The contribution of Visible Near Infrared Reflectance spectroscopy to colour determination: the case of the experimental ceramic briquettes

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Introduction

The aim of this study is to investigate and determine the colour changes in experimental ceramic briquettes through different states (from unfired to be fired at 1050°C) using Visible Near Infrared Reflectance Spectroscopy (VNIR). Initially the studied material was examined in terms of colour following the ordinary method of Munsell Chart (2000). Reflectance spectroscopy has been defined as a technique that uses the excitation energy in the Visible-Near Infrared (350-2500nm) wavelength regions of the electromagnetic spectrum to identify minerals. The Visible Near Infrared spectroscopy (VNIR) contributed to a more accurate determination of colour, since we can obtain tristimulus values from visible region. The main factors which are responsible for the colour changes is the presence of different minerals as well as the conditions during firing. The mineralogical determination was performed by X-ray Powder Diffraction (XRPD) in order to identify and confirm all the primary minerals and the neoformed mineralogical phases as a result of the firing regime.

Materials and Methods

The experimental briquettes were prepared using clayey raw materials (n=4) which were collected from Achaea and Corinth (Northern Peloponnese, Greece) and were fired at three different temperatures (700, 900 and 1050°C) under oxidizing conditions.

Different techniques (X-ray diffraction and VNIR spectroscopy) were performed to investigate the mineralogical composition and evaluate the colour changes. The mineralogy of the unfired and fired materials was studied by XRPD using a BRUKER D8 ADVANCE diffractometer. Spectral curves and colorimetry data of samples were obtained using a SpecTERRA SM-3500 Spectral Evolution portable spectrometer. The calibration was performed using a standard white reference plate. Visual observation of the unfired and fired samples was performed by following the Munsell colour chart (2000). The VNIR region detects effects due to several different electronic processes including crystal field, charge transfer, colour centers and conduction band transitions. Fe-oxide minerals are easily detected in the VNIR region (350–2500 nm) since most electron transitions are caused by various kinds of iron oxides (Fang *et al*., 2018). The process which was been followed for the colour evaluation of the experimental briquettes is based on the transformation of the visible spectra (350-780 nm) to values X, Y, Z according to the International Commission on Illumination (CIE, 1931). Then these values were converted to Munsell and CIE L * a * b * notations using the Munsell Conversion Program (Wallkillcolour, 2019).

The spectra were taken and focused on the visible region (350 to 780 nm) for the colour determination. Thereafter transformed into tristimulus values X, Y, Z according to the International Commission on Illumination (CIE, 1931) using the software DarwinSp by SpecTERRA (Version 1.2). Transformation into absorption spectra was performed (A=log1/R) to the original spectra curves. Savitzky-Golay algorithm was applied for background noise reduction and then 2nd derivative was calculated using the software Origin Pro 9.0.

Results

The examined samples were differentiated in terms of composition based on XRPD and VNIR results. The first sample (C4) is characterized as calcareous clayey raw material due to the abundant participation of calcite; the second one (C13) is rich in calcite and dolomite and is characterized as calcareous-dolomitic whereas the rest of the samples (C9 and HS45) are calcite-free and are characterized as siliceous (Xanthopoulou, 2019). The newly formed mineralogical phases developed in the calcareous and calcareous dolomitic samples are larnite, which was formed at 700°C and diopside and gehlenite which appeared at 900°C. Hematite is the newly formed mineral after the firing of the siliceous samples at 700°C to 1050°C and using 2nd derivative to original spectra (Fig. 1a) the relevant absorption band is visible near 550nm (Deaton & Balsam 1991).VNIR spectrometer results were obtained into tristimulus values X, Y, Z (Fig. 1a) according to the International Commission on Illumination (CIE, 1931) and then converted into Munsell colour notations.

Discussion

The colour of the unfired siliceous sample HS45 was yellowish brown and during firing obtained a reddish yellow hue-yellow red (700°C), a light red hue (900°C) and at the highest temperature (1050°C) obtained a red hue. This is due to the low Ca concentration which allows hematite formation. On the other hand, the sample C9 was reddish brown at the unfired state and during firing the hue became darker red (1050°C). Hematite formed at 900 °C and is responsible for the
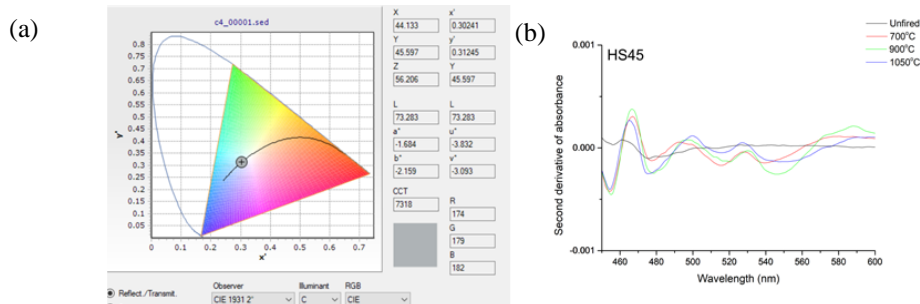
reddish hue.

Figure 1. (a) Illustration of colorimetry results obtained using DarwinSp software and (b) Plot of 2nd derivative absorbance

On the contrary, Ca-rich samples exhibit different hues due to the formation of Ca-silicates minerals. The colour of sample C4 was gray and during firing (700°C) it transformed to very pale brown (900°C) and at the highest temperature to pale yellow (1050°C). XRPD results showed the formation of gehlenite at 900 °C which is responsible for the buff colour (Molera *et al.*, 1998). Sample C13 originally had a pale yellow colour and during firing obtained a light gray hue (700-900°C) and at higher temperature obtained a darker pale yellow colour (1050°C). The formation of diopside during firing is related to the yellowish and creamy colours. The creamy colours are also related to the decomposition of calcite, the development of pyroxenes and to the low presence of iron oxides (Molera *et al.*, 1998). VNIR results specifically for sample C9, contributed to a further discrimination among the firing temperatures, a fact that it was not evitable by visual observation as it is displayed in Fig. 2.
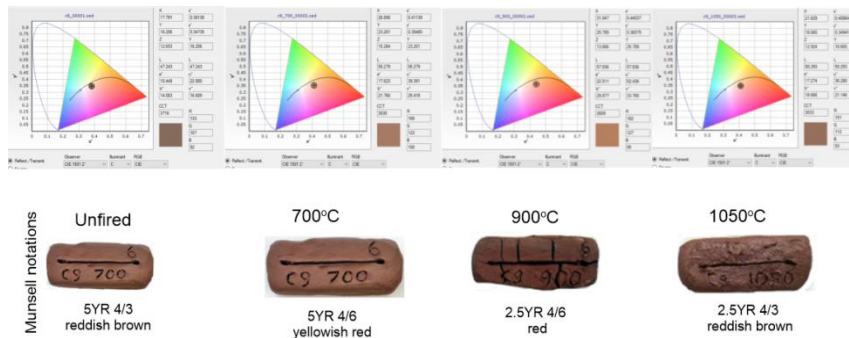

Figure 2 Colorimetry display (above) and munsell notations (below) for sample C9 in all temperatures

Conclusion

VNIR spectra results are obtained into numerical data and thus we acquire a quantitative measurement of colour. On the contrary the Munsell soil chart has limited number of chips for colour determination and offers a qualitative measurement of colour by the visual observation which is considered as a subjective perception among each observer. The use of the NIR spectrometer may provide an alternative untrained approach that can produce results not only for colour coordinates but also about the reflectance spectra, which contain more information about mineral identification.

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