DESY SUMMER STUDENT PROGAMME 2009

Investigations of p-chloroanilinium molybdates

Investigations of pigments

Marta Grzesiak
Karolina Pajak
Julita Sliwinska

Supervisors: **Dariusz Zajac**
Andre Rothkirch

Acknowledgements.

We would like to thank our supervisor Dariusz Zajac for support and advices during this Summer Student Program. Thanks to André Rothkirch, Thomas Wroblewski and Jörn Donges for help during measurements.
We also want to thank Mr Joachim Meyer, Andrea Schrader and others who put a lot effort to organize this program.

Investigations of p-chloroanilinium molybdates.

Molybdenum compounds are interesting as prospective candidates for various applications in catalysis, optoelectronics and anticancer therapy. Many researches are focused on fibrillar or layered materials with organic cations. Layered or fibrillar materials based on polymolybdate anions offer interesting chemical properties and unusual architecture.

Investigations of p-chloranilinium molybdates were focused on three synthesized samples. As reference there were used: anilinium pentamolybdate [1] (sample no 1) and p-bromoanilinium pentamolybdate [2] (sample no 4). All p-chloroanilinium molybdates were synthesized in the same way but time of synthesis was different for all samples (samples no: 2, 3 and 5).

Method of synthesis:

Sample no 2
0.01M of molybdic acid was dissolved in 150ml of hot water. To the boiling solution 0.02M of p-chloroanilinium, 0.02M of hydrochloric acid in 10ml of water was added. The solution was heated for 2 hours. The precipitate was filtered off and dried in air.

Sample no 3
0.01M of molybdic acid was dissolved in 150ml of hot water. To the boiling solution 0.02M of p-chloroanilinium, 0.02M of hydrochloric acid in 10ml of water was added. The solution was heated for 24hours. The precipitate was filtered off and dried in air.

Sample no 5
0.01M of molybdic acid was dissolved in 150ml of hot water. To the boiling solution 0.02M of p-chloroanilinium, 0.02M of hydrochloric acid in 10ml of water was added. The solution was heated for about 7 days. The precipitate was filtered off and dried in air.

At Jagiellonian University in Krakow, Poland the PXRD patterns have been collected using a Philips X'Pert Pro MPD diffractometer.

Measurements performed at G3 beamline:

Parameters:
Wavelength: 8047.15eV (Cu $K\alpha_1$)
2θ range: from 4-125^o (except sample no 5 where range was from 4 to 103^o)
step: 0,01
time per step: 4s

Sample no 1: Anilinium pentamolybdate

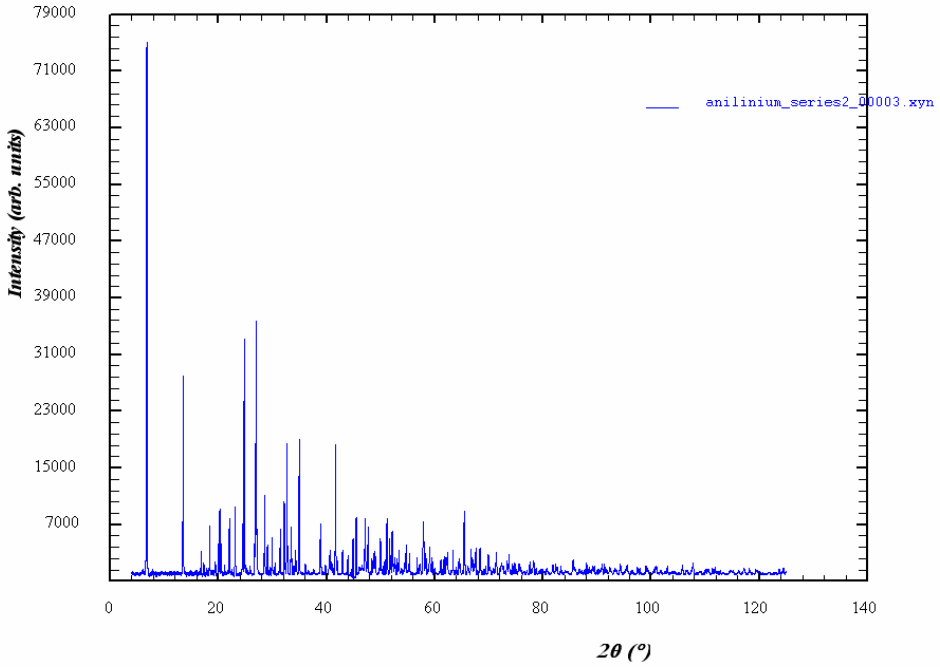

Figure 1. Diffraction pattern of anilinium pentamolybdate measured at beamline G3.

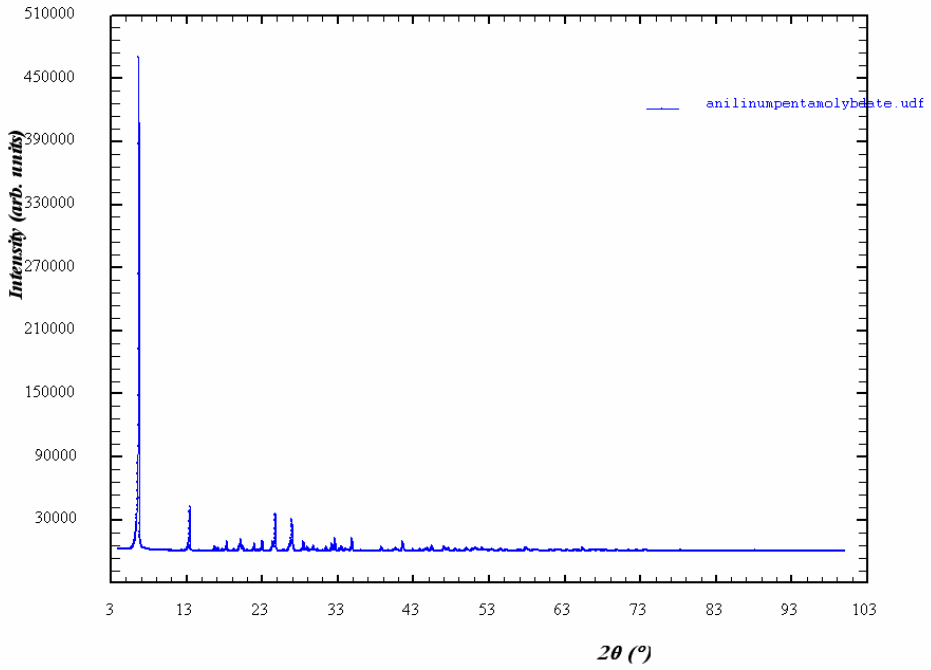

Figure 2. Diffraction pattern of anilinium pentamolybdate measured in Krakow.

Sample no 2: *p*-chloroanilinium trimolybdate

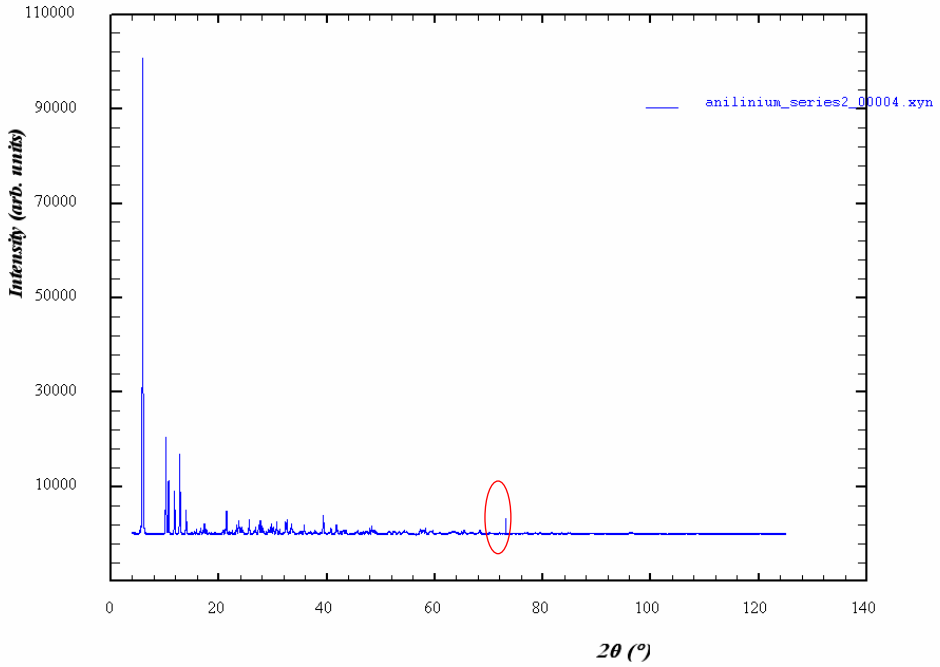

Figure 3. Diffraction pattern of p-chloroanilinium trimolybdate (sample no 2) measured at the beamline G3. Peak about 73 deg occurred due to problems with the beamshutter .

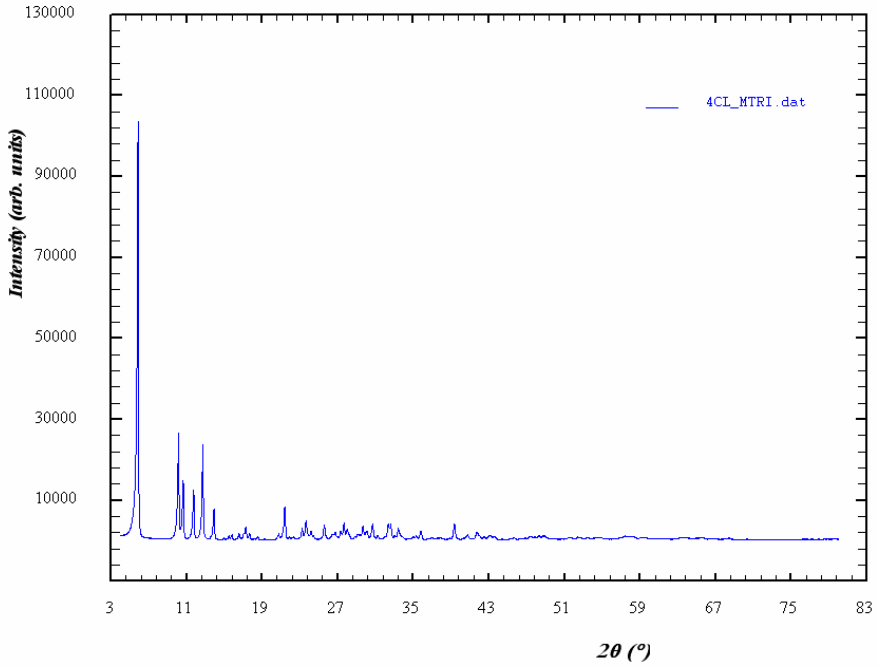

Figure 4. Diffraction pattern of p-chloroanilinium trimolybdate (sample no 2) measured in Krakow.

Sample no 3: *p*-chloroanilinium molybdate (synthesized 24h)

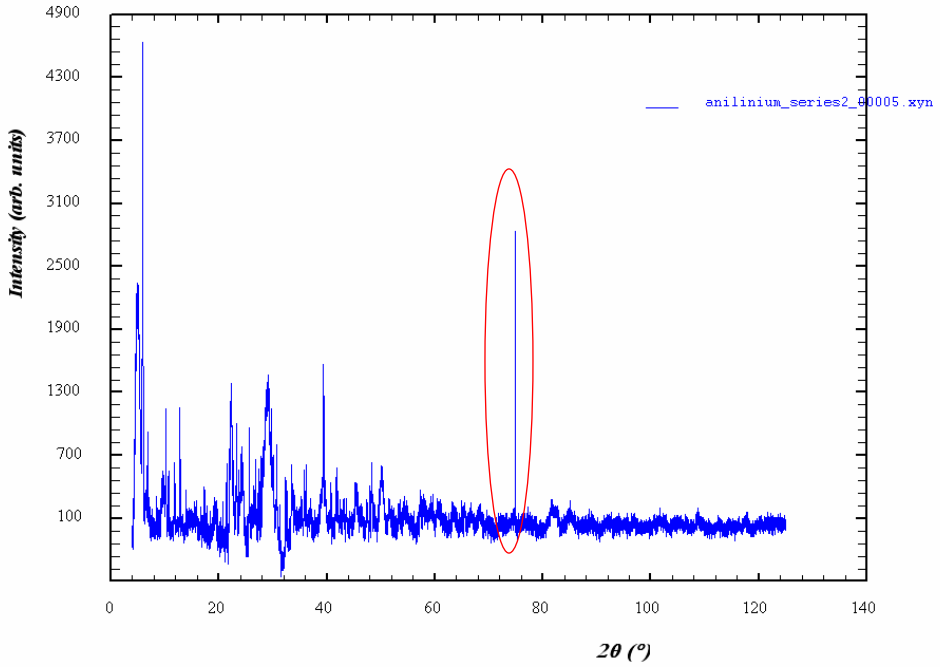

Figure 5. Diffraction pattern of p-chloroanilinium molybdate (sample no 3) measured at the beamline G3. Peak about 75 deg occurred due to the injection.

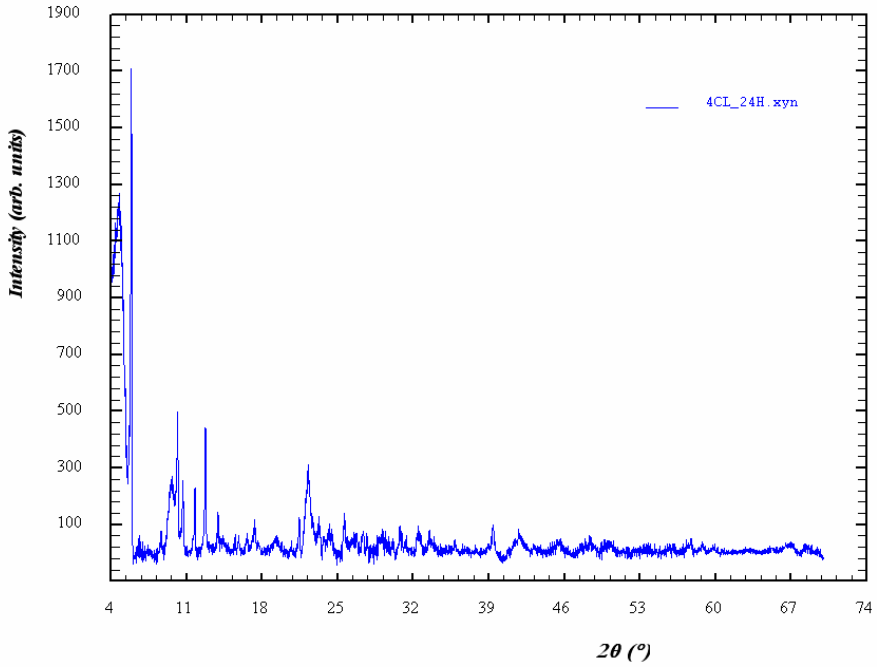

Figure 6. Diffraction pattern of p-chloroanilinium molybdate (sample no 3) measured in Krakow.

Sample no 4: p-bromoanilinium pentamolybdate

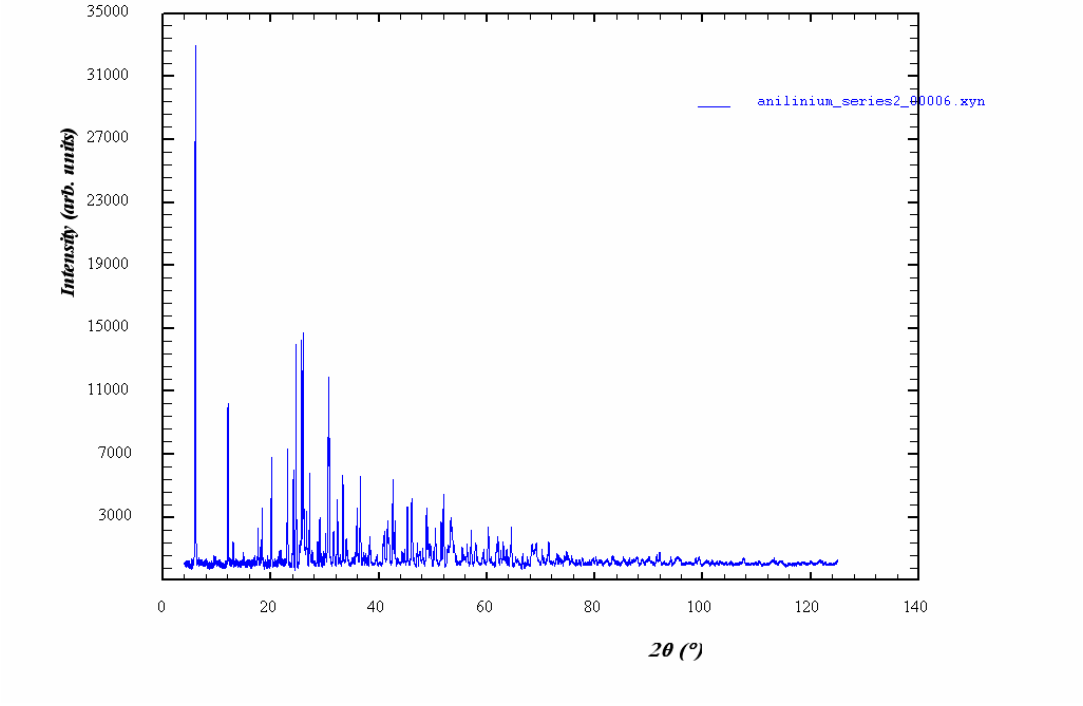

Figure 7. Diffraction pattern of p-bromoanilinium pentamolybdate (sample no 4) measured at beamline G3.

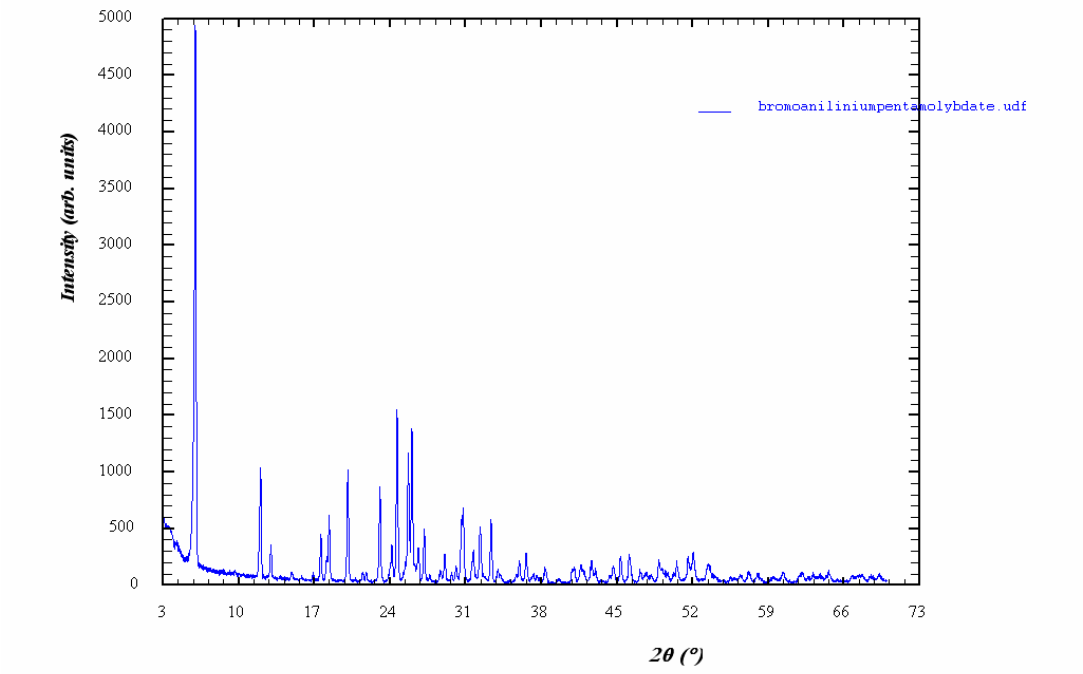

Figure 8. Diffraction pattern of p-bromoanilinium molybdate (sample no 4) measured in Krakow.

Sample no 5: *p*-chloroanilinium molybdate (synthesized 7 days)

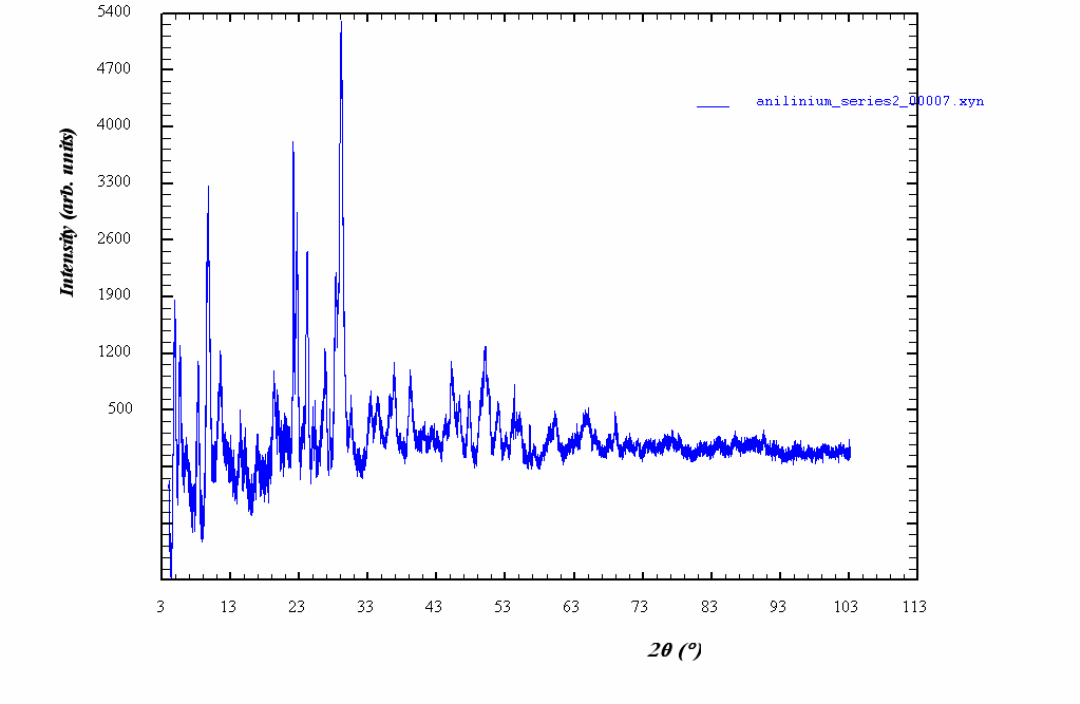

Figure 9. Diffraction pattern of p-chloroanilinium molybdate (sample no 5) measured at beamline G3.

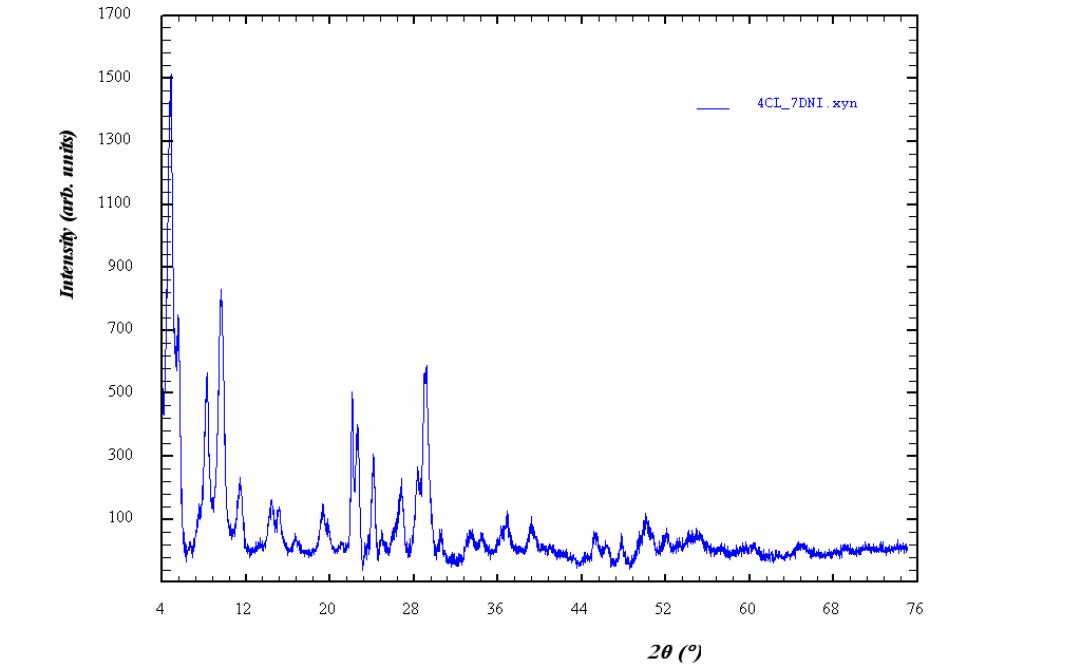

Figure 10. Diffraction pattern of p-chloroanilinium molybdate (sample no 5) measured in Krakow.

In the diffraction patterns obtained at the beamline G3 we observe peaks with higher intensity than patterns received from measurements in Krakow. It occurs especially for weaker reflexes. For samples 1, 4 and 2 received diffraction patterns have good separated and narrow peaks. Peaks from patterns of samples 3 and 5 are wide and lot of them are not good separated.

Analysis of data from diffraction is insufficient to give information about structure of investigated samples. Therefore XAS measurements of molybdates have been performed. Measurements obtained at the beamline C1. All samples have been prepared in the same way. Appropriate amount of sample was mixed with cellulose to have weight about 120mg and pressed into pastilles of 13,3mm diameter. As a reference 20μm Mo foil was used for energy callibration. Measurements have been done in RT and in 77K (liquid nitrogen cryostat).

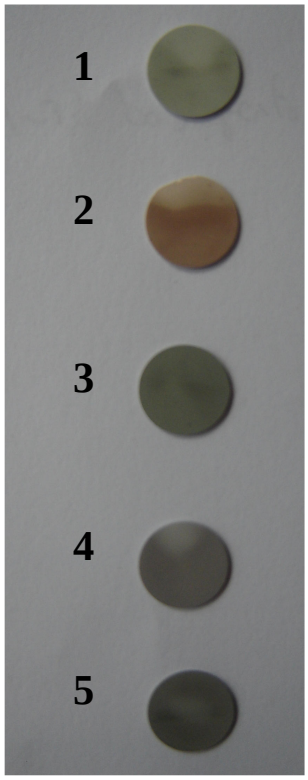

Figure 11. Photo of prepared samples from EXAFS measurements

Measurements performed at beamline C:
Parameters:
Beam size: 2mm × 12mm.

Energy range: 19850 to 21248.22 eV

Measurements have been performed in transmission (absorption) mode.

Three ionization chambers have been filled with following gases to absorb percentage of radiation given in brackets:
I_1 - 753mbar Ar (10%)
I_2 - 367mbar Kr (50%)
I_3 - 910mbar Kr (82%)

Samples:

1. Anilinium pentamolybdate $(C_6H_5NH_2)Mo_5O_{16}$

$m_{sample} = 25{,}2mg$

$m_{cellulose} = 90{,}8mg$

2. *p*-chloroanilinium trimolybdate $(ClC_6H_4NH_2)Mo_3O_{10}$

$m_{sample} = 30{,}5mg$

$m_{cellulose} = 85{,}5mg$

3. *p*-chloroanilinium molybdate (synthesized 24h) $(ClC_6H_4NH_2)Mo_xO_y$

$m_{sample} = 25{,}3mg$

$m_{cellulose} = 90{,}1mg$

4. *p*-bromoanilinium pentamolybdate $(BrC_6H_4NH_2)Mo_5O_{16}$

$m_{sample} = 27{,}2mg$

$m_{cellulose} = 88{,}2mg$

5. *p*-chloroanilinium molybdate (synthesized 7 days) $(ClC_6H_4NH_2)Mo_xO_y$

$m_{sample} = 25{,}8mg$

$m_{cellulose} = 91{,}8mg$

Figure 12 shows 5 spectra. All XANES curves we have got as a result of XAS experiment are very similar. There is no difference in area of the white line and there is no energy shift. It means that local arrangement and valency are unchanged. On all spectrums small pre-edge peak is observed.

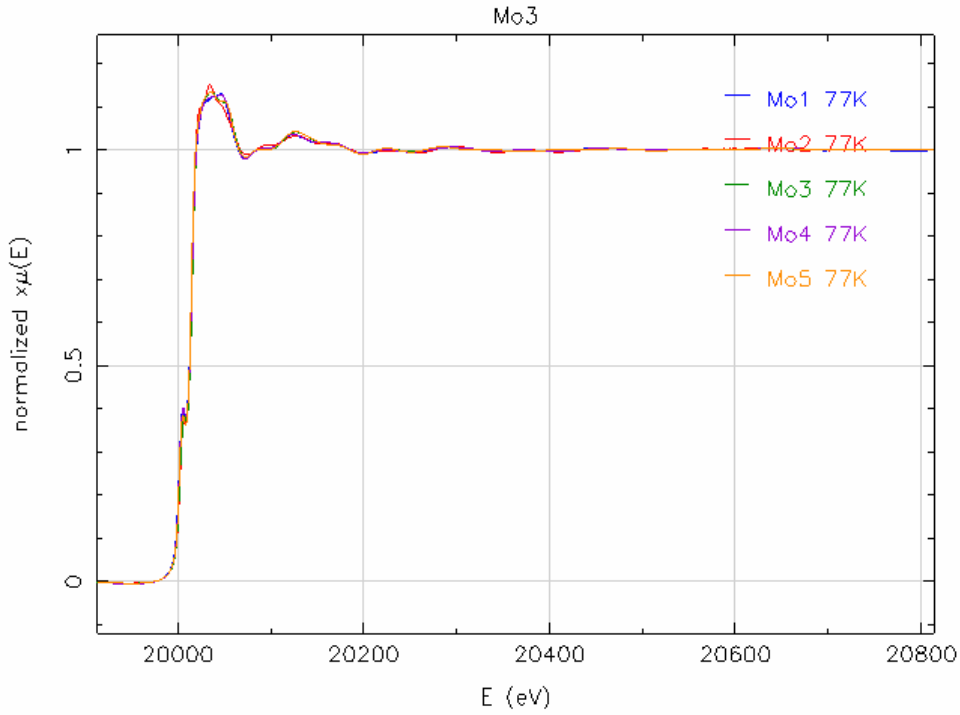

Figure 12. XAFS spectrum for all measured at beamline CEMO samples.

Zoom on XANES region (50eV below and 100eV above molybdenium absorbtion edge).

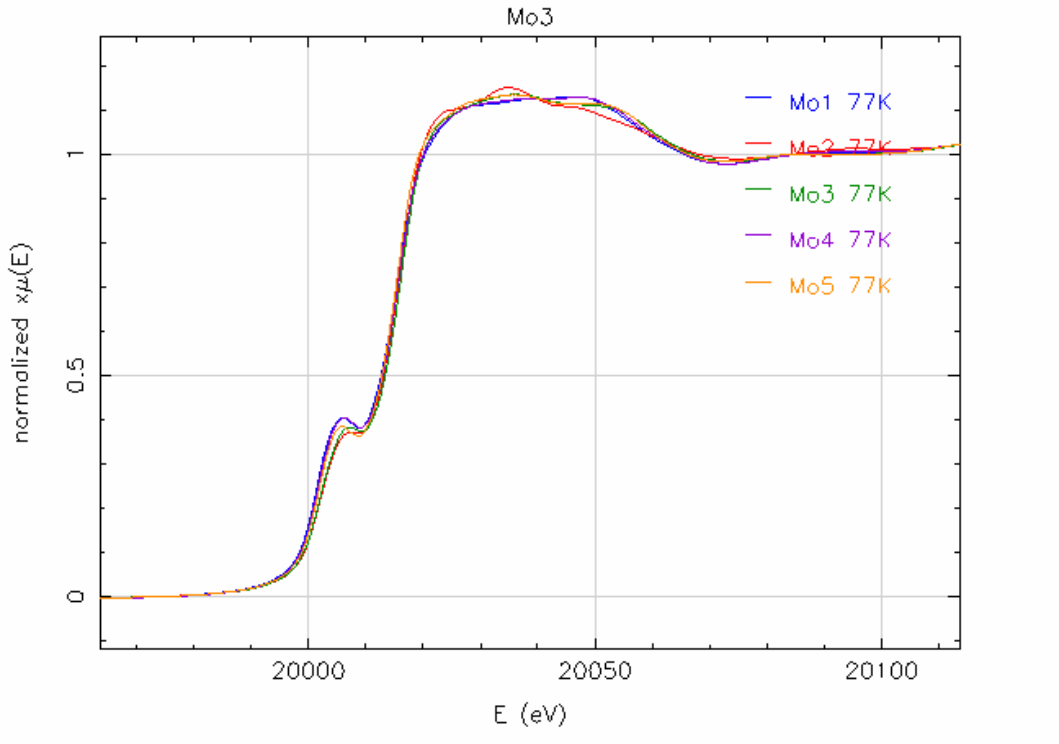

Figure 13. XANES region for all measured samples.

Next plot shows similarities between samples 1 and 4.

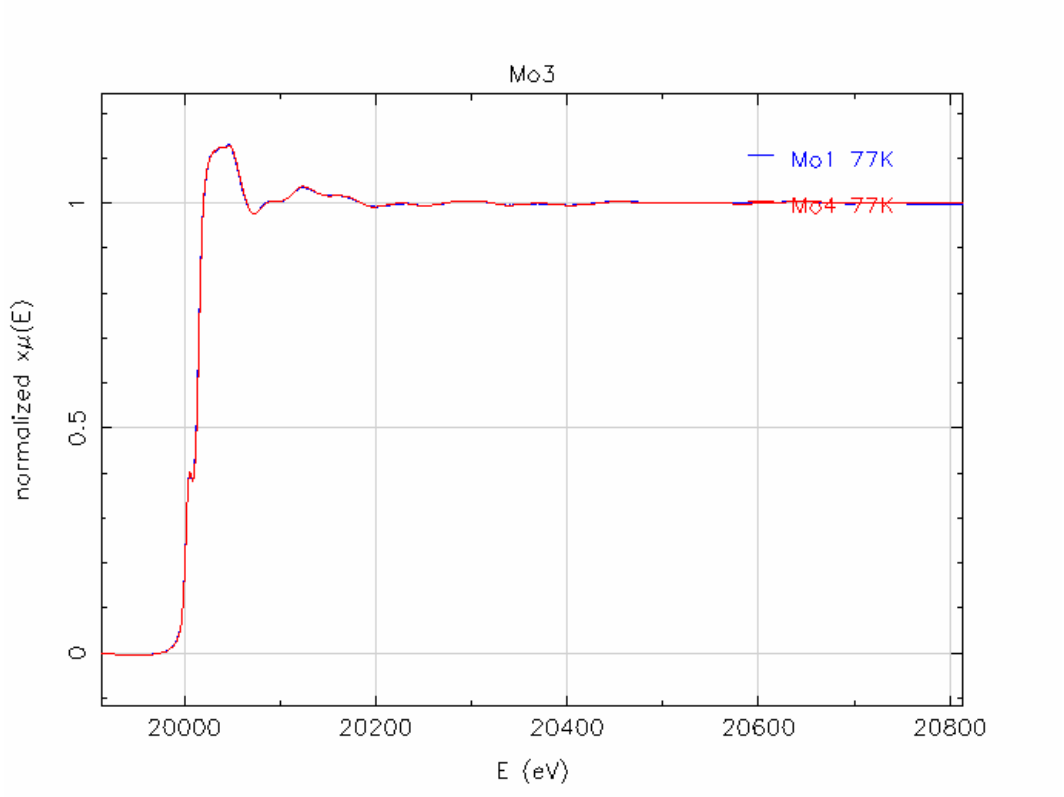

Figure 14. XAFS spectrum for samples number 1 and 4.

Also samples 3 and 5 have the same properties as it is shown on figure 15.

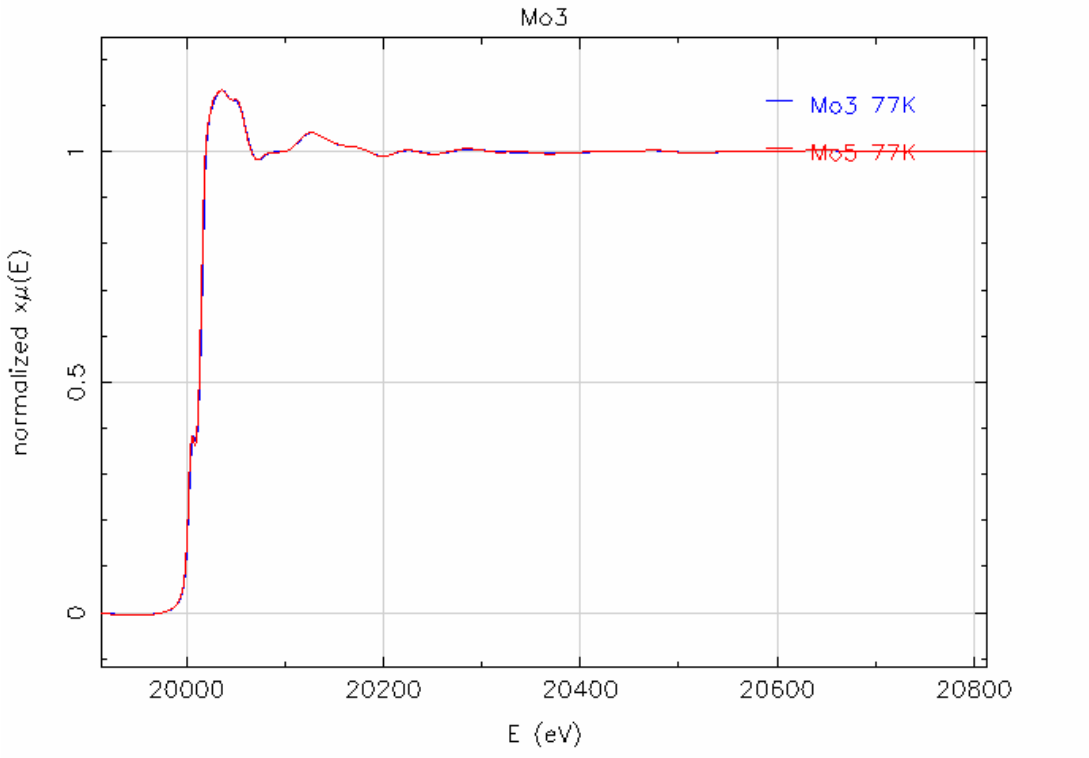

Figure 15. XAFS spectrum for samples number 3 and 5

Conclusion:

Analysis of data from diffraction is insufficient to give an information about structure of investigated samples because obtained diffraction patterns are not good quality due to the samples structure.

Preliminary XANES analysis show that samples 1 and 4 are similar. The same situation is observed for samples 3 and 5. Sample no. 2 is different from others. Obtained data need further long- term analysis which should give information about the local structure of investigated p-chloroanilinium molybdates.

Investigations of pigments

Pigments are coloring agents used in paints in the form of colored powder. Mineral pigments have used since prehistoric times. Since 18th century began to produce synthetic pigments. Identification of the individual pigments and their components are used in dating, signing and authentication of works of art.

1. Investigation of Ruthenian - Byzantine wall paintings from St Mary's Chapel in the Wawel Cathedral

Background of samples

Wawel Hill

Wawel Hill is situated on the left bank of the Vistula River in Cracow (Poland). This is a place of great significance for the Polish people. The Royal Castle with an armoury and the Cathedral are situated on the hill. Polish Royalty and many distinguished Poles are interred in the Wawel Cathedral. Royal coronations took place there also.

Figure 16. Wawel Hill

The Wawel Cathedral

The Wawel Cathedral is Poland's national sanctuary. It was the coronation site of nearly all Polish monarchs.

Figure 17. Southern side of Wawel Cathedral

St Mary's Chapel

St Mary's Chapel is located in the Wawel Cathedral. It was bulit in 14th century.

Samples

During restoration of this chapel remains of Ruthenian – Byzantine wall paintings were discovered. These wall paintings were hidden under the floor.

Figure 18. Discovered Ruthenian – Byzantine wall paintings

Investigated samples

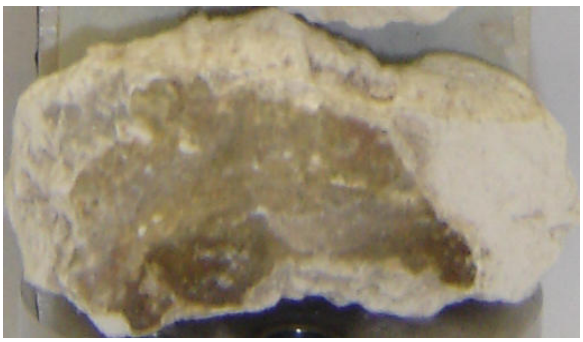

Figure 19. Photo of investigated sample no 1.

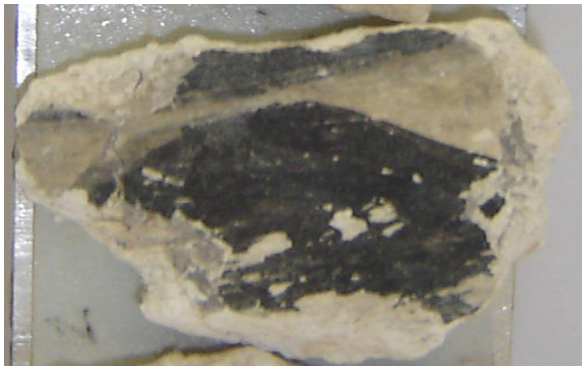

Figure 20. Photo of investigated sample no 2.

.

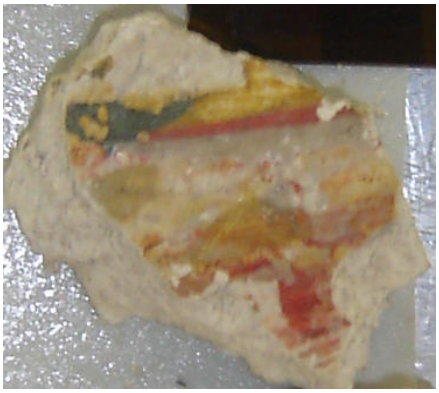

Figure 21. Photo of investigated sample no 3.

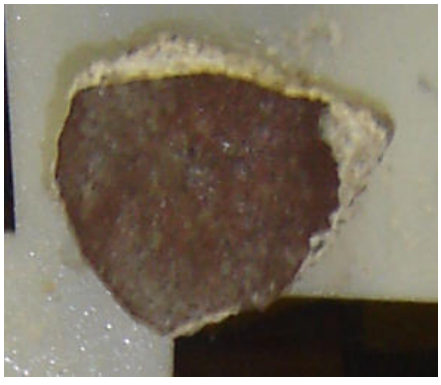

Figure 22 . Photo of investigated sample no 4.

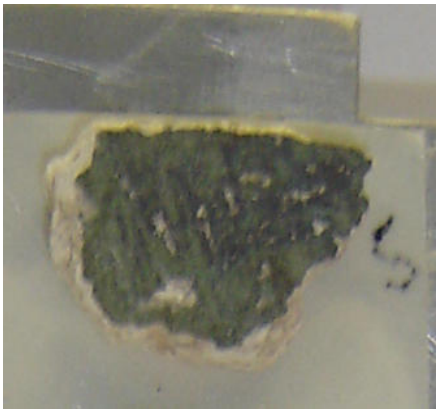

Figure 23. Photo of investigated sample no 5.

At Jagiellonian University the investigations of the materials have revealed:
cinnabar - HgS
azurite - $2CuCO_3 \cdot Cu(OH)_2$
goethite – FeO(OH)

Aim of investigations:
1) to determine which pigment has been used as a green pigment
In the area of Byzantine Empire artists used green earth as a green pigment. In turn Polish artists used malachite.
The main question sounds: "Which pigments were used by painters from St Mary's Chapel?"
There is supposition that artists from St Mary's Chapel used pigments which are more similar to paintings from Byzantine Empire than from Poland.
2) to check if cadmium yellow was used as a yellow pigment
Goethite was used as a yellow pigment in this wall paintings but there might be in two samples cadmium yellow too. There is no information in literature about using of cadmium yellow in this time (when Ruthenian – Byzantine wall paintings were made). Therefore there is necessity to check presence of this pigments in our samples.

Measurements

Measurements performed at beamline G3

MAXIM (materials x-ray imaging)

Beamline parameters:
- beamsize 2.8 x 1.1 mm (FWHM)
- monochromator - fixed-exit double-crystal Ge(111),
  - further crystals available Ge(311), Si(111), Si(511), Si(400)

Beamline equipped with 2D detector setup allows imaging using the radiation diffracted by polycrystalline samples. Used CCD camera behind channel collimator with position resolved investigation gives possibility to image area of more than 1 cm^2. In contrast to conventional µ-beam techniques we can measure large area in one shot. Spatial resolution is from 12µm – 12 mm (proportional to the sample to detector distance).

Detectors

1. CCD-detector
2. Auxiliary scintillation detector with Soller collimator for integrating measurements

Energy:
E = 8047.16 [eV]

1) Sample number 3

Name of sample: **yellow_powder_wawel_wall3**
Description of sample: yellow pigment (powder) from wall painting number 3
Scan from **4° to 80°**
Step: 0.01^o

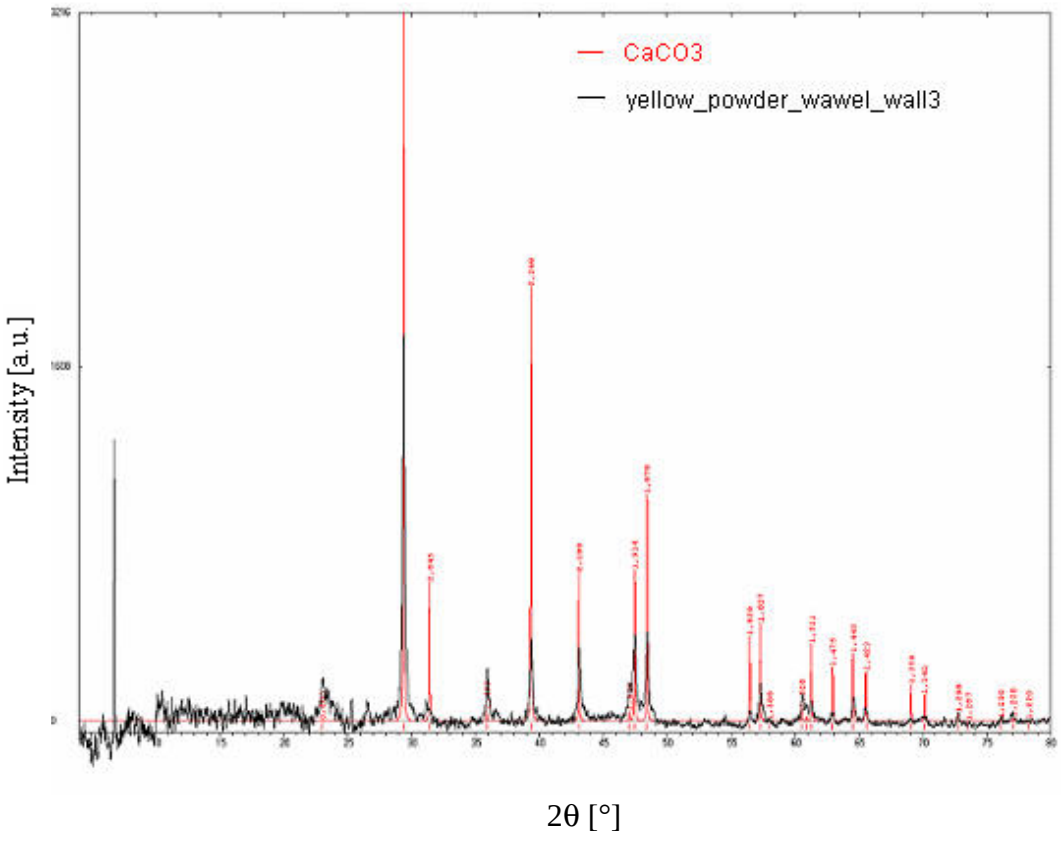

Figure 24. Diffraction pattern of yellow powder from sample number 3 (black solid line) and overlapping diffraction pattern of $CaCO_3$ (red lines).

Name of sample: **fragments_byzantine_00002r2**
Description of sample: colourful wall painting (sample 3)
Scan from **20° to 120°**
Step: 0.01

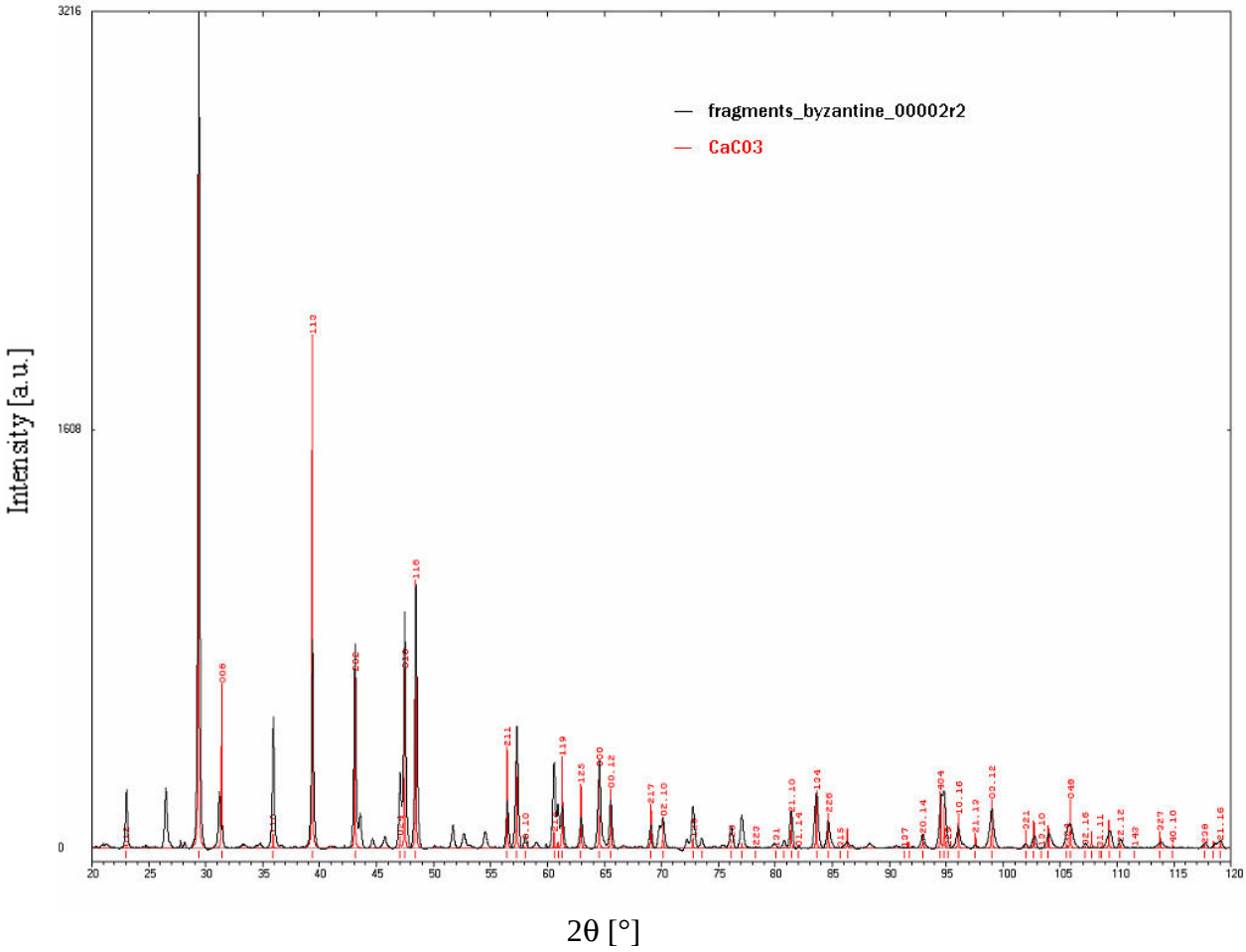

Figure 25. Diffraction pattern of colourful fragment from sample number 3 (black solid line) and overlapping diffraction pattern of $CaCO_3$ (red lines).

MAXIM measurements:

Name of sample: **fragments_byzantine_00006r3**
Description of sample: colourful wall painting (sample 3)
Scan from **77° to 87°**
Step: 0.05°

There is an offset between scintillation counter and CCD camera, which is about 20.4^{o}. Program for calculation of exact offset value was written. Calculated value is 20.3788^{o}.

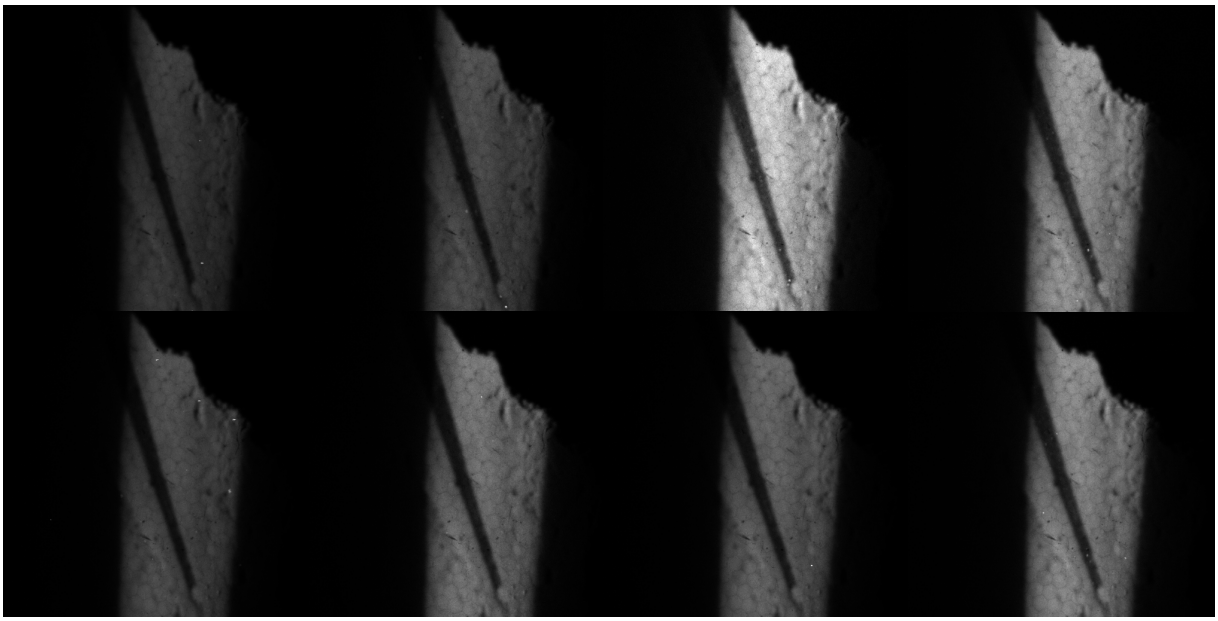

Figure 26. MAXIM images of colourful sample no 3.

MAXIM images show homogenous distribution along all measured area. All observed reflexes belong to the same substance which is homogenous distributed in the sample. It seems to that only main compound of the wall is observed. No distribution of different pigments from sample is seen. It was confirmed by over plotting diffraction pattern of $CaCO_3$ to diffraction pattern from sample (see Figure 25).

2) Sample number 1
Name of sample: **yellow_powder_wawel_wall1**
Description of sample: yellow pigment (powder) from wall painting number 1
Scan from **4° to 80°**
Step: 0.01°

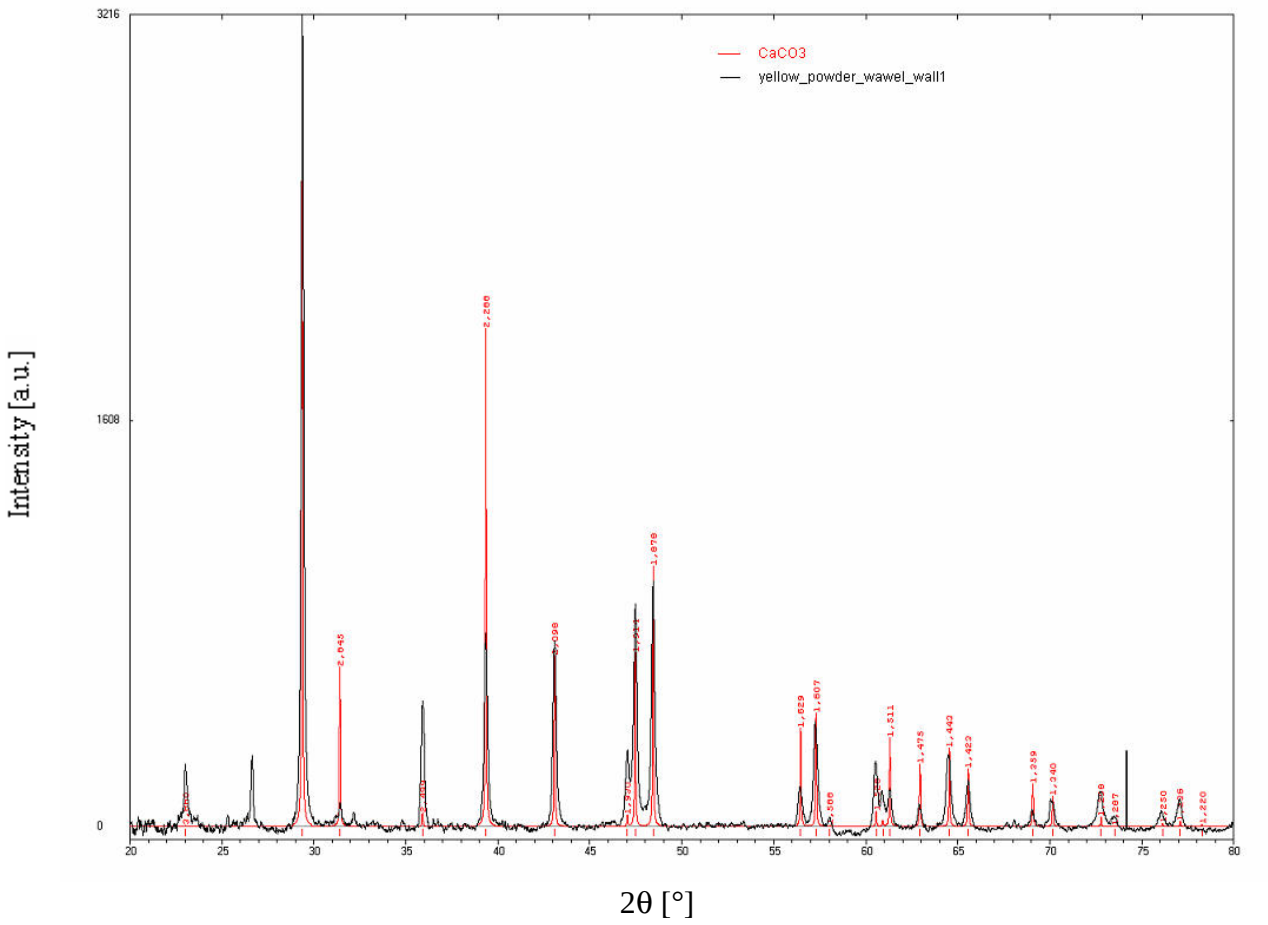

Figure 27. Diffraction pattern of yellow powder from sample number 1 (black solid line) and overlapping diffraction pattern of $CaCO_3$ (red lines).

3) Sample number 5
Name of sample: **fragments_byzantine_00002r1**
Description of sample: green wall painting (sample number 5)
Scan from **20° to 120°**
Step: 0.01°

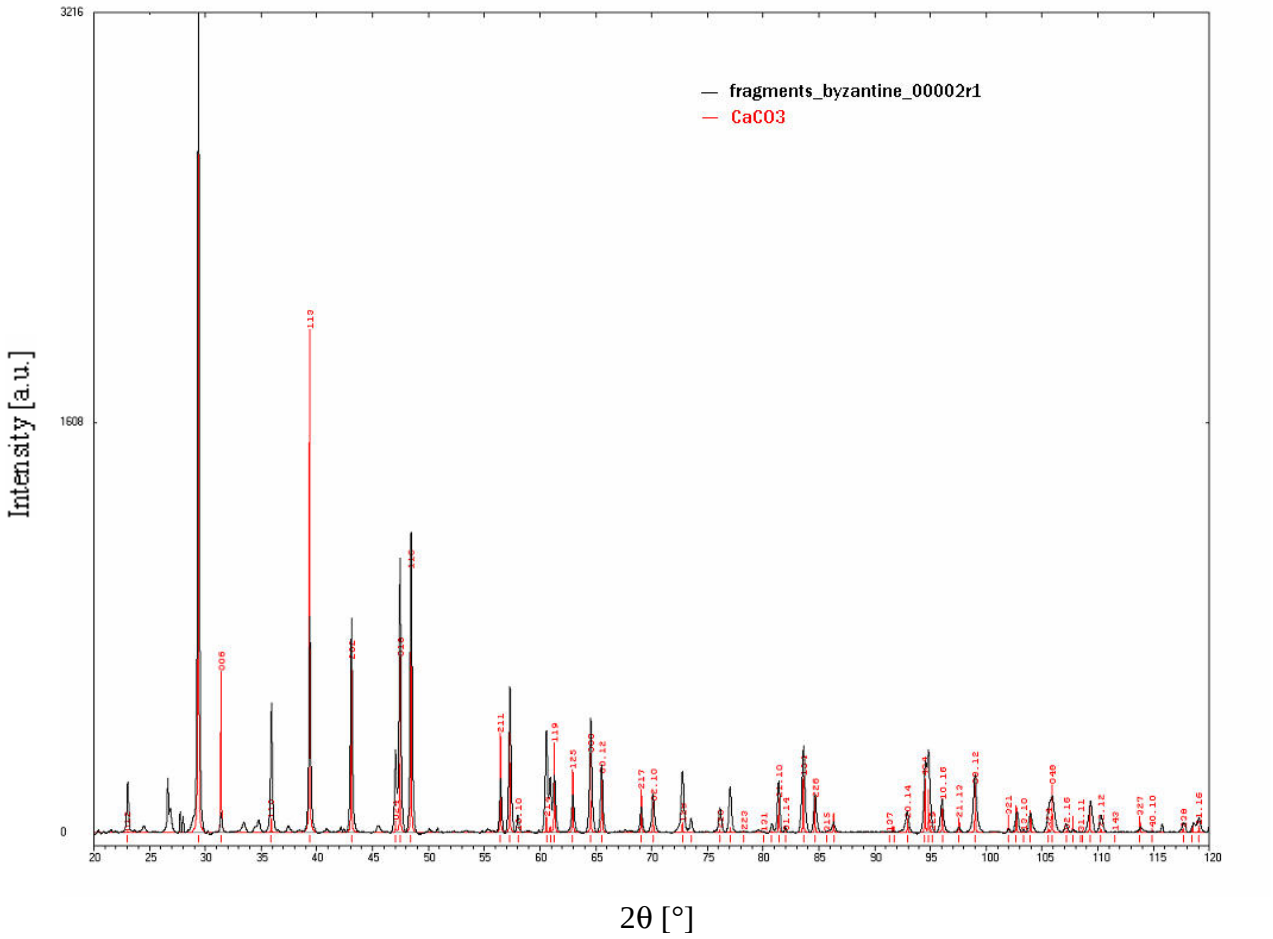

Figure 28. Diffraction pattern of green fragment from sample number 5 (black solid line) and overlapping diffraction pattern of $CaCO_3$ (red lines).

MAXIM measurements:

Name of sample: **fragments_byzantine_00006r1**
Description of sample: green wall painting (sample number 5)
Scan from **77° to 87°**
Step: 0.05°

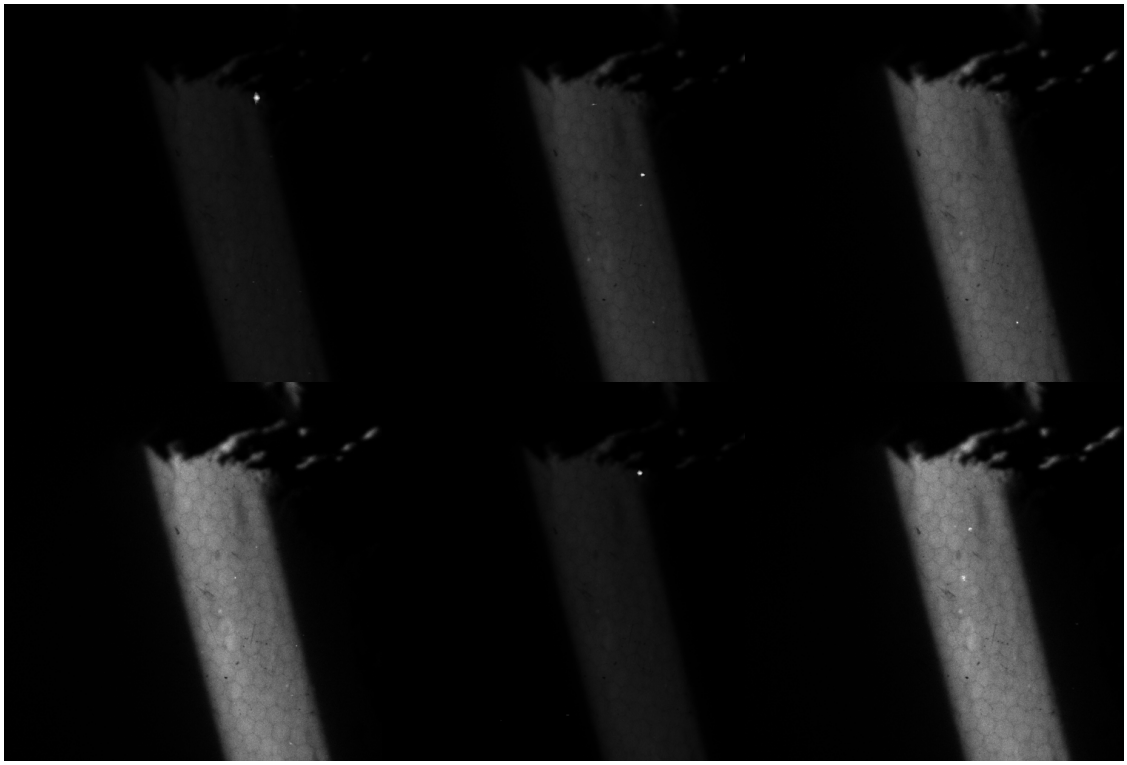

Figure 29. MAXIM images of green sample no5.

MAXIM images show homogenous distribution along all measured area. For sample 5 some images show single grains. Observed reflexes belong probably to the same substance which is homogenous distributed in the sample. It seems that main compound of the wall and some single crystals of this compound are observed. It was confirmed by over plotting diffraction pattern of $CaCO_3$ to diffraction pattern from sample (see Figure 28). Reflexes from green pigment were not observed.

Measurements performed at beamline C

Figure 30. Photo of measured samples.

Results of EXAFS measurements shows lack of the signal from Cd. Lack of the signal of Ti, V, Cr, Mn, Co, Ni and Zn(?) is also noticed. Signal for Fe, Cu, As, Hg and Pb is observed Table 1 shows results corresponding to investigated samples.

Table 1. Results of EXAFS measurements.

Sample	Description	Identified chemical elements
sample 5	green pigment	Fe, Cu, As, Hg, Pb
sample 4	brown-violet pigment	Fe, Cu, As, Pb, Zn(?)
sample 3	multi colour	Fe, Cu, As, Hg
sample 2	black pigment	Fe, Cu, As, Zn(?)
sample 1	yellow-gray pigment	Fe, Cu, As
plaster	-	Fe, Cu

2. Investigation of fragments of vases from Collegium Maius

Background of samples

Collegium Maius

The oldest college of the Polish oldest and best university, was rebuilt by the end of the 15th century as a splendid late-Gothic edifice around a vast courtyard with surrounding arcades and a well of 1517 in the center. Professors lived and worked upstairs, while lecturing downstairs. In the 1490s they had Copernicus among their students, and the astronomer that revolutionized entire European science remains the most illustrious of Krakow university's graduates together with Pope John Paul II.

Figure 31. Courtyard of the Collegium Maius

The Museum of the Jagiellonian University in the Collegium Maius shows upstairs its splendid historic rooms with original furnishings, good collection of the old European art, unique science instruments, and varied memorabilia.

Samples

Figure 32. Photo of all samples stick on the silicon plate.

Aim of investigations:
There are 5 samples from red and green vases. There is no identification about these vases. They have decorations in Chinese and Japanese style and probably they were produced in 19th century in Berlin. Determination of pigments is needed to characterization of these vases.

Measurements

Measurements performed at beamline G3

Parameters:
energy = 8047.16 [eV]

Name of sample: **fragments_vase00001**
Description of sample: vases (5 pieces) from Collegium Maius Museum
Scan from **20^{o} to 120^{o}**
Step: 0.01 ^{o}

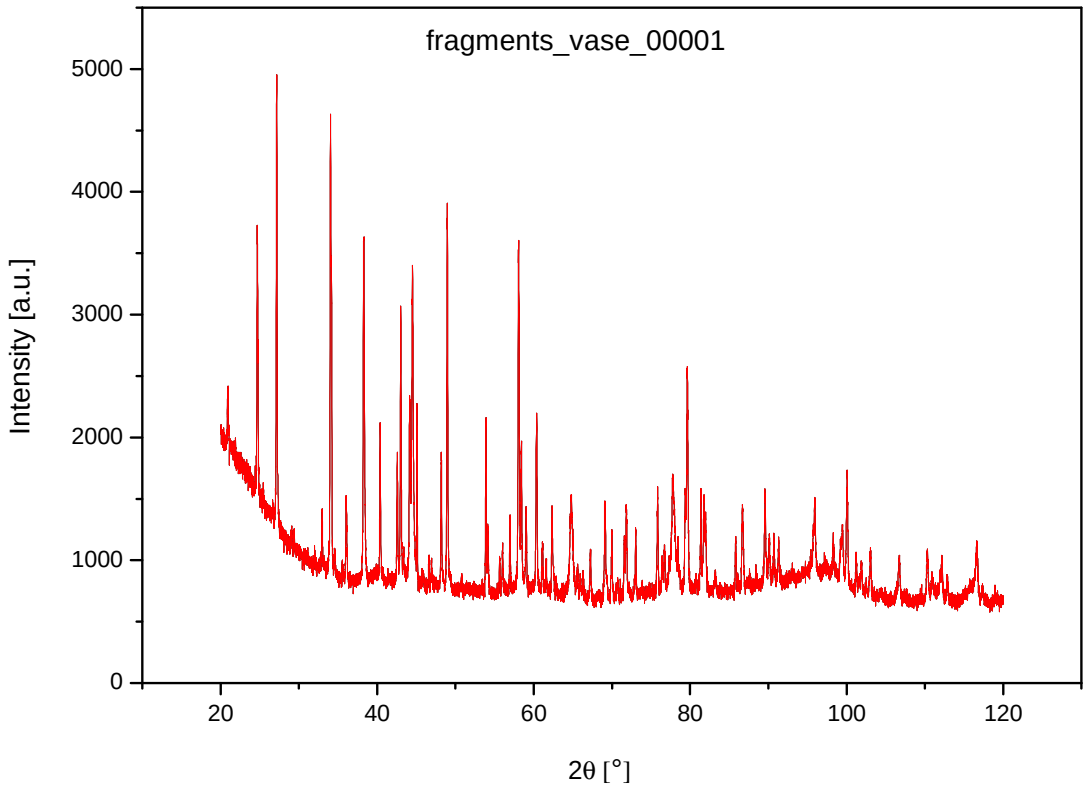

Figure 33. Diffraction pattern of all vases samples.

Sample no 6

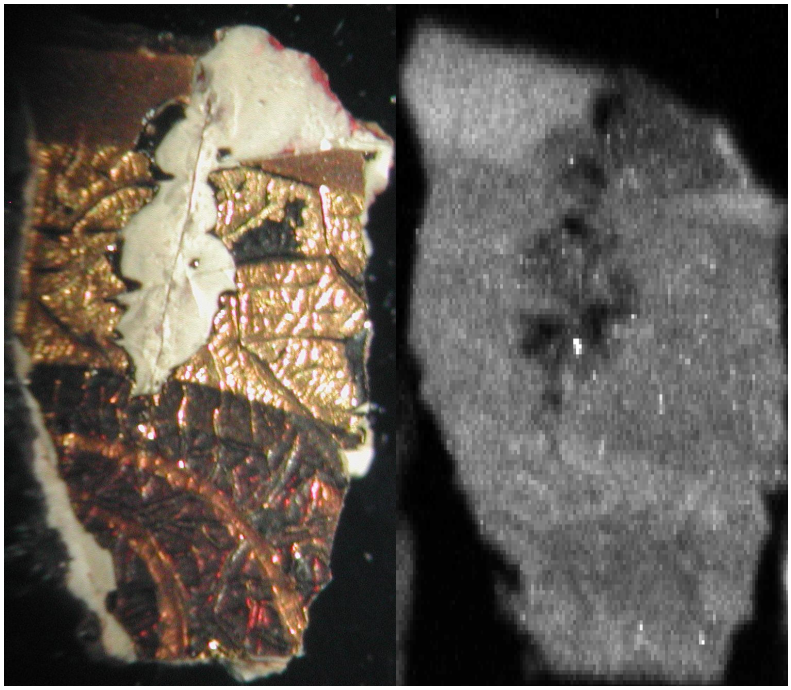

Figure 34. Fragment of vase: photo (left) and MAXIM image from CCD camera (right).

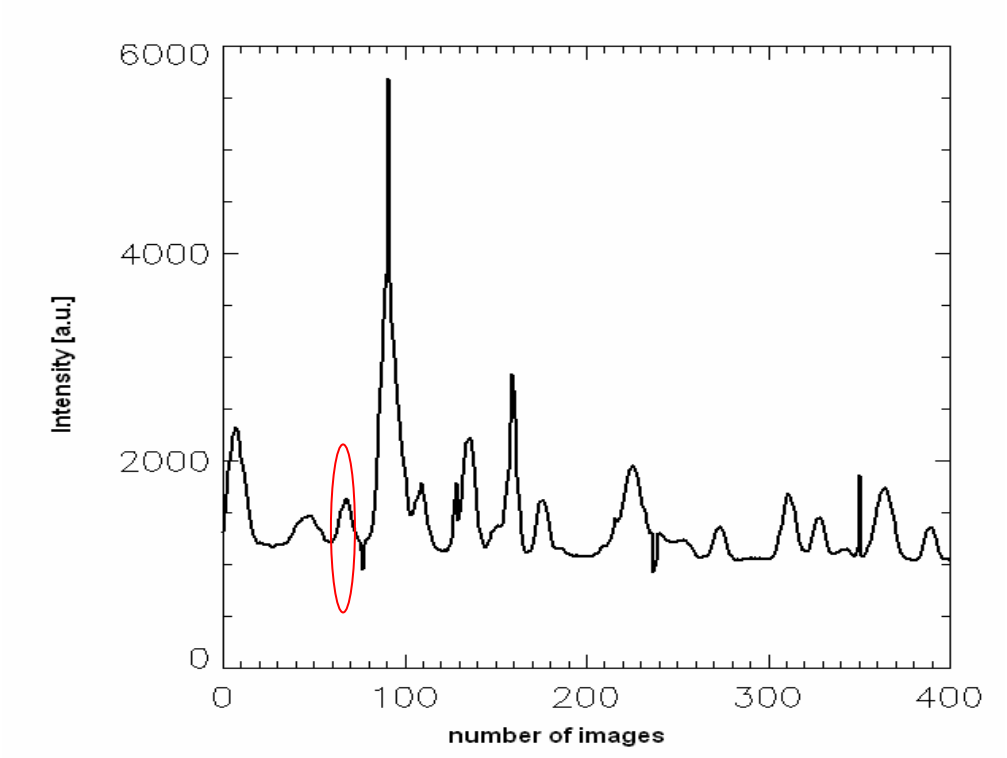

Figure 35. Pattern obtained from MAXIM measurements in function of image number. Selected peak was used to show image from CCD camera in Figure 23.

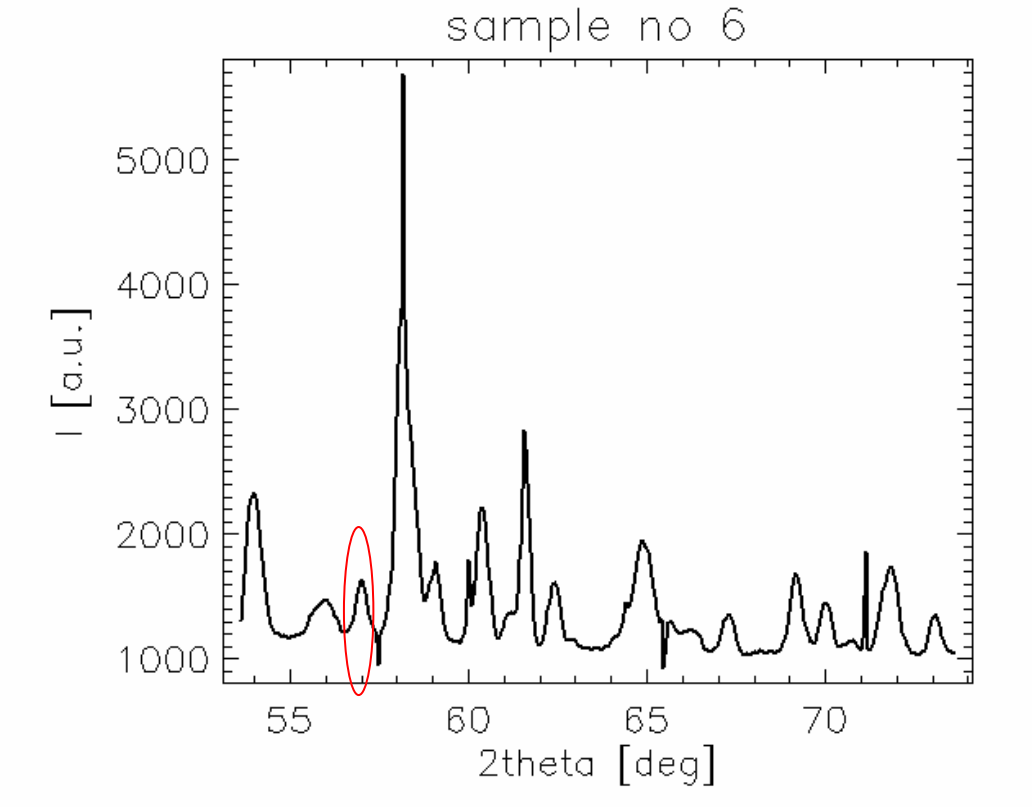

Figure 36. Diffraction pattern for sample 6 in 2θ range from 54° to 74°. Selected peak was used to show image from CCD camera in Figure 23.

MAXIM image of sample 6 shows that some areas on the sample surface are slightly different. Unfortunately it is insufficient for pigments analysis.

Sample no 9

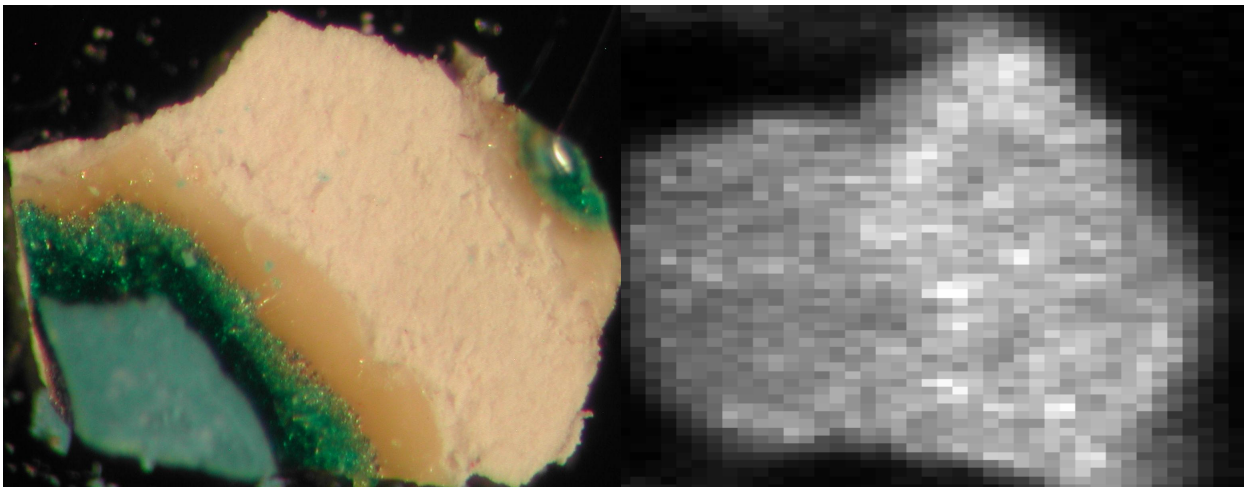

Figure 37. Fragment of vase: photo (left) and MAXIM image from CCD camera (right).

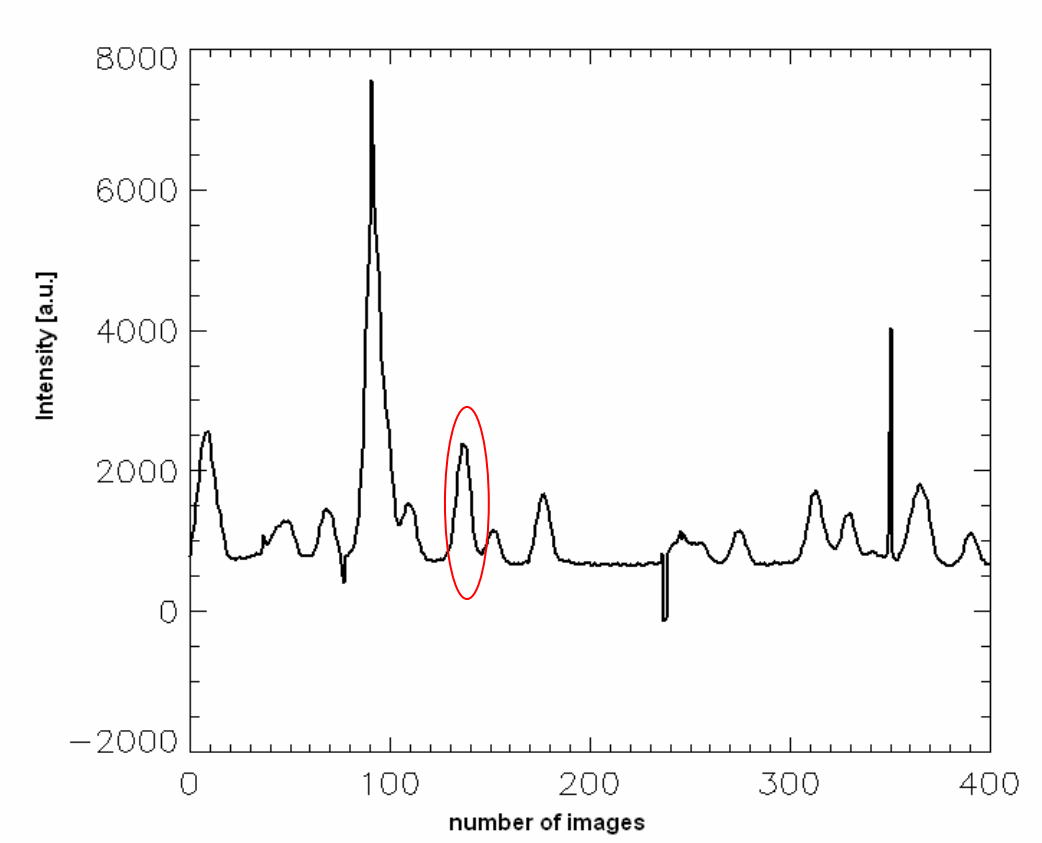

Figure 38. Pattern obtained from MAXIM measurements in function of image number. Selected peak was used to show image from CCD camera in Figure 26.

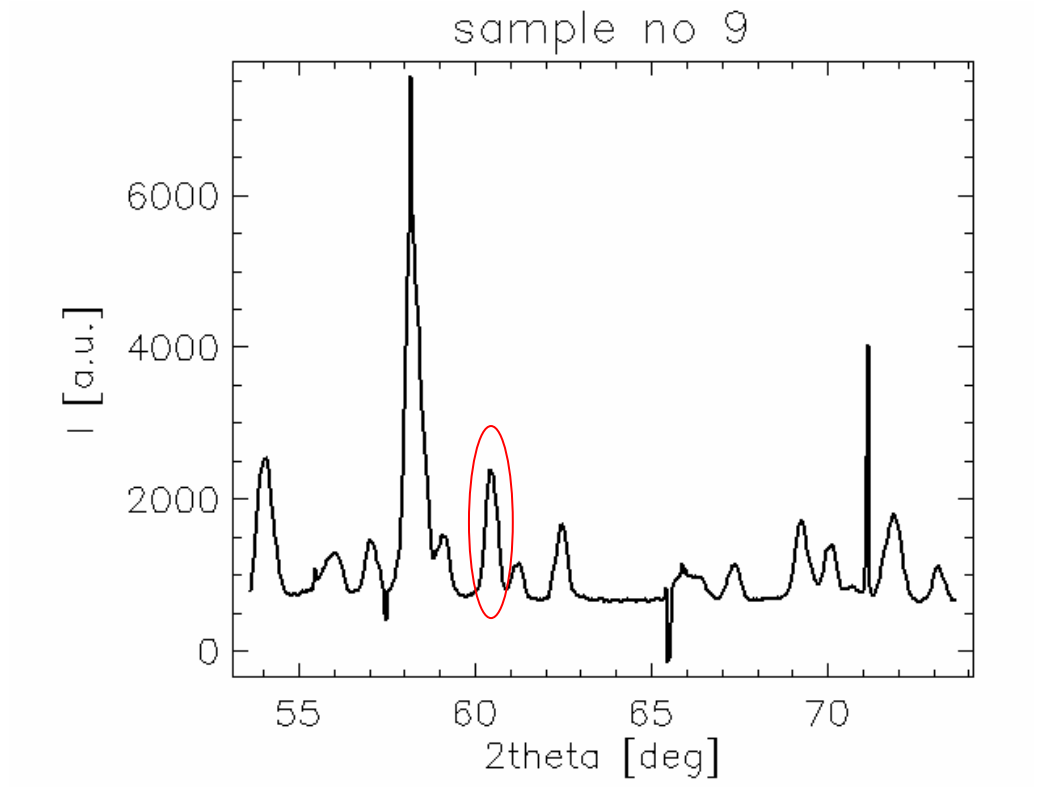

Figure 39. Diffraction pattern for sample 9 in 2θ range from 54° to 74°. Selected peak was used to show image from CCD camera in Figure 26.

MAXIM image of sample 9 does not show any differences on the sample surface which are visible on sample's photo.

Sample no 5

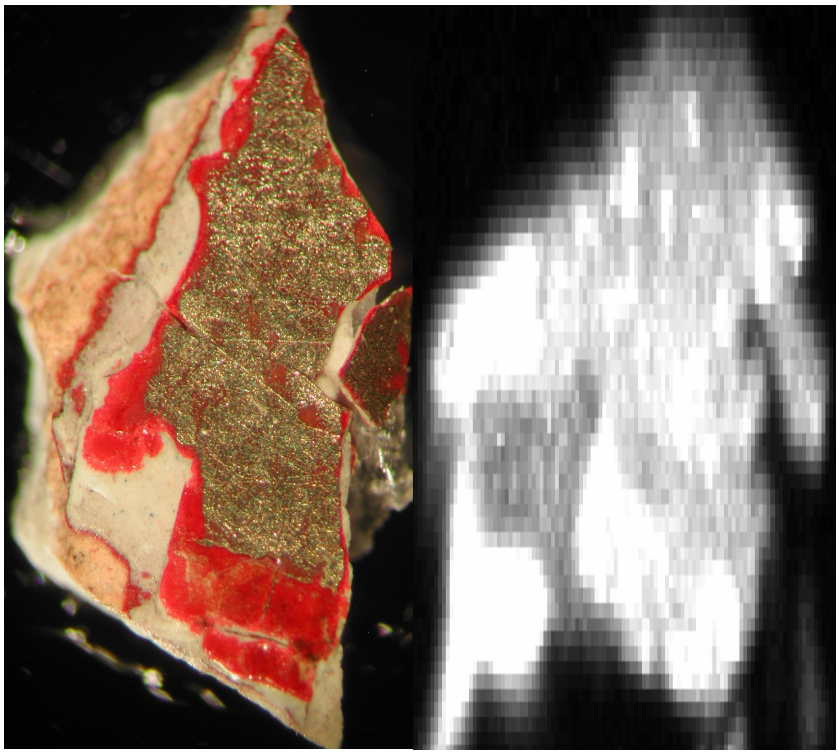

Figure 40. Fragment of vase: photo (left) and MAXIM image from CCD camera (right).

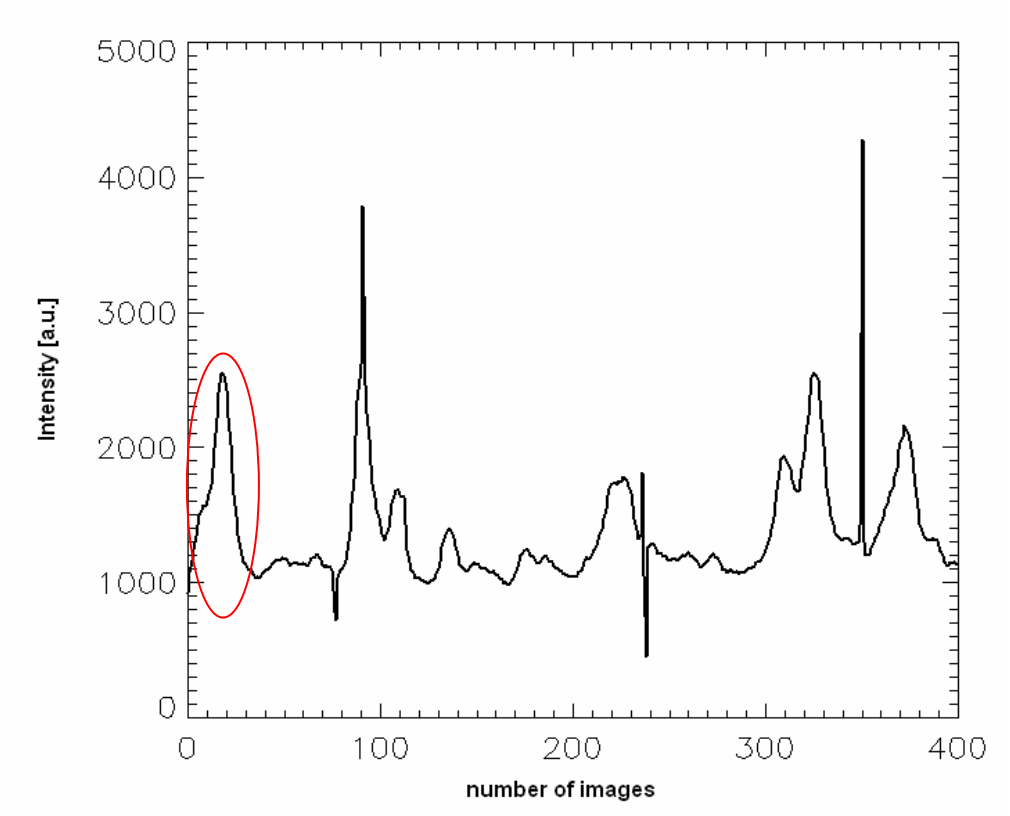

Figure 41. Pattern obtained from MAXIM measurements in function of image number. Selected peak was used to show image from CCD camera in Figure 29.

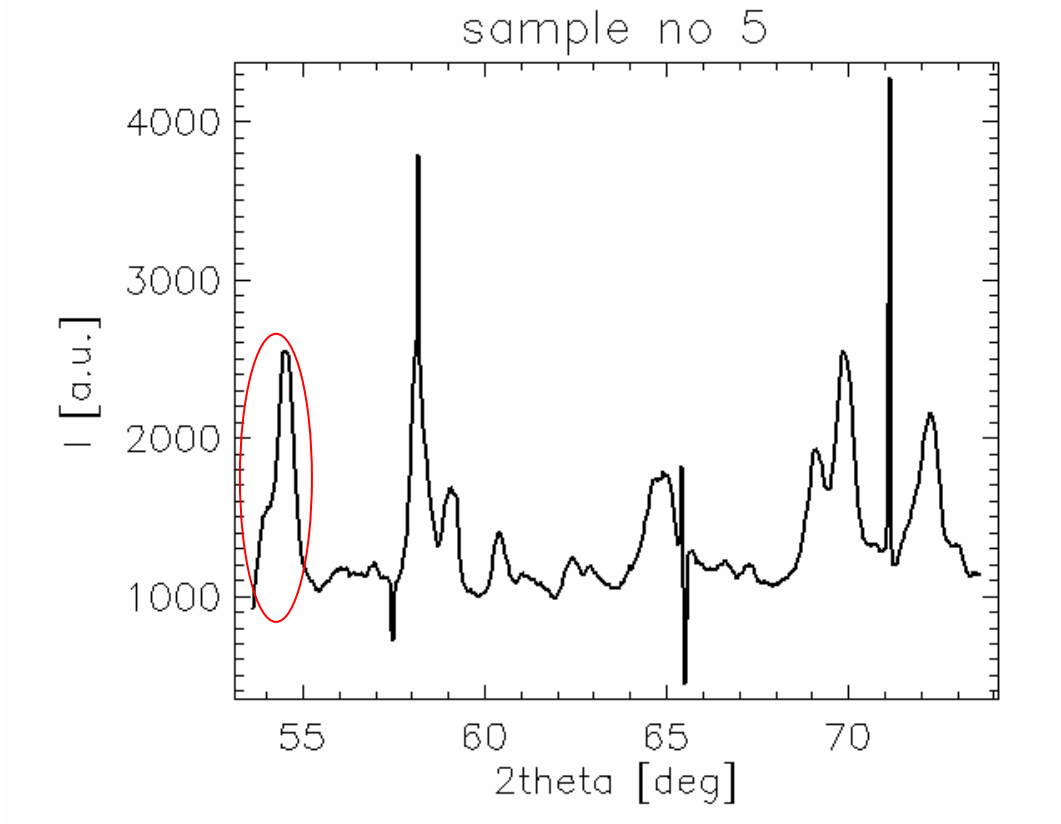

Figure 42. Diffraction pattern for sample 5 in 2θ range from 54° to 74°. Selected peak was used to show image from CCD camera in Figure 29.

MAXIM image of sample 5 shows some brighter areas on sample surface. This is due to fluorescence of some sample compounds. There is no visible difference in diffraction reflexes which could help in pigments identification.

Sample no 7

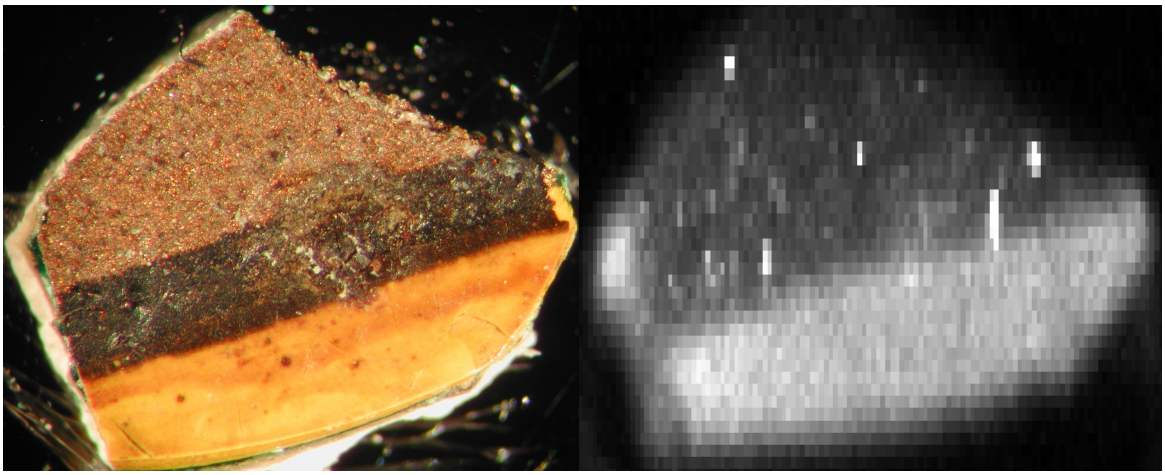

Figure 43. Fragment of vase: photo (left) and MAXIM image from CCD camera (right).

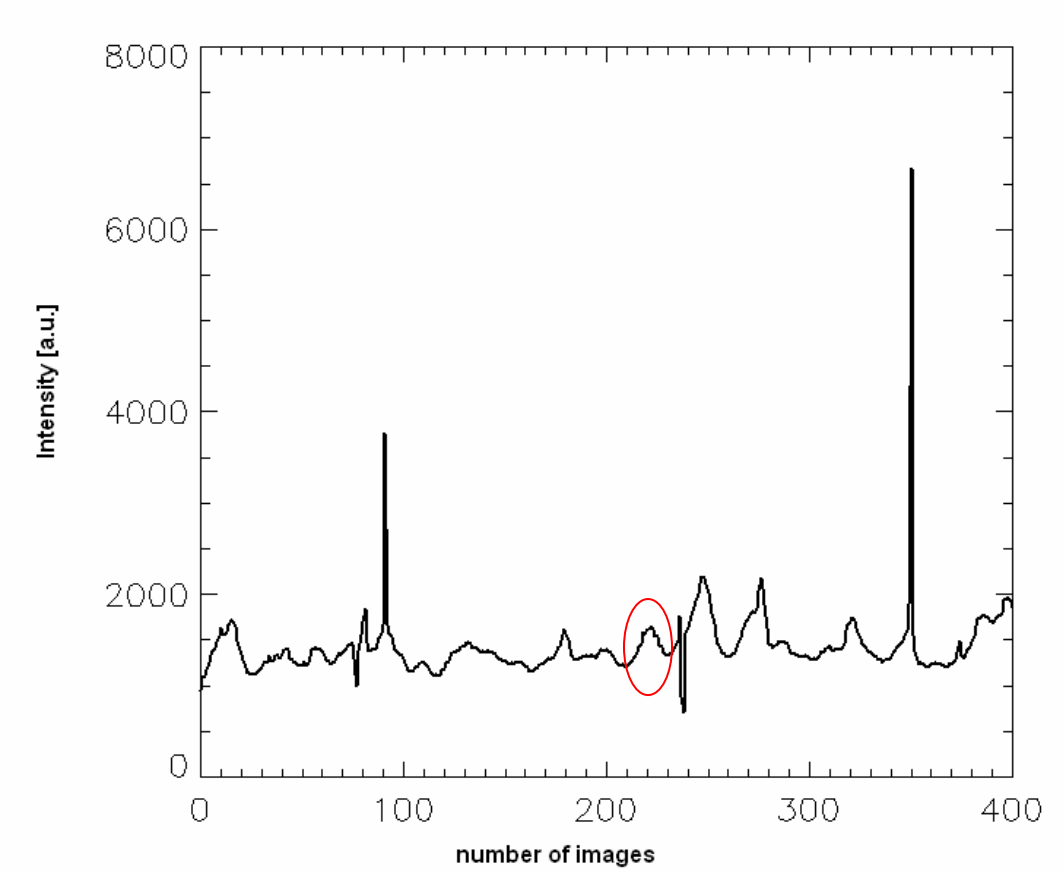

Figure 44. Pattern obtained from MAXIM measurements in function of image number. Selected peak was used to show image from CCD camera in Figure 32.

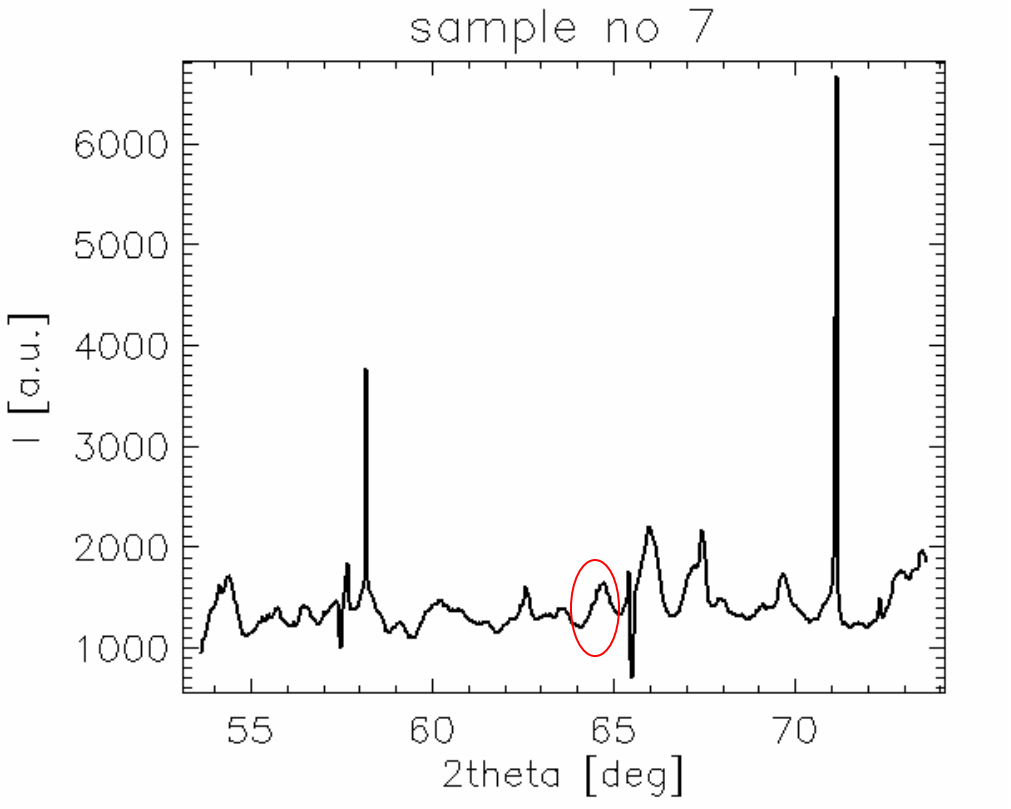

Figure 45. Diffraction pattern for sample 7 in 2θ range from 54° to 74°. Selected peak was used to show image from CCD camera in Figure 29.

MAXIM image of sample 7 shows one brighter area on sample surface. This is due to fluorescence of some sample compounds. Some signal crystal grains are also shown on image from CCD camera. There is no visible difference in diffraction reflexes which could help in pigments identification.

Measurements performed at beamline L

Micro X-ray fluorescence analysis

Smaller beam size was achieved by the use of a collimating glass capillary (polycapillary - focus size: 5µm (30 keV)). A ionisation chamber is used to monitor the incident beam intensity and measure the signal. The signal from the sample is normally measured with fluorescence detector (Ge). Throughout the analysis the sample is supervised with a long distance zoom microscope with a magnification of 500 to 1500x and CCD-camera with a resolution of 3 µm.

Example of analysis for sample number 5

Table 2. Analysis of fluorescence for investigated samples.

Measurement point	Identified chemical element
Red area	
1	Cl, Ca, V, Fe, Cu, Pb, Zn, Sn, Hg
2	Cl, Ca, V, Fe, Cu, Pb, Zn, Sn, Hg
3	Cl, Ca, V, Fe, Cu, Pb, Zn, Sn, , As, Ag
Gold area	
4	Cl, Ca, V, Fe, Cu, Pb, Sr, Ag, Sn, Hg
5	Cl, Ca, V, Fe, Cu, Pb, Ag, Hg
6	Cl, Ca, V, Fe, Cu, Pb, Ag, Hg, Zn
White area	
7	Cl, V, Fe, Cu, Pb, Sn
8	Cl, Ca, V, Fe, Cu, Pb, Sn
9	Cl, Ca, V, Fe, Cu, Pb, Sn
Beige area	
10	Cl, Ca, Fe, Cu, Pb, Sn, Sr
11	Cl, Ca, Fe, Cu, Sr, Zr, Sn, Hg
12	Cl, Ca, Fe, Cu, Sr, Zr, Sn, Pb

Identified chemical elements will use to determine pigments of samples.

3. Investigation of green pigment called verdigris

Background of sample

Chemical name: Copper acetates ranging color from green to blue. Neutral verdigris is **$Cu(CH_3COO)_2 \cdot H_2O$** and basic verdigris contains more $Cu(OH)_2$ and H_2O.

Verdigris is a pigment which was used often, from antiquity through the Middle Ages, Renaissance and Baroque. Verdigris was the most vibrant green available until the 19th century.

Sample

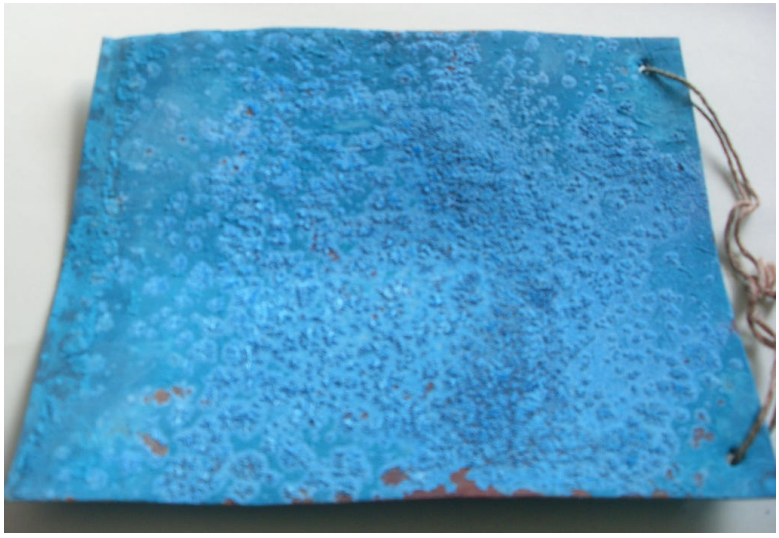

Figure 46. Photo of pigment verdigris.

Measurement

Purpose of measurement: to obtain diffraction pattern
Why? It is very hard to obtain very good diffraction pattern of this green pigment.

Name of sample: verdigris_ov_00003
Description of sample: green pigment called verdigris
Scan from **8° to 140°**
Step: 0.01°

Database ICSD was used to find chemical compound which matches the obtained diffraction pattern.

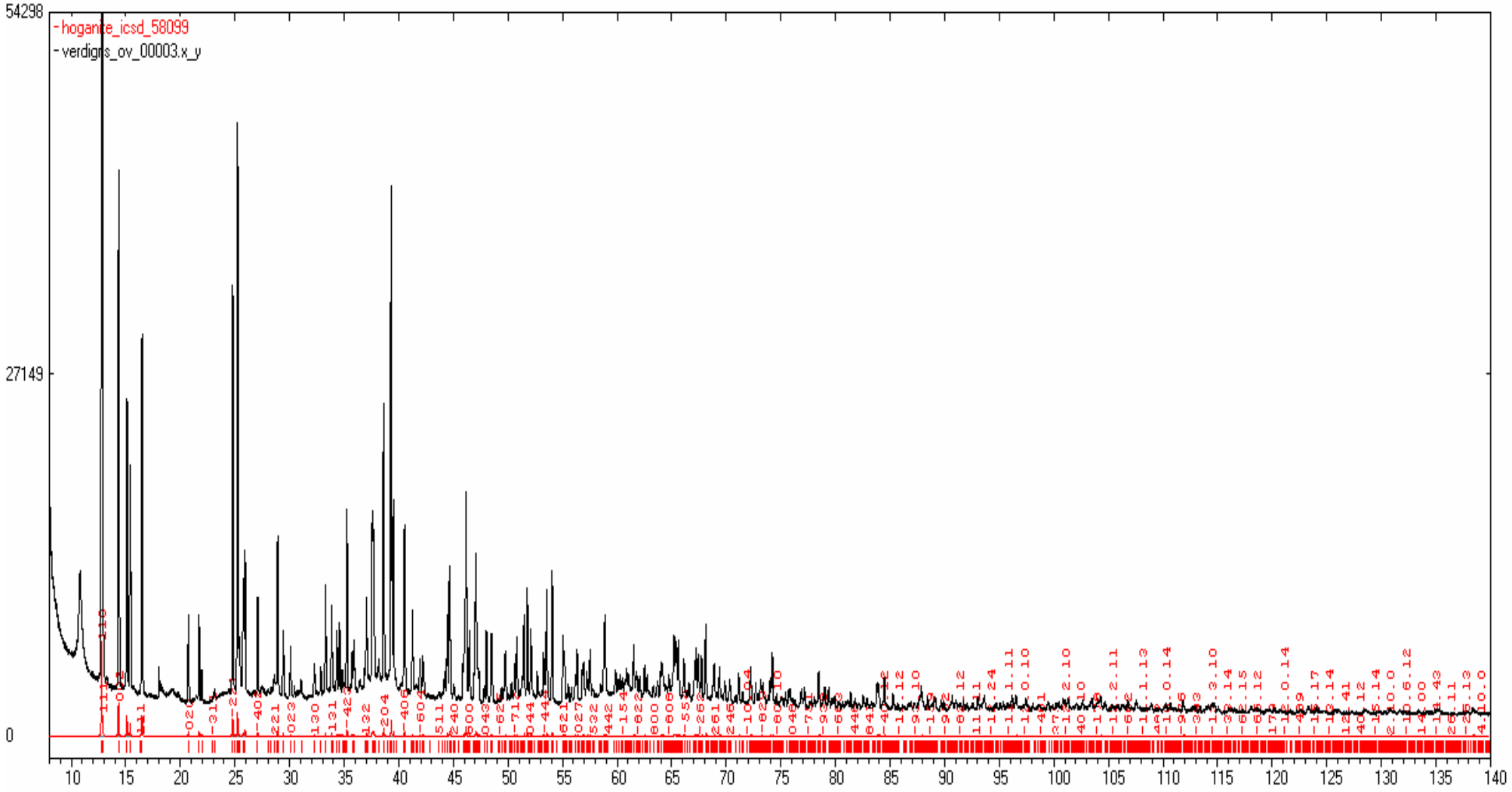

Figure 47. Diffraction pattern of verdigris (black solid line) and overlapping diffraction pattern of hoganite (red lines).

Conclusions

We used three different techniques to investigate our samples.

For Ruthenian – Byzantine wall paintings most information about chemical elements in layers of pigments was taken from EXAFS measurements. We got information that there is no cadmium in yellow parts of samples. In this way one of the main aim of measurement was achieved. Diffraction measurement didn't allow us to know composition of pigments on the sample surface. Obtained diffraction patterns show principal reflexes from chalk ($CaCO_3$). Further analysis of EXAFS data is needed to know better which exactly pigments (especially green) were used by artists in these wall paintings.

In case investigation of fragments of vases from Collegium Maius we used micro X-ray fluorescence analysis. Thanks to this method we knew chemical elements of pigments in our samples. This is beginning of research on these samples. Obtained diffraction patterns are going to be analyze at Jagiellonian University by using database PDF-4 (Powder Diffraction Data) from International Centre for Diffraction Data (ICDD).

Thanks to this we were here preliminary tests of our samples were carried out. Knowledge gained here will allow us to continue our research and create in the future full characterization of pigments in Ruthenian – Byzantine wall paintings and vases.

References:

1. *Crystal structure of Anilinium Pentamolybdate from Powder Diffraction Data. The Solution of the Crystal Structure by Direct Methods Package POWSIM.*, W. Lasocha, H. Schenk, *J. Appl. Cryst.* (1997) **30**, 90-914
2. *Molybdates of p-bromoanilinium – Synthesis and Crystal Structure of New Catalytic Materials.* W. Lasocha, M. Grzywa, M. Oszajca, *Z. Kristallogr. Suppl*. **30** (2009) 387-394