

⁵⁷Fe Mössbauer, SEM/EDX, p-XRF and μ -XRF studies on a Dutch painting

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Abstract The painting of a rich Jewish merchant “Bildnis eines jüdischen Kaufmanns” from the Netherlands is dated presumably to the 16th century. After a vivid historical background, i.e. robbed by the Nazis by order of Hermann Göring, it was recently discovered on an Austrian flea market. Different analysis methods were combined to identify the time of the production of this historically interesting looted art. Non-destructive MIMOS II Fe-57 Mössbauer spectroscopy was utilised for measurements in selected spots. This mainly revealed haematite (α -Fe₂O₃) in the red curtain. In spots of the brown jacket Mössbauer spectra indicated the presence of mainly Iron(III) in super-paramagnetic oxide or oxide-hydroxide. Consecutively SEM measurements revealed a restoration by partly over-painting. The elementary composition of the pigments was examined by a portable-X-ray

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fluorescence. μ -XRF analysis for element distribution at different areas was performed. The look into a crack showed Zinc-white at the bottom of the crack. Traces of Titanium-white could be found within some locations on the surface of the painting. In terms of provenance of the artwork, the presence of Zinc-white suggests that the painting was painted around the 19th century. Titanium-white indicates a reconstruction during the 20th century, approximately between 1917 and 1958.

Keywords Painted artwork · Pigments · Mössbauer spectroscopy · SEM/EDX · p-XRF · μ -XRF

1 Introduction

The analyzed picture shows an old man and appears to date back to the 16th century. Some hints suggest a formerly ownership by a Jewish collector from the Netherlands. He had been expropriated by order of Hermann Göring and later died on the run.

Recently the portrait has been discovered on an Austrian flea market and identified as looted art. In case of authenticity the painting could be worth millions of Euros [1]. The portrait has been painted on wood and it also has a big wooden frame. It shows an old man and is called “Bildnis eines jüdischen Kaufmanns”, picture of a Jewish merchant (Fig. 1, nearly 30 x 22 cm).

The goal of our scientific study was to collect evidence for the provenance of the artwork by combining different analytical techniques. For this we applied various methods such as Mössbauer spectroscopy (MS), scanning electron microscopy/ energy dispersive X-ray spectroscopy (SEM/EDX), portable X-ray-fluorescence (p-XRF), micro X-ray-fluorescence (μ -XRF) and Raman-spectroscopy. After assignment a restitution to the heir in law is planned.

2 Experimental procedures

The MIMOS II Fe-57 Mössbauer spectroscopy [2] was applied to identify the iron containing materials in the artwork. Mössbauer spectra were recorded at room temperature with a MIMOS II spectrometer detecting both 6 keV and 14.4 keV radiation in gamma-ray backscattering mode and a $^{57}\text{Co}(\text{Rh})$ source with an activity of about 80 mCi. No sample preparation was done to carry out the measurements. Several spots of the painting, corresponding to different colour pigments were measured. The fitting procedure of the spectra was carried out using a set of Lorentzian lines and parameters determined by the least squares method. The isomer shifts are given relative to α -Fe at RT.

Raman-spectroscopy measurements were performed at some spots of the brown jacket of the man portrayed in the artwork, with a portable spectrometer based on commercial components illuminated at 785 nm (BWTEK BRM-OEM-785) and with a spectrometer having a spectral resolution of 5 cm^{-1} . The optical probe head was coupled with the spectrometer by an optical fibre and the spot size on the sample was around 100 microns in diameter. The irradiance on the sample was kept below the thermal damage threshold which was visually and spectrally controlled.

Portable-X-ray fluorescence (p-XRF) spectrometry was utilized in the identification of pigments. Measurement parameters: 40 kV, 0,1 mA, 30 sec live time, 7 mm^2 beam, information depth is some hundred μm in organic layers.

Fig. 1 Picture of a Jewish merchant



μ -X-ray fluorescence (μ -XRF, Eagle II, Roentgenanalytik) with micro focus beam ($50\ \mu\text{m}$, by using glass fiber capillary optics) allows stationary observation of the distribution of chemical elements with reasonable accuracy and good local resolution in a small spot of the sample. Measurement parameters: 40 kV, $150\ \mu\text{A}$, resolution 144 eV, 1000 msec live time per measurement point. By scanning a matrix of points it is possible to generate element distribution maps (similar to SEM/EDX but with better limits of detection).

The SEM-measurements were accomplished by the use of two identical instruments (Zeiss LEO 1455 (Germany)), with a secondary electron and a backscattering detector. Measurement conditions: 40 kV, $250\ \mu\text{A}$, $0,008\ \text{mm}^2$ beam. The depth of the measurement is some $100\ \mu\text{m}$. The backscattering-electron-detector is from K.E. Development Limited, the secondary-electron-detector is from Zeiss LEO and the EDX-detector is from Oxford. The program INCA was used for evaluation. Because the painting was too large for the SEM chamber, by using a hollow needle samples were taken (about $500\ \mu\text{m}$ size). The damage was not visible on the painting. To make the surface conductive the samples were coated with a several nanometer thick layer of gold.

3 Mössbauer-spectroscopy results

Mössbauer data (Table 1) were collected on a spot of the red curtain on the painting as shown in Fig. 2 (Fig. 5 location 2) and on two areas on the brown jacket (Fig. 2; Fig. 5, location 10 and 12) the man portrayed is dressed with. One is situated on the left side (location 10) of the person and the other on the right side (location 12). Hyperfine parameters and site occupancies (%) obtained in the fitting of the spectra are shown in Figs. 2 and 3. IS is given relative to α -Fe (Table 1). The spectra were collected with 6 keV radiation as well as 14.4 keV radiation, providing depth selective information on surface layers and substrate layers. There were no differences in the information obtained from the spectra collected with the two radiations. The figures show spectra collected with 14.4 keV.

Figure 3 shows the spectrum obtained on a point of the red curtain. Table 1 gives the hyperfine parameters obtained in the fitting procedure. The parameters are consistent with

Table 1 Mössbauer data

IS (mm/s)	QS (mm/s)	H (T)	WID (mm/s)	%	
Red curtain					
0.37(1)	-0.20(1)	51.2(2)	0.32(1)	100	haematite
Brown jacket – left side					
0.34(1)	-0.11(2)	51.6(2)	0.33(1)	10.0	haematite
0.37(1)	0.68(1)	–	0.49(1)	70.86	Fe(III) doublet
0.43(2)	-0.28(2)	32.4(2)	0.40(1)	19.14	goethite
Brown jacket – right side					
0.28(2)	0.08(1)	49.8(2)	0.30(2)	2.46	haematite
0.37(2)	0.66(29)	–	0.45(2)	81.79	Fe(III) doublet
0.38(1)	0.21(1)	33.6(1)	0.40(1)	15.75	goethite ?

Fig. 2 Picture of a Jewish merchant” with MIMOS II equipment while positioned in front of the red curtain



haematite (α -Fe₂O₃) which is known to be a red pigment. The spectrum obtained for α -Fe₂O₃ shows peak areas that are in the theoretical ratios 3:2:1:1:2:3. Differences can be explained by the moderate statistical accuracy of the spectrum [3].

In Fig. 4 the Mössbauer spectra obtained by measuring the spots on the brown jacket are shown. The spectrum acquired in the left side has a better signal-to-noise ratio, therefore the magnetic subspectra in minority are hardly seen. The parameters obtained in the fitting procedure, for both spectra, are given in Table 1. The magnetic sub-spectra correspond to haematite and likely Goethite [4]. The quadrupole shift for the right side spot of the brown jacket is unfortunately positive for Goethite. Perhaps this may be an effect of the poor statistic. Most probably it is Goethite with rather large grains that gives a magnetic splitting at ambient temperature. The Iron(III) doublet that consists of 70–80 % of the spectrum can

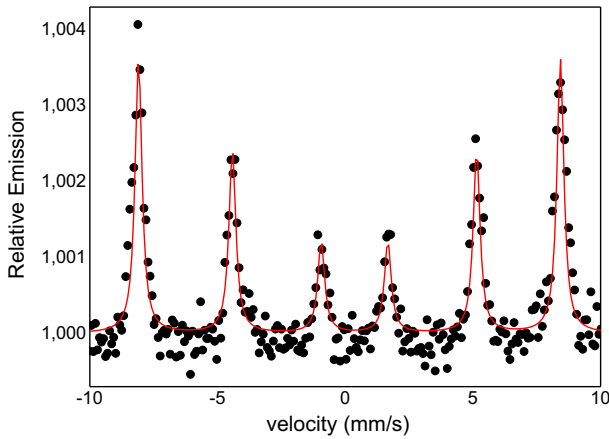


Fig. 3 ⁵⁷Fe Mössbauer backscattering spectrum (a) taken at a spot of the red curtain of the painting (see location 2 at Fig. 5)

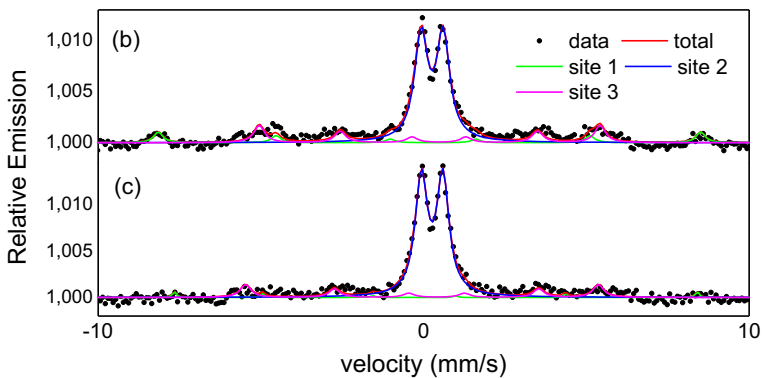


Fig. 4 ⁵⁷Fe Mössbauer backscattering spectra taken at spots of the brown jacket of the man portrayed in the painting: (b) on the left side (see location 10 at Fig. 5), (c) on the right side (see location 12 at Fig. 5)

be assigned to a super-paramagnetic oxide or oxide-hydroxide, most probably to Goethite in a superparamagnetic small particle size (with a wide distribution of grain sizes) which has an orange/yellowish colour [5]. Raman spectroscopy measurements on the brown jacket reveal Cinnabar (HgS) having a red colour.

4 Portable X-ray fluorescence analysis (p-XRF) results

By using portable-X-ray fluorescence the elementary composition of the pigments was examined. The results should help to check the interpretation of the Mössbauer data. The p-XRF measurements (Table 2) were performed at various spots on the artwork as seen in Fig. 5. Only some selected spots are explored and discussed in the following. In location 19 the main signals show a mixture of mostly Iron (brown, 0,7 %) and Mercury (red, 0,9 %) on the background wall. In location 1 to 3 the measurements show mostly Mercury (red,

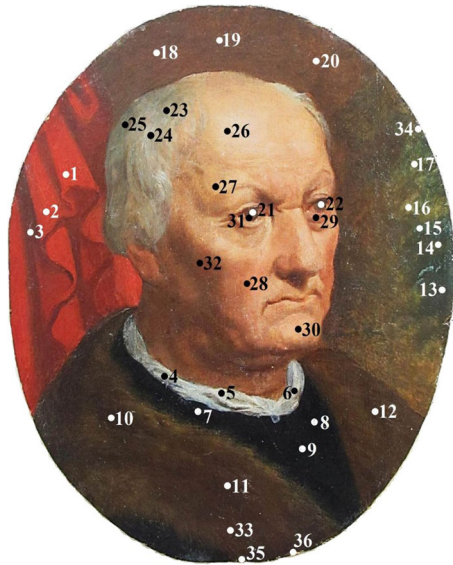
Table 2 p-XRF data in mg/kg and interpretation according to Fig. 5

No.	Color	Fe	Cu	Hg	Pb	Pigment
1	Red curtain	10050	100	70500	22000	Cinnabar, iron oxide
2	Red curtain	31400	480	486400	58900	Cinnabar, iron oxide
3	Red curtain, dark area	39300	2550	100000	43800	Cinnabar, iron oxide
4	White collar	2700	530	400	60800	White lead and white zinc
5	White collar	1030	700	590	138400	White lead
6	White collar	700	130	110	54900	White lead
7	Black clothes	1700	440	32	10200	Carbon black
8	Black clothes	1100	240	<DL	18700	Carbon black
9	Black clothes	920	170	70	12600	Carbon black
10	Brown fur	40400	490	770	21400	Iron oxide brown
11	Brown fur	28200	40	310	17300	Iron oxide brown
12	Brown fur	29600	90	290	26000	Iron oxide brown
13	Dark green background	10900	86400	1900	51300	Mountain green (malachite)
14	Dark green background	5700	47500	1130	34400	Mountain green (malachite)
15	Dark green background	4000	49200	950	33100	Mountain green (malachite)
16	Light green background	2200	12400	1270	12600	Mountain green (malachite)
17	Light green background	2300	14200	1290	16800	Mountain green (malachite)
18	Brown background	7300	2900	7600	15000	Iron oxide brown and cinnabar
19	Brown background	7100	5900	8940	23400	Iron oxide brown and cinnabar
20	Brown background	9000	1580	5540	25400	Iron oxide brown and cinnabar
21	Black pupil	12400	120	2370	25300	Carbon black/ iron oxide black
22	Black pupil	7590	130	2250	30100	Carbon black/ iron oxide black
23	Gray hair	2340	5850	710	31300	Carbon black with white lead
24	Gray hair	1340	5050	530	29700	Carbon black with white lead
25	Gray hair	3700	16200	950	43900	Carbon black with white lead
26	Light yellow skin	1450	110	3470	104300	White lead, cinnabar, iron oxide
27	Light yellow skin	2610	80	3480	46600	White lead, cinnabar, iron oxide
28	Rose skin	2290	210	800	59300	Cinnabar, white lead, iron oxide
29	Rose skin	4000	180	27200	62900	Cinnabar, white lead, iron oxide
30	Skin	1380	50	3350	45600	White lead, cinnabar, iron oxide
31	Brown eye	6000	100	2320	26600	Iron oxide brown with cinnabar
32	Brown skin	7130	90	6640	38300	Iron oxide brown with cinnabar
33	Spalling with brown	47700	110	530	41100	Iron oxide on white lead
34	Spalling with green	5400	6860	530	10600	Mountain green on white lead
35	Spalling with brown	7300	50	100	10700	Iron oxide on white lead
36	Spalling with brown	3100	< DL	80	4200	Iron oxide on white lead

LD means below detection limits (about 10 mg/kg). Measurement error about 5 % below 10 000 mg/kg, about 10 % above 10 000 mg/kg

cinnabar, 7 to 10 %) and Iron pigments (red, 1 to 4 %) in the curtain. These results confirm the interpretation of the Mössbauer data. Not only one red pigment was used (cinnabar) but a second red iron pigment, too. In location 26 the signal reveals mostly Lead (white, 10 %)

Fig. 5 Picture of a Jewish merchant with selected locations for measurements with p-XRF, Mössbauer spectroscopy (location: 2,10 and 12) and other methods



and Mercury (red, 0,3 %), which contributes to the skin color. The observation in location 13 indicates dominantly Copper (green background, 8,6 %). The data in location 11 shows Iron (brown jacket, 2,8 %). The main result is the use of iron pigments as brown and red pigment.

5 μ -X-ray-fluorescence and SEM/EDX results

The goal of the analysis by μ -XRF and SEM/EDX was to identify different layers and determine their composition. The composition gives a hint to the pigments used. Because different pigments were used at different times, the results can help to discuss the time of the production of the painting [6]. The entire painting was placed in the vacuum chamber of the device (Fig. 6). Due to the size of the picture only the centre region of the painting was measured by the use of μ -XRF.

5.1 Sector with eye

The identification of Titanium (Fig. 7) in the top layer indicates a restoration in the beginning of the 20th century by using Titanium-white. Titanium-white has been technically produced from 1917 onwards [6]. At this time Titanium-white contained up to 10 % Zinc for various reasons [6] which can be seen in the top right picture of Fig. 7. After a change in production methods Titanium-white was produced in an industrial process in pure form since 1958.

5.2 Sector with crack

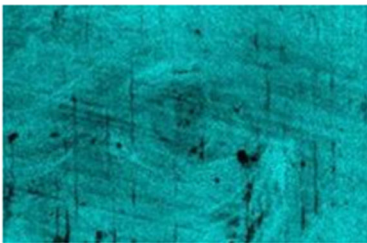
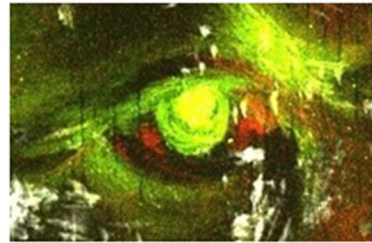
The tested crack area (Fig. 8) is situated at the neck of the merchant. In the crack signals for Calcium and Zinc are visible. These signals are hints for gypsum (calcium sulfate) and Zinc white (Zinc oxide) in the bottom layer. In the crack no signal for iron or Lead white



Fig. 6 The analyzed artwork “Bildnis eines jüdischen Kaufmans”, in situ in the opened large measurement chamber of μ -XRF (Eagle II)

Analysed sektor

Overlay: Zn: white; Fe: yellow;
Mn: green; Hg: red



Distribution of Pb

Distribution of Ti

Fig. 7 Distribution of elements in the eye region, measured by μ -XRF, measurement matrix 256 x 200 pixel (3,4 x 2,5 cm), 1000 msec measurement time for each pixel

is detectable. The layered structure of this sample has been tested concerning the elements of: Iron mixed with Lead lying above Zinc and Calcium. The same result was obtained by analyzing other areas of the painting too. The presence of Zinc in the bottom color layer is a hint to a production in the 19th century. Zinc oxide was used as a white pigment since about 1840. These observations are strong indications that the painting is a 19th century reproduction or a fake rather than a 16th century original. Perhaps this masterpiece forgery

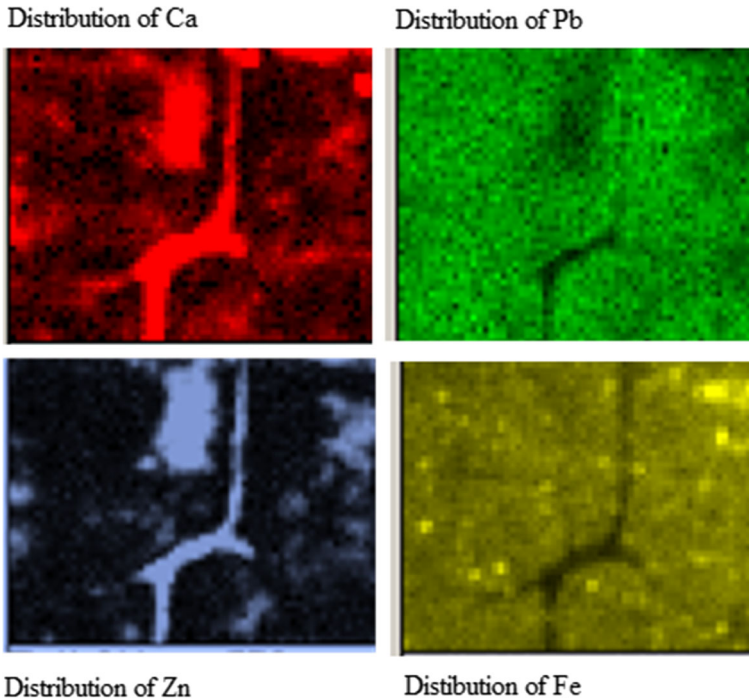


Fig. 8 False colour images: Distribution of selected elements in and around the neck crack. Measured by μ -XRF, measurement matrix 128 x 100 pixel (2,1 x 1,6 mm), 1000 msec measurement time for each pixel

was presented to the Nazis to cheat them and to keep the original painting. This was a known procedure in the time of expropriation.

6 Conclusions

Mössbauer is a powerful tool for the analysis of art works to identify iron pigments. The combination with traditional analytical techniques (XRF, RAMAN) can result in an all in all powerful tool for art works analysis. The results for the old Dutch portrait are consistent with haematite (α - Fe_2O_3) which is known to be a red pigment and to Goethite which has an orange/yellowish colour.

Using μ -XRF the p-XRF-results various pigments are identified at various spots on the artwork. The main result is that iron was mainly used as brown pigment. Only the Mössbauer data could show that the red colour is caused by haematite in addition to the red mercury pigment cinnabar. The use of Mössbauer spectroscopy is a reasonable addition to traditional techniques.

By local area scanning mode of μ -XRF the distribution of color giving elements is resolved, especially on the bottom of cracks. The presence of Titanium- and Zinc-containing areas could be shown by using μ -XRF. By applying SEM and μ -XRF the reconstruction of pigment layers was possible. The Zinc white pigments are located at the bottom of the pigment layers, the Titanium white pigments on the top of the painting.

Concerning the provenance of the artwork, the presence of Zinc-white at the bottom of a crack suggests that the painting was created around the 19th century. Titanium-white on the top layer furthermore indicates that there has been a reconstruction performed during the 20th century, approximately between 1917 and 1958. Probably this copy of an older painting was used to cheat the Nazis. This practice is known since the discovery of art depots from the Nazi time with forged paintings which were sold to or expropriated by the Nazis.

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