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Multi-analytical study of artist felt-tip pen inks

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Abstract – **A multi-analytical study on the composition of commercial felt-tip pens commonly used by contemporary artists was carried out. The inks were investigated by the use of complementary analytical techniques, such as µ-Raman spectroscopy, Fourier transform infrared spectroscopy and pyrolysis-gas chromatography-mass spectrometry. The results provided data for the identification of binders, pigments, solvents, and additives. Various synthetic pigments were recognised, such as PV23 and blue phthalocyanines. The binder seems to be mainly based on a styrene-acrylic copolymer in combination with polyamide. In addition, solvents and additives could be efficiently identified.**

This study illustrates a methodology based on the use of an integrated analytical approach for the characterisation of commercial ink-based artistic media.

I. INTRODUCTION

Contemporary artists, architects and industrial designers frequently use felt-tip pens for their sketches, drawings, copies, architectural and technical designs. Unfortunately, these inks are usually very sensitive to light and chemical agents and the exact knowledge of their composition may be important to define the optimal conservation treatment and/or storage conditions. So far, few studies have been addressed to the chemical characterisation of these materials [1-3] and often information on binders, fillers, dyes and pigments is lacking.

Here felt-tip PITT artist pens (Faber-Castell) used by Ane-Flore Cabanis, a contemporary French artist, were investigated by using a multi-technique approach: the inks have been analysed with Fourier transform infrared (FTIR) and µ-Raman spectroscopy and pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS). These analyses aimed to perform a complete identification of the ink components, i.e., solvents, binders, additives, dyes and pigments.

II. EXPERIMENTAL

A. Samples and materials

A selection of four PITT artist pens (Faber-Castell) (Cadmium yellow 107 (Cy-107), Pink madder lake 129 (Pml-129), Purple violet 136 (Pv-136), Light cobalt turquoise 154 (Lct-154)) was investigated. The inks were applied to glass slides and µ-Raman spectroscopy was directly performed on the film. Small amounts were scraped off and could be subjected to Py-GC-MS. For variable angle reflectance (VAR) FTIR spectroscopy the inks were applied on the shiny side of aluminium foil.

Fig. 1 Faber-Castell PITT artist pens.

B. µ-Raman spectroscopy

µ-Raman spectra were recorded with an Xplora (Horiba JobinYvon) instrument equipped with three lasers (λ_0 = 532, 638 and 785 nm). Sample irradiation was accomplished using the 50× microscope objectives of an Olympus BX41 microscope. The exposure time, beampower and accumulations were selected to get sufficiently informative spectra. The laser spot size was adjusted between 1 and 3 µm. Raman scattering was filtered by a double holographic notch filter system and collected by an air-cooled CCD detector. The wavelength scale was calibrated using a Si(111) standard (520.5 cm^{-1}).

For the identification of the blue copper phthalocyanine (CuPc) pigments special care was taken to use a constant setting in order to allow for comparison with reference pigments [4, 5].

C. VAR-FTIR spectroscopy

FTIR spectroscopy was carried out with a BIORAD FTS6000 spectrophotometer, equipped with a KBr beamsplitter and DTGS detector.

Ink films on aluminium foil were analysed in VAR mode with a reflectance angle of 45°. Spectra were acquired in the 4000 and 400 cm^{-1} range at a resolution of 4 cm^{-1} and by summing 64 scans.

D. Py-GC-MS

The pyrolysis experiments were carried out with a microfurnace pyrolyser injection system Pyrojector II (SGE, USA). Small amounts of sample were inserted into a quartz tube (4 cm × 0.53 mm) which was then introduced into the microfurnace operating at a temperature of 550 °C and at a pressure of 15.0 psi. The pyrolysis chamber was directly connected to the injection port (T = 280 °C) of a Perkin Elmer Clarus 680 chromatograph coupled with a Perkin Elmer Clarus SQ8T single quadrupole mass spectrometer. The MS transfer line temperature was 290 °C, and the MS ion source temperature was kept at 250 °C. The mass spectrometer was operating in the EI positive mode (70eV) with a scan range of 45–400 *m/z*. For the gas chromatographic separation, a 5% diphenyl–95% dimethyl polysiloxane column (Perkin Elmer Elite-5MS; 30 m × 0.25 mm i.d. 0.25 µm film thickness) was used. The injector was operated in split mode, the split ratio being dependent on the sample size. The column oven temperature programme was 40 °C (4 min hold) to 250 °C at a heating rate of 15 °C/min (7 min hold). The carrier gas (He) was used in constant pressure mode at 10.0 psi. Identification of compounds was performed with the NIST11 MS library search and comparison with literature data.

III. RESULTS AND DISCUSSION

A. Pigments

All pigments present in the inks of the felt-tip pens could be identified with µ-Raman spectroscopy. In particular, the two azo pigments PR146 (naphthol AS) [6] and PY81 (arylide) [7] were found in the pink Pml-129 and in the yellow Cy-107, respectively. The Raman spectrum of sample Cy-107 is reported in Figure 2.

In the violet pen Pv-136 the dioxazine pigment PV23 could be identified [6] (Fig. 3), whereas in the blue pen Lct-154 the presence of a blue copper phthalocyanine was established. The polymorphs of the blue phthalos (PB15:x) can be discerned on the basis of their Raman spectra [6], although increasing laser power may induce peak shifting [4] and unambiguous discrimination of CuPc polymorphs in paint and ink samples may be difficult. The Raman spectrum of Lct-154 was compared with those of reference pigments (PB15:1, PB15:3, PB15:6). In this way β-CuPc (PB15:3) could be successfully identified (Fig. 4).

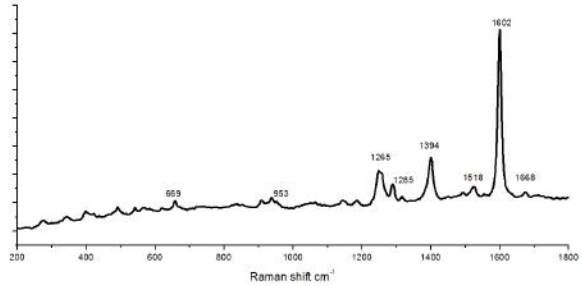


Fig. 2 Raman spectrum of PY81 as identified in Cy-107.

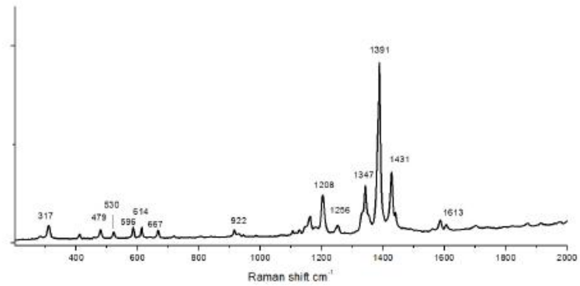


Fig. 3 Raman spectrum of PV23 as identified in Pv-136.

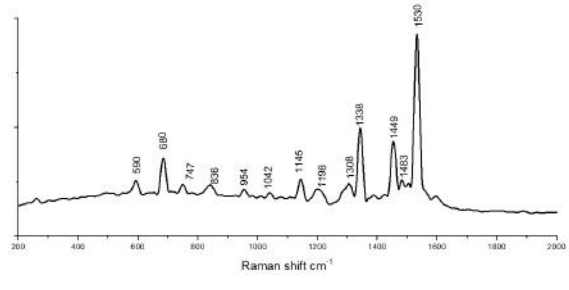


Fig.4 Raman spectrum of PB15:3 as identified in Lct-154

The presence of these pigments could be confirmed by the FTIR spectra as well as by the pyrograms. For example, in sample Cy-107 the occurrence of the yellow pigment PY81 is clearly visible in the FTIR spectrum which shows specific bands at 1668, 1598, 1552, 1526, 1492, 1357, 1312, 1280, 1248, 1211, 1179, 1047, 954, 828, 778 cm^{-1} (Figure 5).

Fig. 5 FTIR spectrum of sample Cy-107

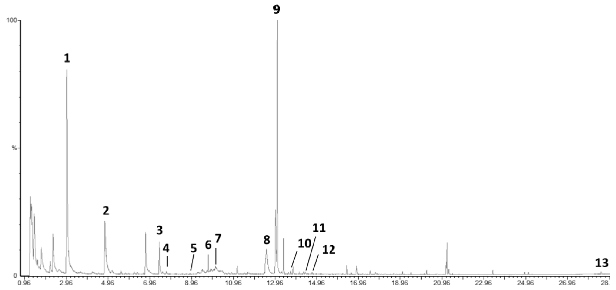
In the pyrogram of sample Pml-129 the occurrence of PR146 is testified by the following pyrolysis products: β-naphthol, 5-chloro-2,4-dimethoxyphenyl isocyanate and 4-chloro-2,5-dimethoxy benzenamine. These products are considered to be characteristic for this naphthol AS pigment [8], which is prepared by combining 2-hydroxy-3-naphthoic acid and N-arylamide (coupling component), whereas analytical pyrolysis at 550°C of PY81 yields 3,4-dimethyl benzenamine and 3,5-dimethylphenyl isocyanate [9]. The latter were clearly detected in sample Cy-107 (see the pyrogram in Figure 6).

In the pyrogram of sample Pv-136 the detection of 1,4-dichloro benzene, 1-ethyl-1H-indole and 9-ethyl-9H-carbazole seems to confirm the presence of the violet dioxazine PV23 in this ink (see pyrogram in Figure 7).

The presence of the blue phthalocyanine in sample Lct-154 is simply testified by a rather intense peak assigned to 1,2-dibenzenedicarbonitrile, but Py-GC-MS does not allow for distinction between the blue polymorphs.

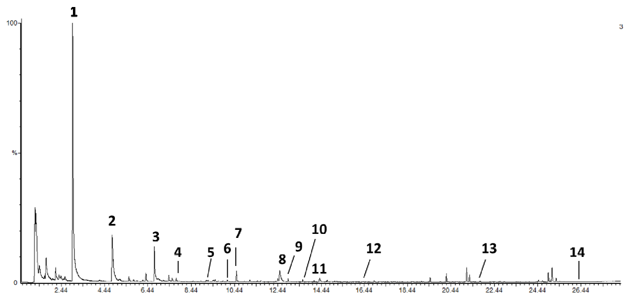
B. Binders

The most exhaustive information on the chemical nature of modern paint and ink binders can generally be obtained by performing Py-GC-MS. The pyrograms that were obtained for the felt-tip pen ink samples (Figures 6-7) indicate the presence of a copolymer of styrene and methylmethacrylate (MMA). Indeed, methacrylate-based polymers produce rather simple pyrograms, since pyrolysis generates a typical “unzipping” depolymerization mechanism leading to the formation of the constituent monomers [10]. Moreover, the presence of cyclopentanone and ε-caprolactam suggest the addition of a polyamide binder. This type of medium has been reported in water-based printing ink patents.



Legend: 1 = mehyl methacrylate; 2 = cyclopentanone; 3 = styrene; 4 = 2-butoxy ethanol; 5 = phenol; 6 = α-methylstyrene; 7 = glycerol; 8 = 2,4-dimethyl benzenamine; 9 = 2,4-dimethylphenyl isocyanate; 10 = diethylen glycol; 11 = 2,3,6-trimethyl phenol; 12 = ε-caprolactam; 13 = diisoctyl phthalate

Fig. 6 Pyrogram of sample Cy-107



Legend: 1= mehyl methacrylate;2 = cyclopentanone; 3= styrene; 4 = 2-butoxy ethanol; 5= phenol;6 = α-methylstyrene; 7 = glycerol; 8 = 1,4-dichloro benzene; 9 = diethylen glycol; 10 = 2,3,6 trimethyl phenol; 11 = ε-caprolactam; 12 =1-ethyl-1-H-indole; 13 = 9-ethyl-9-H-carbazole; 14 = diisoctyl phthalate

Fig. 7 Pyrogram of sample Pv-136

The presence of an acrylic binder is confirmed by the FTIR spectra where the C=O stretching absorption at 1730 cm^{-1} is relatively intense, as well as the C-H stretching vibrations at 2926 and 2858 cm^{-1}. The aromatic C-H stretchings at wavenumbers between 3100 and 3000 cm^{-1} are both due to the styrene of the binder as well as to the pigments bearing aryl rings (see FTIR spectrum of sample Cy-107 in Figure 5). Other characteristic peaks are hidden by the rather intense peaks of the pigment.

C. Solvents and additives

Glycerol and diethylene glycol, used as solvent, could be detected in all pyrograms, especially when the ink was analysed immediately after its application. Moreover, the use of phenolic antioxidants is confirmed by the presence of phenols [11] and diisooctyl phthalate plasticiser was identified as well as an intact molecule at the end of the pyrogram.

The occurrence of these solvents and antioxidants was confirmed by the broad band at 3320 cm^{-1} due to the hydroxyl stretching in the FTIR spectra.

IV. CONCLUSIONS

The chemical characterisation of modern paints and inks, being multi-component systems containing one or more polymeric binders, pigments and additives, requires high resolution and sensitive techniques. Therefore, in this study we proposed the use of FTIR spectroscopy, Py-GC–MS and micro-Raman spectroscopy as complementary techniques for a complete identification of all components.

The felt-tip pens analysed in this study are commonly used by modern artists. FTIR spectroscopy and Py-GC–MS permitted to determine the solvents, binders and additives. The advantage of Py-GC–MS relies in its capability to reveal also minor and trace components to unambiguously identfy acrylic monomers. As to the analysis of pigments, although FTIR spectroscopy and Py/GC–MS may provide some information on the presence and nature of these compounds, the most informative technique is micro-Raman spectroscopy. It was possible to recognise a range of synthetic organic pigments of the mono- and disazo, phthalocyanine and dioxazine classes.

In conclusion, in this study compositional data of an important type of felt-tip artist pens were provided as well as a methodology based on a multi-technique approach, which could remarkably help investigations in a broad panorama of case studies, ranging from forensic science to cultural heritage.

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