Application of Fibre Optics Reflectance Spectroscopy (FORS) for the determination of mineral pigments in jasper

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The identification of pigments is carried out routinely mostly by X-ray diffraction, FTIR and Raman spectroscopy as well as visible absorption. An optical method which frequently is used in archaeology and art history has the advantages of quick, non-destructive and portable testing: Fibre Optics Reflectance Spectroscopy (FORS). Its wide application spectrum includes the determination of inorganic and organic pigments in e.g. antique ceramics, glass and paintings (Picollo *et al*., 2000; Cosentino, 2014). Gemmological application of FORS covers investigations of opaque gem materials i.e. the determination of colour causes, the proof of colour modifications and the detection of imitations.

Micro-crystalline quartz and especially the colourful group of jaspers offer a broad spectrum of applications in determination of colour causes by mineral pigments.

As an example, jaspers from the region of Idar-Oberstein, Germany were investigated by using an Ocean Optics FORS system (Figure 1), which consists of a halogen light source (1) and an Ocean Insight Flame Miniature Spectrometer (190-1100 nm) (2), both connected with a UV-visible bifurcated optical fibre (3) at the end of which the reflection probe (4) is coupled. This consists of six illumination fibres around one read fibre which is held over the smooth surface of the sample (5) in a distance of approx. 1 cm.

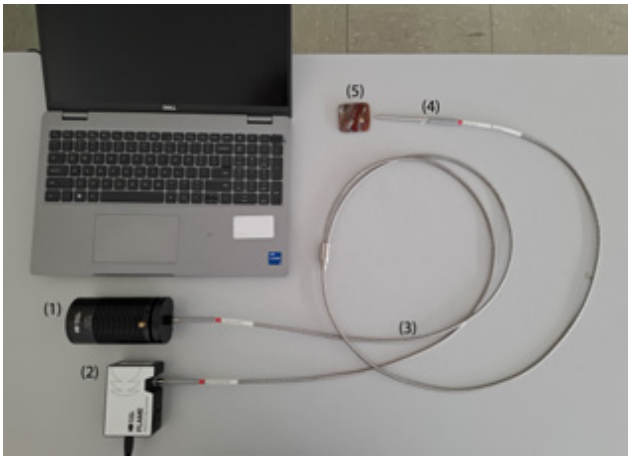


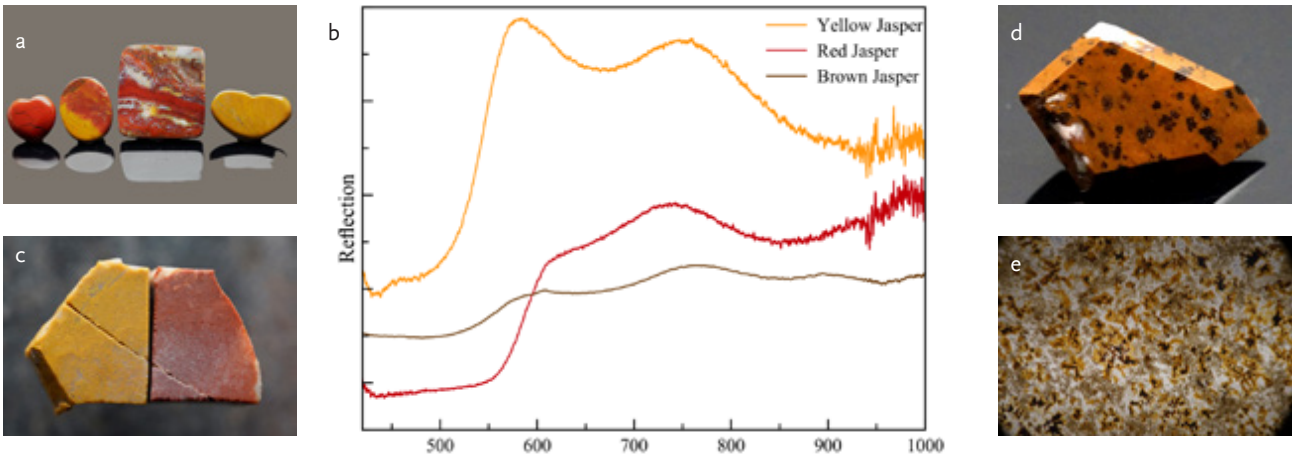
Figure 1. Fibre Optics Reflectance Spectroscopy (FORS). Ocean Optics system, described in the text.

The investigated samples originate from jasper veins in Permian intermediate volcanic rocks of the Saar-Nahe region and cover red, yellow, brown and green colours. Generally, colours of jaspers are caused by mineral impurities (Kostov, 2010). Red, yellow and brown colours are due to iron oxides or hydroxides, green to phyllosilicates.
Three representative types of Permian jasper from the Saar-Nahe region have been selected to demonstrate the results of FORS measurements. Indications of the respective pigments were additionally confirmed by Raman spectroscopy and chemical investigations.

Red and yellow jasper

Red and yellow jasper (Figure 2a) is frequently found in the Permian volcanic rocks of the Saar-Nahe region and a historically significant mining place is the Steinkaulenberg in Idar-Oberstein. There red and yellow jasper is found together with agate and moss agate in veins of an andesite. Generally, such material is known as jasp-agate (Campos-Venuti, 2012).

The reflection spectrum of the red jasper (Figure 2b) is characterized by a broad absorption in the range 550 nm to shorter wavelengths followed by a gradient between 550 and 600 nm with an inflection point at 580 nm. A second broad absorption band in the near infrared has a maximum at 850 nm. Between the two absorptions there is a broad reflection region with maximum at 740 nm which is responsible for the red colour.



a. Red and yellow jasper from the Steinkaulenberg in Idar-Oberstein. Size of the large jasp-agate 47 x 42 mm.
b. Reflectance spectra of red, yellow and brown jasper.
c. Iron-rich jasper before (left) and after heating (right).
d. Dark spotted brown Panthera-jasper from Baumholder. Size 30 x 20 mm.
e. Thin section of Panthera-jasper. Size of the brownish-yellow, grey-brown and brownish-black pigments 0.1 – 0.5 mm.

In the reflection spectrum of the yellow jasper (Figure 2b) the main absorption lies in the range 500 nm to shorter wavelengths with a maximum at 430 nm. The inflection point of the following gradient is at 540 nm. Two more absorption bands have maxima at 660 and 950 nm. The reflection maximum is located at 575 nm in the yellow spectral range.

The spectral characteristics of the red and yellow jasper arise from crystal field transitions of Fe^{3+} and can be clearly attributed to hematite (red ochre) in the red material and goethite (yellow ochre) in the yellow one (Torrent & Barrón, 2002; Elias *et al*., 2006).

Heating the yellow jasper at 230°C causes a colour modification to red (Figure 2c), effected by a dehydration process which causes the transformation of the iron hydroxide goethite to the iron oxide hematite: $2\ FeO(OH) + Fe_2O_3 + H_2O$.

Brown jasper

A particular dark spotted brown jasper (Figure 2d) occurs near Baumholder, approximately 10 km south of Idar-Oberstein. The material is called Panthera jasper and is associated with baryte deposits. Even under magnification, various pigments could be observed, including brownish-yellow, grey-brown and brownish-black partly flake-like impurities (Figure 2e) in the fine-grained SiO_2 matrix.

The reflection spectrum (Figure 2b) is mostly characterized by the spectral features of goethite and differs mainly in the lower reflectance intensity. The curve is flatter in the 500 to 600 nm range and the subsequent edge shifts to longer wavelengths. An additional absorption band with a maximum at 850 nm can be assigned to hematite which suggests the presence of limonite as a goethite dominated mixture of iron hydroxides and oxides.

The brown colour impression is finally caused by these brownish-yellow pigments in combination with the grey-brown and brownish-black pigments composed of manganese oxides (probably hollandite and romanechite).

Similar to the yellow jasper from the Steinkaulenberg a colour modification from brown to red is produced by heat treatment which underlines the dominance of goethite as the main pigment.

Green jasper

A rarely found variety is the green jasper (Figure 3a) from a locality near Oberkirchen, aproxiamately 20 km south of Idar-Oberstein. These are also heterogeneously composed veins with jasper, moss agate and agate as well as zeolites and alteration products, e.g. phyllosilicates.

The reflection spectrum of the green jasper (Figure 3b) is characterized by a broad reflection band with maximum at 550 nm in the green spectral range and a second reflection peak at 830 nm. In between lies an absorption band with a maximum at 750 nm.

These features are typical for the green phyllosilicate celadonite (green earth) $K(Mg,Fe^{2+})(Fe^{3+},Al)Si_4O_{10}(OH)_2$ (Radpour *et al*., 2019). The 750 nm absorption band is caused by a Fe^{2+}-Fe^{3+} electron transition (Platonov *et al*., 2009) and the absorption band visible just before 1000 nm (approx. 980nm) is probably due to isolated Fe^{2+}.

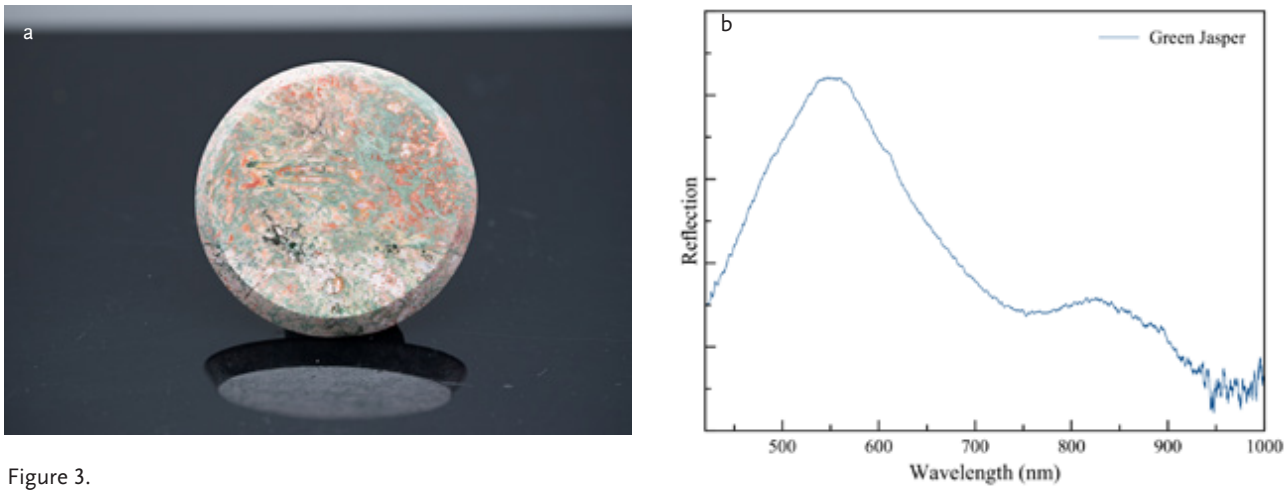


Figure 3.
a. Jasp-agate plate with green jasper from Pfeffelbach. Diameter 7 cm.
b. Reflectance spectrum of green jasper.

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