Introduction
The examination of works of art is carried out preferably by non-destructive means and directly on the object. Simple analyses of the composition of elements can be carried out using a “hand-held” XRF spectrometer. However, for the characterization of differences within fine structures a spatially resolved analysis is necessary. Bruker’s Micro-XRF spectrometer ARTAX fulfills all the requirements mentioned above. In this paper tests carried out on the painting “The Holy Family” by Piero di Cosimo are discussed (Figure 1).

Existing damage
The blue areas on the painting indicated various stages of preservation. While the sky and mountains in the background were bright blue and appeared to be in very good condition, the blue robe worn by the Madonna was monochromatic and almost shapeless. Especially, the half-lights in the garment folds, which were transparent and full of binding agents, appeared altered as a result of fading and greying. Furthermore, there were dark brown shadows on the right side and at the bottom of the robe. This area seemed to be heavily restored.

Objectives of the examination
The materials used in the blue areas of the painting were characterized. Whether discoloration or degradation of the color lending pigments took place in parts of the painting had to be analyzed. The so-called “blue diseases” or the discoloration of smalt could be of interest. The main points to be taken into consideration were the types of blue pigment, the layer structure of the various tones of light and shadow in the Madonna’s robe and comparative tests of further colored areas of the painting.

Methods
The ARTAX was set up using the following settings:

- Low-power X-ray tube, 30 W, Mo-target
- Excitation: U = 45 kV, I = 600 µA
- Measuring time: 180 s per testing point
- Helium purge: 6 litres min⁻¹ (light elements)

A line-scan using 3 measurements over a distance of ca. 1 mm was carried out each time. The spectra were added in order to balance inhomogeneities in the distribution of the pigment.
Results - Blue Pigments

- The lights and half-lights of the Madonna’s robe consisted of natural lapis lazuli pigment (Al, Si, Figure 2).
- The shape of the garment folds was achieved through various mixing ratios of lapis lazuli and white lead.
- The brownish shadows in the Madonna’s robe contained a copper pigment as well as lapis lazuli.
- The sky and mountains in the background were painted solely using lapis lazuli.

Results - Other Pigments

- A gesso foundation (plaster) customary for the period served as a primer.
- Copper green was identified on the clothing of the left angel. Ochres (Fe) and lead white (Pb) were used for the flesh-colors.
- Other than Pb from white lead particles the red garments showed no inorganic constituents. The characteristic red tone indicated an organic color lacquer (madder).

Conclusions

- The damage cannot be attributed to the real blue diseases (discoloration of smalt or ultramarine).
- Changes in the painting due to degenerative effects of other pigments can be excluded because of the material-technical evidence.

A micro-sample from the area of the grey half-lights in the Madonna’s robe, which had already been characterized with regard to its material components during the XRF test, was extracted for further examination in the HfBK laboratory. The polished sample surface was examined under strong magnification. Various types of cracks could be seen in the binding agent and/or varnish. The effects of organic solvents used for the removal and application of varnish in the past should be taken into consideration as a possible cause for this damage. For a definite clarification of the damage further tests, above all on the binding agent, are necessary.

Figure 2: Micro-XRF spectrum of the half-light area of the robe

Bibliography

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