Synthetic organic pigments of the 20th and 21st century relevant to artist’s paints: Raman spectra reference collection

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Abstract

Some 170 organic pigments relevant to artist’s paints have been collected from historical collections and modern manufactories. The number includes multiples of the same pigment from different sources and comprises 118 different color indices (C.I.). All of them have been analyzed with FTIR spectroscopy and 125 pigments (93 different C.I. No.s) of particular relevance to artist’s paints have been characterised with Raman spectroscopy so far. The pigment collection encompasses the following pigment classes and subgroups: monomeric monazo pigments represented by azoaromatic yellow (hansa yellow), β-naphthol, BON, naphthol AS and benzimidazozone; disperse pigments with disperse condensation, diaryl, bisacetocarbocyclic, pyrroline; azo-arnemethazol complexes; non-azo, polycyclic pigments such as phthalocyanines, diketoerythrine-pyroles (DPP), porphyrins and porphines, quinacridones, isokleinolines, polycarbocyclic anthraquinones and dioxazines. The selection of references was based on availability (historic collections) and current use in 16 acrylic, alkyd oil-based artist’s paints, and it covers pigment colors PY yellow (27 C.I. No.s), PR red (38), PO orange (9), PB blue (8), PV violet (6), PG green (3) and PB brown (2). Besides peak tables and spectra patterns, flow charts based on color, pigment class, group and individual color index are presented to help identification of unknowns and mixed paint samples. While Raman could isolate all of the synthetic organic pigment, which is readily identified with Raman. 

Introduction

The use of synthetic organic pigments in an artist’s paint products has dramatically increased and is now well established. In the early 30th century, there has been an enormous expansion of synthetic pigment developments, with examples where new organic pigments were found in artworks shortly after their introduction to the market. While organic pigment usage in artist’s paint products has been conservative for a long time, a survey of current (2008) artist’s paint products by Schmiz and Wiser & Newton has revealed that almost 60% of pigments within those 16 product palettes are synthetic. Furthermore, the combination of pigments to achieve a specific hue varies largely across the products. This, of course, generates new analytical challenges for forensic and art technological laboratories.

Methods

Based on current artist’s paint brochures (Tab. 1), literature on the early 20th century pigment developments, early colour swatches and artist’s correspondence, as well as sampling of historic pigment collections, a comprehensive collection of reference material has been assembled. These materials were systematically recorded with all relevant information available (C.I. Name, C.I. Number, Product Name, Pigment Class, Group, Manufacturer, Source Collection, Year of discovery, ...) FTIR and Raman spectra were acquired (Tab. 2) to be compiled in a reference database and generate tools for the identification of unknowns taken from real artwork.

Results and discussion

FTIR and Raman spectra from pure reference compounds and mixed paint from real artwork were compared and the results clearly emphasize the complementary nature of FTIR and Raman (Fig. 1), recommending FTIR to identify binders, ageing products, filter ratios and many pigments in an efficient survey, while Raman delivers great performance when it comes to identifying both inorganic and synthetic organic pigments, as well as mixtures thereof. Raman has proven high reproducibility to within 1 wavenumber, allowing separation of different C.I. numbers using a flowchart (Fig. 2). Distinction of identical C.I. numbers from different manufacturers or batches, however, is not feasible (Fig. 3).

Conclusion

Raman spectroscopy is a powerful tool to identify organic pigments in artist’s paints, yet identification of unknowns stands and falls with a comprehensive reference spectra collection, preferrentially generated with 785nm excitation.

Tab. 1. This is an excerpt of table 1 of the full text article. The aim of this table is to list all of pigments and pigment combinations declared in current artist’s paint products by Schmiz, Tinten and Wiser-Newton in 2008. It highlights the growing importance of synthetic organic pigments in such products and gives a first grasp of the pigments that need to be included in such a reference collection. Further differentiation was made on pigments used only in combination with other pigments.

Tab. 2. Example of reference spectra including peak tables and molecular structures across the pigment classes and groups compiled by this collection. The general approach was to use 785nm excitation. Other wavelengths available came into action when 785nm could not deliver a suitable response. The main reason for choosing this strategy was the fact that the use of 784 or 632nm excitation on real paint samples is very often strongly limited by fluorescence contribution of binder or ageing products.

Fig. 1. Comparison of FTIR and Raman data of a red paint sample taken from the artwork “Glass-Fassade”, 1940, by Paul Klee. This example demonstrates the choice of pigments, filter and binding media - and intensity ratios thereof. While FTIR is able to record all components of the paint, it suffers from fluorescence and the low intensity of the synthetic organic pigment, which is readily identified with Raman.

Fig. 2. Example of a systematic workflow applicable to the dataset of orange pigments. Due to the multiple peaks of organic pigments, identification of a sample paint table is not the use of systematic flowcharts, however, is always limited by the dataset included. With the growing number of pigments, spectral database systems using matching algorithms is the most feasible strategy.

Fig. 3. Comparing Raman spectra of pigment yellow PY7-3 of variable age and different sources, analysed on the same instrument or separate days. The peak precision is within 1 wavenumber for all peaks. One significant difference, though, is the spectral fluorescence background observed on historic reference samples. This example hints at potential information hidden in the baseline.