



# Pigments Checker version 3.0, a handy set for conservation scientists: A free online Raman spectra database



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## ABSTRACT

Pigments Checker is a collection of swatches of historical and modern pigments that offers art professionals, conservation scientists, conservators and fine art photographers, a tool to evaluate and test their imaging and spectroscopic methodologies for pigment identification. "Pigments Checker Free Spectra Database" is an ongoing project to thoroughly characterize each pigment in the collection with a series of spectroscopic and imaging techniques and to make the data open access. This paper presents the free and downloadable database of Raman spectra, adding to the reflectance spectral database already published. The Raman analysis is in agreement with the information provided by the pigments' manufacturers since most of the pigments could be identified by their Raman spectra which were consistent with the expected content reported in literature.

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## 1. Introduction

Museums, libraries, historical archives and conservation laboratories are in need of scientific examination performed on their art, archaeology and archival collections in order to gain information of their constituent materials. These data allow to understand how, when and where they were made, and they are of great interest to art historians and curators which can have unprecedented insights into their collections. Conservators use this information to devise more effective preservation procedures. There are plenty of scientific analytical techniques which have been tested on museums' collections and among them non-invasive and non-destructive methods are particularly appreciated since they do not require any sampling and do not cause any damage to the objects. Conservation scientists are specialized in art and archaeology examination and they use both Spectroscopy (such as Raman spectroscopy [1], XRF spectroscopy [2], neutron spectroscopy [3]) and Imaging methods (such as Technical photography [4], Terahertz [5] and Multispectral Imaging (MSI) [6]). Raman Spectroscopy has proved to be one of the most valuable methods to determine provenance and authenticity of artefacts of artistic, archeological or historical significance. It is used to characterize very diverse objects, from biological materials to jewellery, and to comprehend their degradation processes. Its more popular application is for the identification of dyes and pigments. Raman spectroscopy is non-destructive, non-invasive and can be implemented as mobile and relatively lightweight equipment.

In the late 1990's when Raman spectroscopy started to show its potential in art conservation, a major issue was the lack of databases of reference Raman spectra which are necessary to compare spectra of unknown materials and properly interpret spectral features. Spectral libraries were published on scientific journals since then [7–10] and even recently new libraries on more specific pigments and dyes collections have been presented [11].

Only in the early 2000's the first Raman databases of pigments were available online. University College London [12] was among the first to upload on their website a collection of spectra acquired with dispersive Raman at 514 nm and 632 nm; IRUG (Infrared and Raman users group) [13] is certainly the most extensive database with a supporting community submitting new spectra acquired with different equipment from the numerous partner institutions; E-Visart [14] is a database developed by University of the Basque Country (Spain) and it covers pigments and archeological materials with FT-Raman and dispersive Raman with excitation at 780 nm. The Romanian Database of Raman Spectroscopy [15] uses a 532 nm laser. Some Institutions also published large databases of minerals including pigments, such as University of Arizona [16] and University of Parma [17].

This paper presents and discusses a new online Raman database of the pigments contained in Pigments Checker [18], a collection of swatches of standard historical and modern pigments (Fig. 1). The pigments are milled into the binder (acrylic) which is added as needed for each pigment and applied with brush. Among all the pigments and their varieties ever used in art these selected pigments represent the most used ones from antiquity to early 1950's. A swatch of just gum arabic is added as a reference. Pigments are painted over a cellulose and cotton

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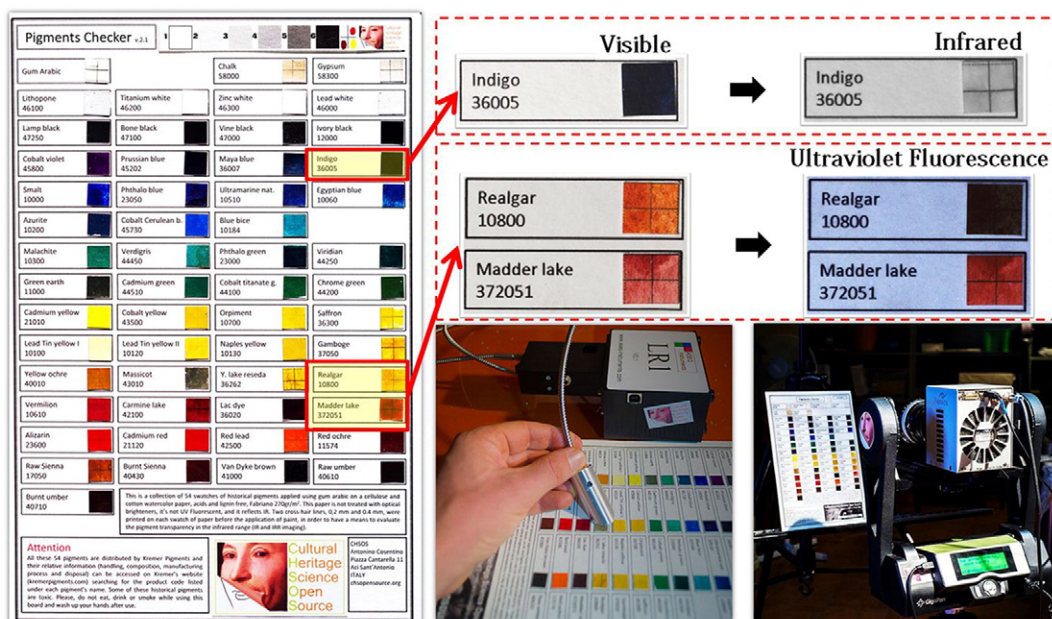


Fig. 1. Pigments Checker is a tool to evaluate and practice imaging and spectroscopic methods for pigments identification.

cardboard, which is acid and lignin free, not treated with optical brighteners, slightly fluorescent in the UV and reflects infrared radiation. Two cross-hairs (0.2 mm) are printed on each swatch of cardboard before paint application in order to evaluate each pigment's transparency to infrared imaging.

Pigments Checker is an ongoing project which aims to select the best quality of the pigments and add new ones to the collection after careful research. Started in 2014, Pigments Checker has now reached version 3.0. Pigments Checker's project is pursued by CHSOS (Cultural Heritage Science Open Source), an initiative to promote innovative, affordable and sustainable technologies for art examination for the art professional community.

"Pigments Checker Free Spectra Database" is a collaborative effort to develop a free and downloadable spectral database of the pigments contained in Pigments Checker: Reflectance, XRF and Raman. The Reflectance spectra database [19] is already available for download. This paper presents the new Raman database and discusses the results.

The goals of the "Pigments Checker Free Spectra Database" are:

1. Define a standard set of historical and modern pigments. All of the Raman databases introduced so far have been collected on samples of different origins. Some pigments belong to collections owned by some institutions, others are manufactured by companies specialized in historical pigments, while others are minerals collected over different geographical locations. Such a variety implies that the pigments' chemical composition could be different due to a number of factors. For example, mineral pigments usually have specific impurities related to different origins and artificial pigments can have been produced with slightly different formulations, as often happened across their history. Pigments Checker provides a standard set of historical pigments that can be used by researchers and art professionals across different institutions and geographical locations to evaluate and practice their diagnostic methods.
2. Provide a complete characterization of Pigments Checker's samples. The set of Reflectance, Raman and XRF spectra will provide deep understanding of the chemical composition of the set of standard pigments and will allow to confirm their composition.
3. Test different wavelength excitations. Pigments have been tested with 3 lasers and the database shows how each pigment responds

to the 3 excitations. This information is useful to inform an actual analysis of the pigments on works of art.

## 2. Materials and methods

### 2.1. Pigments

Raman spectra were collected on the 54 pigments in Pigments Checker v.2 and on 4 pigments that have been added to v. 3. The 58 pigments are listed in Table 1.

### 2.2. Raman spectroscopy

The samples were analyzed in powder by means of the Xplora (Horiba) spectrometer (spectral resolution:  $2\text{ cm}^{-1}$ ) equipped with 532, 638 and 785 nm lasers and an Olympus microscope (spatial resolution  $2\text{ }\mu\text{m}$ ) using an Olympus objective  $50\times$  (N.A. = 0.75). All the spectra were acquired in the spectral range  $100\text{--}3200\text{ cm}^{-1}$  with all the 3 laser excitations. The excitation power was chosen depending on the wavelength used and the analyzed pigment, starting from very low values and increasing it gradually where possible. Time and accumulations were optimized for each sample. Calibration was performed using a Si wafer and a linear baseline was subtracted by means of the LabSpec6 software.

When the pigments are applied with a binder and a varnish, their identification becomes much more difficult than that achieved on pure powder samples, as done for this database. Indeed, these organic materials generate a strong fluorescence emission which covers the weak Raman peaks emitted by the pigments and often even the stronger ones, making it impossible their identification. However, it is possible to improve the signal-to-noise ratio by using a specific excitation wavelength which weakens the fluorescence emission or increase the Raman signal. The most effective wavelength depends on each combination of pigments and binders.

There are some Raman databases which report the spectra of the powder pigments acquired with different lasers [7,8,16] and it was also compiled a database of a collection of 99 pigments applied with different painting binders (fresco, egg tempera, casein tempera and linseed oil) and with 3 different excitation wavelengths [20]. That study

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