Exploiting reflectance FTIR spectroscopy for the in situ identification of pigments in illuminated manuscripts

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Introduction

The non-destructive identification of pigments used in pictorial works is of great interest in the field of the study of cultural heritage, in particular when it is applied in situ. For this aim, in the present study a portable instrumentation for reflectance FTIR spectroscopy is used. The reflectance FTIR spectra of several inorganic pigments spread on parchment with different binders were recorded and converted to the more conventional absorbance FTIR spectra. This spectral database was used to recognize the pigments used in some northern-Italian illuminations dating to the XVI century. Moreover, as some green areas of the illuminations showed different spectral features with respect to those of the more common green pigments, the basic copper sulfates brochantite (CuSO₄·3Cu(OH)₂) and posnjakite (CuSO₄·3Cu(OH)₂·H₂O) were synthesized and characterized. Then reflectance FTIR spectra of these compounds spread on parchment were recorded and they resulted very useful for the identification of the pigments of the green details.

Reflectance FTIR spectroscopy

Specular reflection is a type of external reflection that occurs when the surface of the sample reflects the infrared radiation so that the angle of reflection is equal to the angle of the incident beam.

The total reflectance of smooth surfaces, as an illuminated manuscript can be considered, is almost entirely composed of the specular component.

In this case, the reflection FTIR spectrum can be converted in an absorbance spectrum, through the Kramers-Kronig transformation: this conversion resulted to be fundamental in order to characterize a material, as the IR spectra of the most databases are measured in the transmission mode.

Advantages of reflection FTIR instrumentation (Alpha Bruker):

- completely non-invasive analyses
- in situ analyses, portable size,
- spectral range: 7500 - 375 cm⁻¹
- detection of the overtones and combination bands

Basic copper sulfates brochantite and posnjakite as a case study

Synthesis of brochantite (CuSO₄·3Cu(OH)₂)

Addition of a 0.2 M NaOH solution to CuSO₄ 0.1 M at different temperatures, end-point pH=8. [Themochim. Acta, 133 (1988) 221-226]

Synthesis of posnjakite (CuSO₄·3Cu(OH)₂·H₂O)

Addition of a 0.1 M NaOH solution to CuSO₄ 0.01 M at room temperature, end-point pH=6. [Chem. Erde, 73 (2013) 39-50]

Posnjakite recognized on illuminations!

The origin of these compounds on works of art is still an open question, as they could possibly be:
- natural, or
- artificial pigments used on purpose, or even
- degradation products of malachite CuCO₃·Cu(OH)₂.

Conclusions

The present investigation of the occurrence of posnjakite on a northern-Italian illuminated manuscript dated to the XVI century reveals its presence both as a pure compound and as a component of mixtures of pigments, together with malachite. This latter circumstance leaves obviously open the hypothesis of the formation of the basic copper sulfate from the degradation of the copper carbonate, but besides this fact, we can not exclude that, being the "verde-azzurro" quoted by the ancient treatises a mixtures of not well defined copper-based minerals, posnjakite and malachite could be occasionally co-existent in the raw materials used to obtain this pigment.

Reflection FTIR analyses:

The reflectance FTIR spectra of these basic copper sulfates are reported here for the first time!