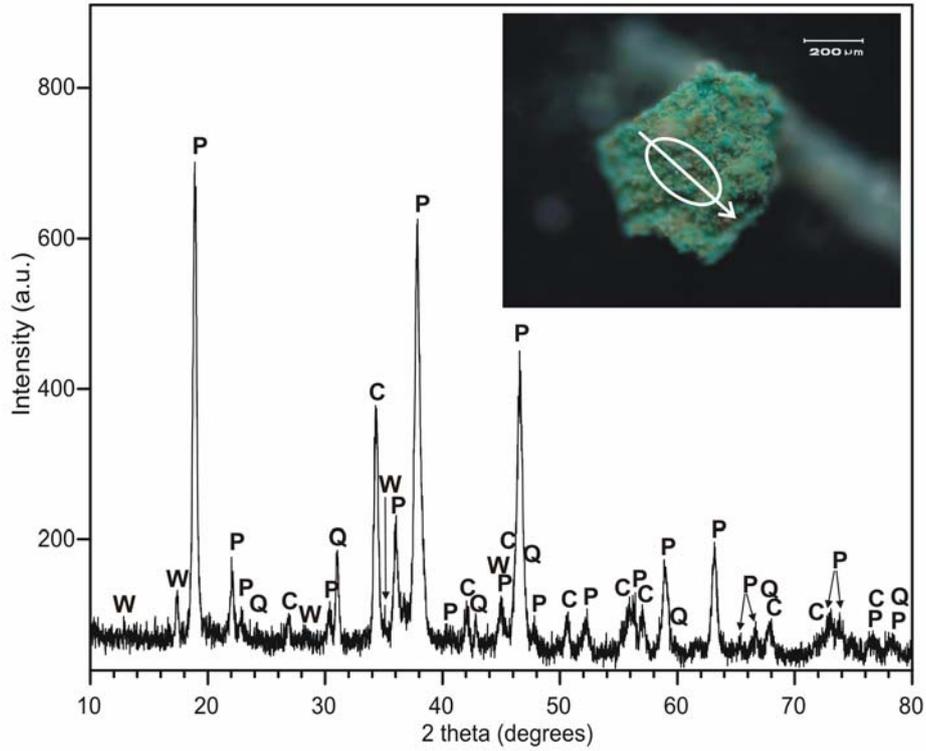


Figure 3. X-ray diffraction pattern of sample 1. Phase abbreviations: **P** paratacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), **C** calcite (CaCO_3), **Q** quartz (SiO_2), **W** whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$). In right corner micrograph of sample 1, ellipse marks off estimated irradiated area, arrow marks off direction of incident X-ray beam.

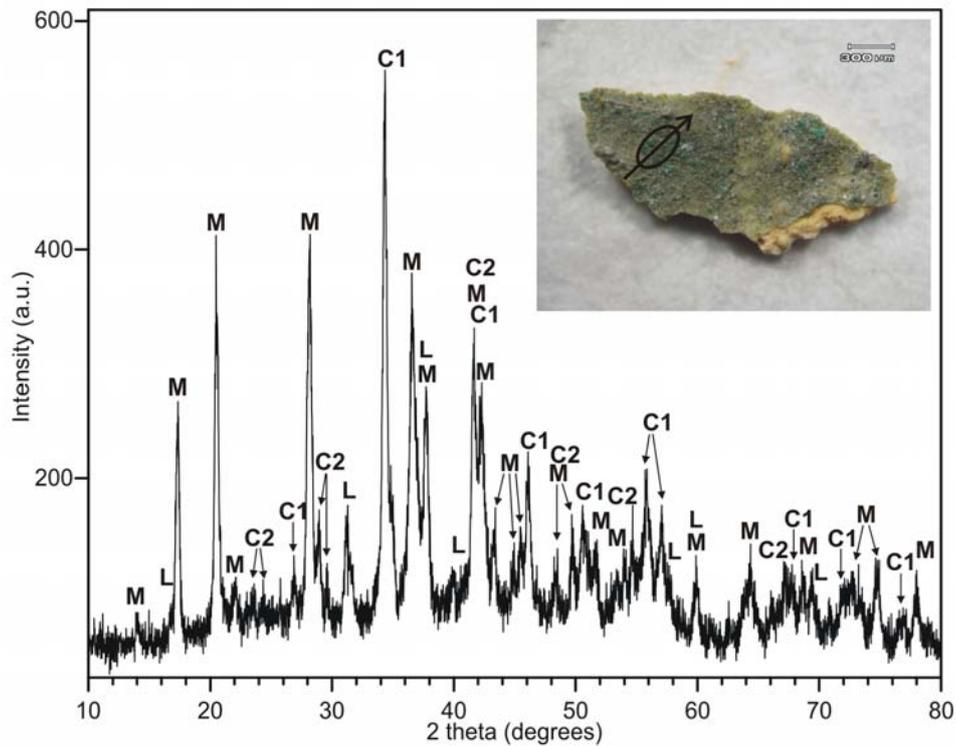


Figure 4. X-ray diffraction pattern of sample 2. Phase abbreviations: **M** malachite ($\text{Cu}_2\text{CO}_3 \cdot \text{Cu}(\text{OH})_2$), **C1** calcite (CaCO_3), **C2** cerussite (PbCO_3 , lead white), **L** lead tin oxide. (Pb_2SnO_4 , lead tin yellow I). In right corner micrograph of sample 2, ellipse marks off estimated irradiated area, arrow marks off direction of incident X-ray beam.

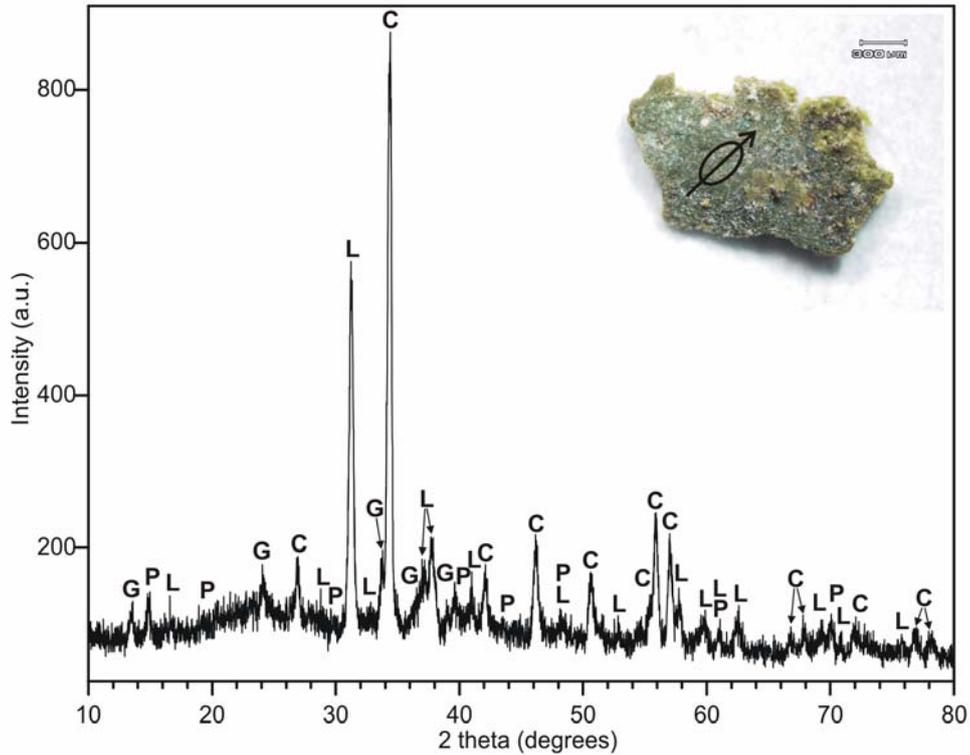


Figure 5. X-ray diffraction pattern of sample 3. Phase abbreviations: **C** calcite (CaCO_3), **L** lead tin oxide (Pb_2SnO_4 , lead tin yellow I), **P** posnjakite ($\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$), **G** gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). In right corner micrograph of sample 3, ellipse marks off estimated irradiated area, arrow marks off direction of incident X-ray beam.

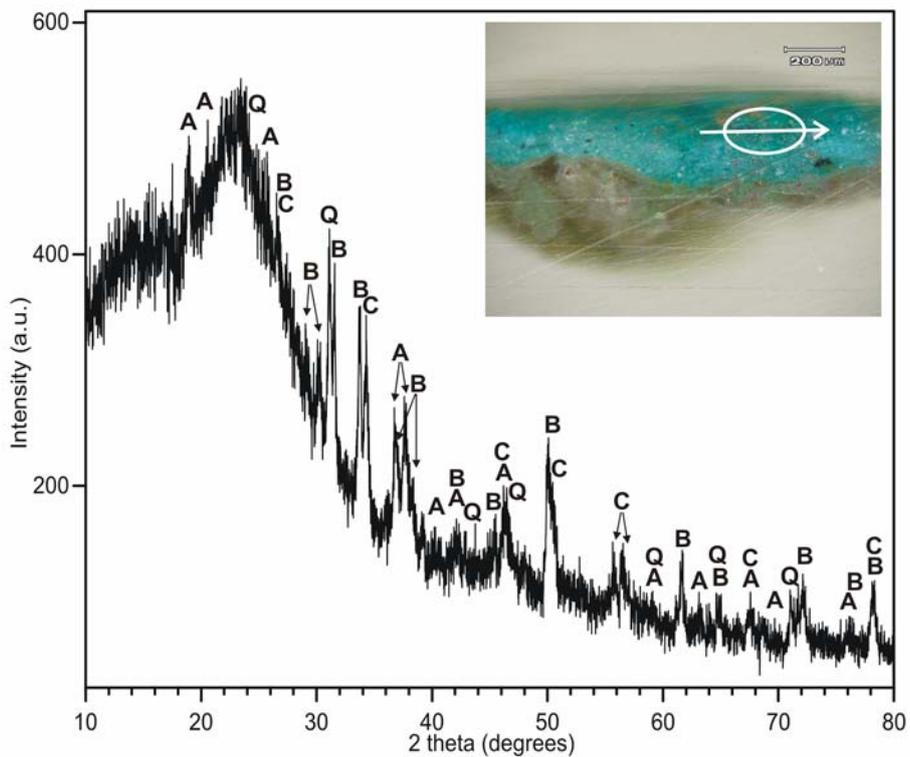


Figure 6. X-ray diffraction pattern of sample 4. Phase abbreviations: **A** atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), **C** calcite (CaCO_3), **Q** quartz (SiO_2), **B** barium sulphate (BaSO_4). In right corner micrograph of sample 4, ellipse marks off estimated irradiated area, arrow marks off direction of incident X-ray beam.

CONCLUSION

The laboratory powder X-ray microdiffraction is a very efficient non-destructive method for direct phase analysis of small samples containing mineral constituents. It is useful complementary tool to microscopic methods for materials analysis of artworks in cases when the knowledge of elemental composition is not sufficient for evaluation of present phases. We used micro-pXRD successfully for identification of green copper-based pigments in fragments of Gothic wall paintings. We found uncommon phases such as atacamite, paratacamite and posnjakite that could indicate the corrosion of originally used copper-based pigments as malachite or azurite.

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