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Klimt artwork: red-pigment material investigation by backscattering Fe-57 Mössbauer spectroscopy, SEM and p-XRF

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ABSTRACT

Material tests were performed on a rediscovered Klimt-artwork “*Trompetender Putto*”. We performed studies on the red colored spots, mainly taken from non-restored parts. MIMOS II Fe-57 Mössbauer spectroscopy (novelty in art-pigment analysis) mainly reveals haematite and crystallized goethite in red colors. Electron microscopy can identify various layers of the original and overpainting of an artwork. The number of layers fluctuates between three and four chemically painted areas. The portable X-ray fluorescence analysis enables to reduce the pigment list to containing mercury (cinnabar), lead, zinc, iron and titanium. Infrared-light-irradiation visualizes the different age of the pigments.

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Klimt: “*Trompetender Putto*”; Mössbauer spectroscopy; scanning electron microscopy; X-ray fluorescence analysis; pigments; infra-red-light investigation

Introduction

At the end of the 19th century, Klimt’s painting “*Trompetender Putto*” greeted visitors at the entrance of the artist workshop “Künstler Compagnie” in Vienna, an association of Gustav Klimt, Ernst Klimt and Franz Matsch. Recent studies suggest that the painting probably originated in the early 1880’s and that it was unskillfully overpainted in the 1950’s with the same motif (Nebehay 1969). A valuable painting such as this has to be examined as nondestructively as possible in order to restore the original of the Viennese artist’s company (Nagy et al. 2015). Many red pigments are poisonous, such as those containing mercury (cinnabar), cadmium (cadmium-red), lead (Paris red, minerie), realgar (arsenic-red) or chromium (chromium-red). By detecting the use of these pigments and knowing when they were prohibited, the period this work of art was created can be narrowed down. In addition to frequently used methods, a miniaturized Fe-57 Mössbauer spectroscopy with the MIMOS II is particularly suitable. It is very small, mobile and usable everywhere. This analysis is suitable mainly because of the presence of iron pigments (many yellow-, brown- and red-tones are iron pigments). The portable X-ray fluorescence analysis (p-XRF) can be applied well on surfaces and reveals used chemical elements from the PSE (Nagy

et al. 2015). Irradiation with IR light is revealing as well. IR light goes very deep and a hidden motif is detectable under the last painting layer. The number and composition of the different color layers is determined by the scanning electron microscope (SEM) and energy dispersive X-ray fluorescence (EDX).

Goal

The main objectives were given as follow:

We determined the chemical composition of many pigments, especially the red color.

This composition gives information about the source of the pigments and thus also of the provenance of the artwork.

To confirm the artwork as an early masterpiece of e.g. Gustav Klimt or one of the members of the “Künstler Compagnie”, the red color is very important. Many red pigments consist of toxic ingredients like lead, arsenic or chromium and were forbidden in the 20th century. And now, knowing both the kind of pigment and the date of the ban, one can narrow down the period this masterpiece was created. It can thus be assigned to one of the two Klimt-brothers (Gustav and Ernst) or Franz Matsch, the three members of the “Künstler-Compagnie”.

Mössbauer spectroscopy for painting analysis

Instrumentation

Valuable paintings or finest rock paintings can be examined without damage by spectroscopic methods, using the transportable, miniaturized Fe-57 Mössbauer spectrometer MIMOS II. This device, used on planet Mars during NASA “Spirit” and “Opportunity” missions, showed hydrated minerals - water on the red planet (Figure 1).

The Mössbauer spectrometer, in its portable MIMOS II version, is approximately the size of a cigarette box. For analysing art, the Mössbauer spectrometer is equipped with a Co-57 source, which has an activity of 80 mCi. The spectra are recorded with 6 keV and 14.4 keV. The environment is protected with a lead cover against gamma radiation (Costa et al. 2014 and Costa et al. 2016).

The Mössbauer spectroscopy is particularly suitable for the determination of a wide variety of iron compounds. Many red, brown, yellow and earth pigments are composed of iron. This analysis allows to draw conclusions on age determination and applied painting methods. The Mössbauer spectra of many iron compounds are tabulated and documented in various databases. By comparing and matching the experimentally obtained spectra with those from the catalogue, a phase analysis can be carried out and thus an assignment to the iron compounds.

Mössbauer spectroscopy: results and discussion

The parameters of the magnetic sub-spectra are consistent with haematite and probable goethite (Cornell



Figure 1. MIMOS II device in action (Fig.: Prof. B. Costa).

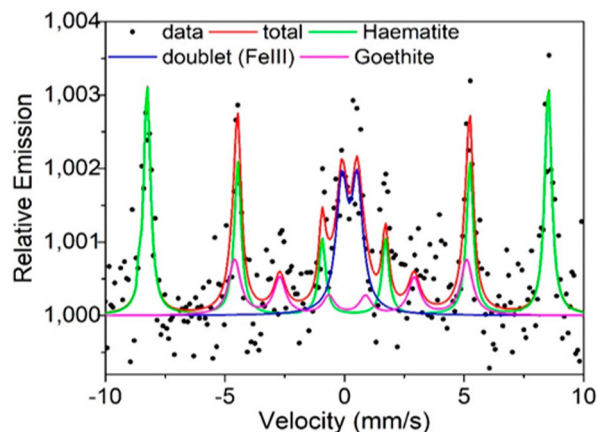


Figure 2. Fe-57 Mössbauer backscattering spectrum at a spot of the red scarf of the “Putto”. For this, the hyperfine parameters obtained in the fitting procedure are shown in Table 1. (Fig.: Prof. B. Costa).

and Schwertmann 2003) (Figure 2). Haematite (α - Fe_2O_3) is known to be a red pigment. The spectrum obtained for α - Fe_2O_3 and goethite shows peak areas that are in the theoretical ratios of 3:2:1:1:2:3. Differences can be explained by the poor statistical accuracy of the spectrum (Keisch 1974).

Most probably it is goethite with rather large grains, which gives a magnetic splitting at ambient temperature. The iron(III) doublet can 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) (Murad and Cashion 2011) (Table 1).

The Mössbauer parameters consist at the iron sites of IS, QS, H, Wid, which correspond to isomer shift, quadrupole splitting, magnetic field and full width at half maximum, respectively. IS is given relative to α -Fe at room temperature. % stands for the relative amount.

Portable X-ray fluorescence analysis (p-XRF) for painting analysis

Instrumentation

X-ray fluorescence analysis allows a non-destructive material analysis with qualitative and quantitative results. The portable XRF is used, in particular in difficult to access situations like non-transportable artworks or large-scale paintings. Even if direct analysis on the ground outside is necessary, this technique is suitable for an immediate element analysis (Granite 2012).

Table 1: Hyperfine parameters, obtained of the spectrum shown in Fig. 2 (Table: Prof. B.Costa)

IS(mm/s)	QS (mm/s)	H(T)	Wid (mm/s)	%	Mineral
0.37(1)	-0.25(1)	51.9(2)	0.35(1)	53.64	Haematite
0.31(2)	0.63(2)	-	0.57(1)	24.05	Fe^{3+} octahedral
0.29(2)	0.15(1)	30.1(2)	0.59(1)	22.31	Goethite

The atoms of the object are stimulated with energetic X-ray radiation and electrons are removed near the nucleus. Electrons from more distant shells are able to fall into these gaps. They emit energy in form of light by fluorescence radiation, which is characteristic of each element. All elements of the periodic system can be identified in nature and concentration by this portable version, except for hydrogen and helium (Figure 3).

This XRF handheld device, here the DELTA X Dynamic XRF Premium by InnovX Systems, is one of our two devices. It has been adapted to our special needs in cooperation with the producing company InnovX Systems. The device I used is exclusively for trace element analysis.

In the p-XRF-pistol, the miniature X-ray tube source (10–40 kV, cathode current up to 100 μ A) produces an X-ray beam.

In the XRF handheld device, such as the DELTA X Dynamic XRF Premium from the company InnovX Systems, the miniature X-ray tube source (10–40 kV, cathode current up to 100 μ A) produces an X-ray beam. This beam reaches to the sample with a focus of 8 mm or 3 mm in diameter. The X-ray fluorescence radiation, generated in the sample, is recorded by a silicon drift detector (SDD) with Peltier cooling and converted into electrical pulses. These continuously collected data yield the X-ray spectrum, which is evaluated with the software Delta User Interface (factory-calibrated with pure element standards).

Portable X-ray fluorescence analysis (p-XRF): results and discussion

The data obtained here is intended to confirm the data obtained from the SEM / EDX and is a fast and simple method.

High values of mercury indicate cinnabar red (vermilion) (HgS) as one coloring pigment for the “red scarf.” This red appears to be a mixture of different red pigments. Iron is found as well and indicates the use of iron pigments. The high values of lead suggest minium (Pb_3O_4), another frequently used red pigment in the 1880s.

To develop a high color-luminosity, artists like to add a white. In this case, it can be zinc white (ZnO) or lead white ($2 PbCO_3 \cdot Pb(OH)_2$), because both values can be detected. From about 1840, zinc white began to be used as a substitute oil-color for the highly toxic lead-white. But the opacity and brightening power is not as good as lead-white, which might explain a mixture of both. Lead white was banned in Austria from 1924 onwards as painting pigment and limited to 2% in railway stations and commercial premises on request (“Bundesgesetzblatt für die” 1924) (Table 2).

SEM/EDX for painting analysis

Instrumentation

To obtain an analysis of the sample’s surface as accurately as possible, a scanning electron microscope is well suited. In addition, it is possible to identify the chemical elements of the sample by means of an EDX detector. The scanning electron microscopy (SEM) (Zeiss Leo VP 1455, Germany) is used.

SEM/EDX: results and discussion

SEM investigations show four layers of paint in this sample (red scarf, near elbow) (Figure 4). EDX results indicate, that these layers are zinc-white (ZnO) (layer 1), cinnabar (HgS), minium (Pb_3O_4) or/

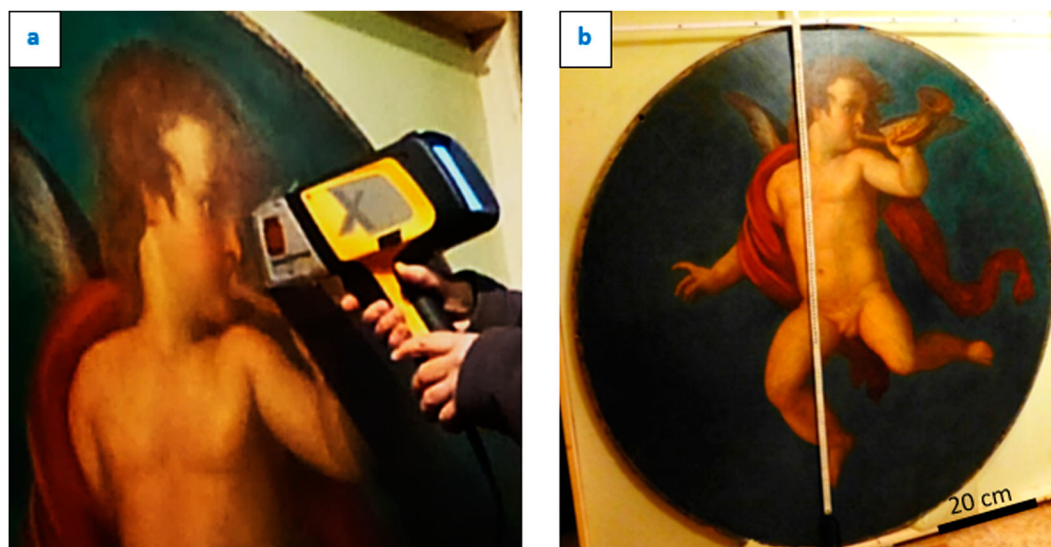


Figure 3. a. Portable XRF device in use (Fig.: H.J. Schmidt), b. Klimt artwork prepared for non-destructive use with the p-XRF device (Fig.: D. Wengerowsky).

Table 2: Results of the p-XRF at a measuring spot on the red scarf (Table: D. Wengerowsky)

Element	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe
Cps	53975	343941	24748	4628	23671	831	3468	162	8157
Element	Ni	Cu	Zn	As	Sr	Cd	Sn	Sb	I
Cps	142	50	34733	17184	1144	102	34	3803	4539
Element	Ba	Hg	Pb						
Cps	1483	73319	77543						

Cps: Counts per second

and lead-white ($2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$) (layer 2), organic compounds (layer 3) and titanium white (TiO_2) (layer 4). Layer 1 is the oldest. EDX-measurements show that the main component of this layer is zinc. Consequently at this point zinc-white has been employed. The main components of layer 2 are lead, oxygen and sulfur and medium quantities of mercury. It can be expected, that cinnabar and/or minium are used to obtain the reddish coloration. Lead suggests that lead-white is used at this point, to give a luminous effect to the red color. In layer 3, a lot of carbon has been found, but no other metals for pigments. It can be assumed, that this is an organic coating layer. Layer 4 is the youngest one and contains carbon and oxygen and a small amount of titanium. This could be a recently restored layer with carbon compounds and titanium-white, whereas the carbon compounds could be organic colors. Titanium white was used as a color pigment for oil colors after 1930 (Kühn 1983) (Figure 5).

Infra-red-light for painting analysis

Instrumentation

Infrared light (IR-light) is electromagnetic radiation in the wavelength range of more than 700 nm. The radiation can be indicated either in the wavelength λ [nm] or by its reciprocal value, that is the wave number $\tilde{\nu}$ in [cm^{-1}]. The wave number is proportional to frequency and energy (Lehmann 2010).

A single lens reflex camera (SLR) with an objective filter OG 590 nm red was used at a color temperature

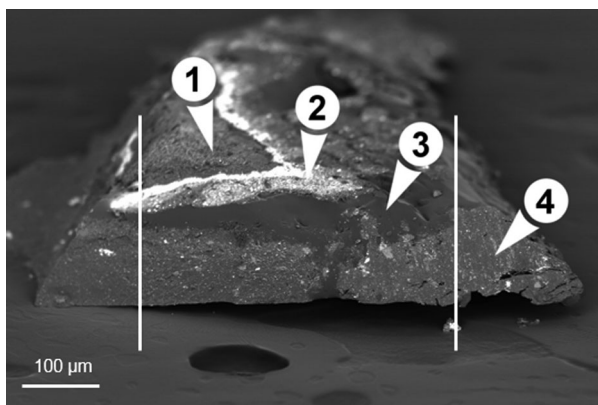


Figure 4. SEM taken at a spot of the red scarf (near elbow) (Fig.: F. Dencker).

of 4000 K (white balance) and an excitation light of 500–550 nm.

Infra-red-light: results and discussion

Infrared light is more energy-efficient than white visible light. The IR-light penetrates the top layer. You can see that the second picture that is underneath has the same motif and has been painted relatively accurately - but with uneven thick paint application. Most of the bright areas consist of a thicker color layer than the dark ones (Dopita 2012 and broux et Lewis Larmore 1959) (Figure 6).

The colors contain organic substances (oils, paraffins) as pigment carriers. These form a heat-insulating layer. The heat radiation appears pale red and lighter in infrared light. Dark black surfaces are rough, they devour the light. There are different reasons for this. One reason is, the overpaints are missing and these are not heat-emitting original colors. Also, storage of heat radiation from pigment to pigment is different. This can be noticed in the restored facial area, which consists only of original colors (Cockburn 1976).

Where mercury is present as a pigment, the right side of the scarf appears very dark. The IR rays are absorbed by the trigonal modification of the mercury sulfide (cinnabar). The heat radiation in the areas where more than 200 °C is reached, converts the red cinnabar (HgS) into the orthorhombic modification or finely divided elemental mercury. These appear dark in the IR light. More white pigments (zinc oxide or titanium dioxide) were added to the left portion of the scarf. As a result, the IR radiation is no longer absorbed, but radiated back. Due to this, the scarf appears brighter in these areas.

Two areas of the chest and trumpet-bearing upper arm appear in a still paler yellow light. These areas have already been released by the restorer. Due to the long time that has elapsed, the old oil paints contain many radicals, that return the radiation.

Conclusion

The red colour of the scarf of „*Trompetender Putto*” by Klimt is particularly important for the provenance research. MIMOS II - Mössbauer spectroscopy revealed the iron minerals haematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite, as well as octahedral iron-III oxide. In measurements with the portable X-ray gun, lead and

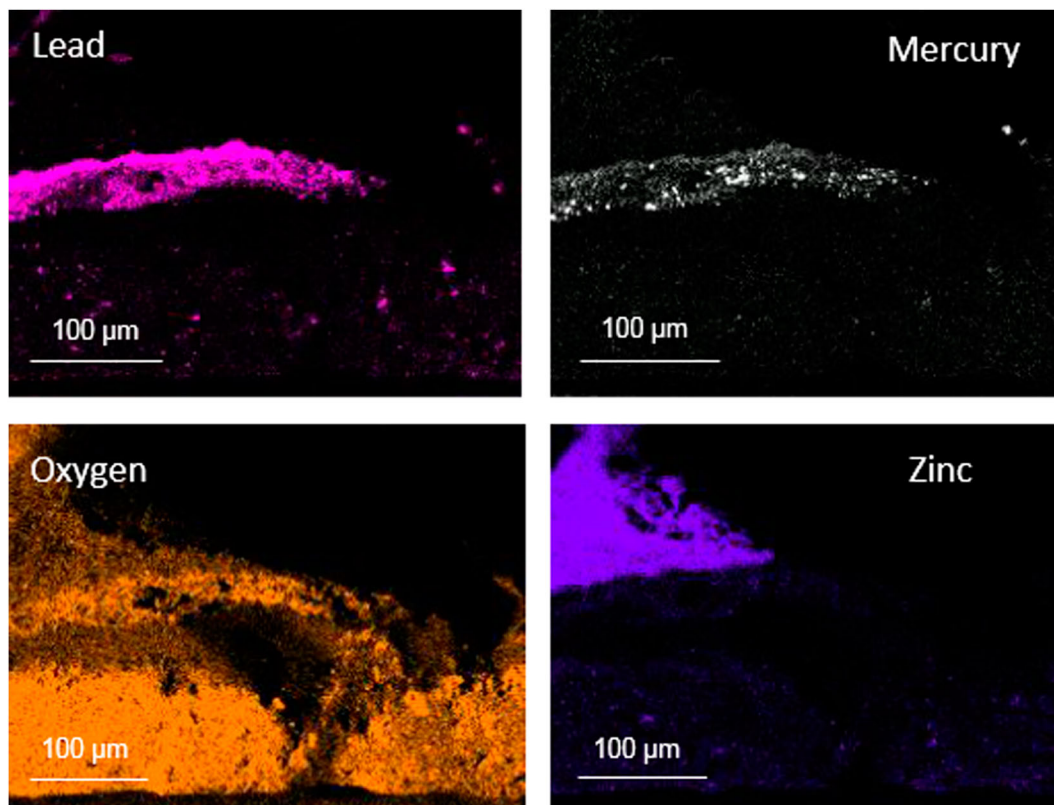


Figure 5. EDX-recordings taken at a spot of the red scarf (near elbow) (Fig.: F. Dencker).



Figure 6. IR-Picture depth analysis with a camera (4000 K); objective filter (OG 590 nm yellow-red); excitation light (500-500 nm green) (Fig.: LKA Hannover).

mercury elements are found in particularly large amounts, suggesting the presence of cinnabar red (HgS) and/or minium (Pb_3O_4) for the red color. Iron is also detected and indicates iron pigments. SEM allows the reconstruction of the sequence of pigment layers, particle size and homogeneity of the pigment distribution. The age of the pigments can be deduced from the storage of the irradiation with IR-light.

These analyses show the pigments used in the original and overpainted work of art. The combination of applied pigments indicates the late 19th century as origination date of the artwork. This correlates with the literature on this subject (Nebhay 1969).

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Notes on contributors

Dr. Robert Lehmann planned the whole experiment and carried out the Infra-red-light painting analysis.

Mrs. Dagmar Wengerowsky performed the Portable X-ray fluorescence analysis (p-XRF).

Mr. Hans-Jörg Schmidt performed the Portable X-ray fluorescence analysis (p-XRF).

Dr. Manish Kumar supported in planning and evaluation of data.

Mr. Folke Dencker contributed in the SEM/EDX analysis.

Mr. Andre Niebur contributed in the SEM/EDX analysis.

Dr. Göstar Klingelhöfer participated in the Mössbauer spectroscopy analysis.

Prof. Dr. Benilde F.O. Costa participated in the Mössbauer spectroscopy analysis.

Mrs. Dagmar Wengerowsky wrote the manuscript.

Dr. Manish Kumar wrote the manuscript.

Prof. Ralf Sindelar supervised the project and commented on the manuscript. All authors discussed the results and approved the manuscript.

Prof. Dr. Franz Renz supervised the project and commented on the manuscript. All authors discussed the results and approved the manuscript.

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