

Towards the identification of original dyes in chromogenic films: the development of an approach based on chemical analyses

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Abstract

Four colour movie films of different brands and with different polymeric support, dated from 1990 to 2006, were studied from the point of view of the chemical structure of the chromogenic dyes. Both spectroscopic (Raman and surface-enhanced Raman) and chromatographic (thin-layer chromatography and high-performance liquid chromatography-mass spectrometry) techniques were used, and it was possible to establish a comparison between the dyes in the different films, together with a tentative attribution to couplers of different molecular classes.

Keywords: chromogenic films; dyes; chemical analyses.

Introduction

The main problem that conservators have to face with regard to the latest generation of cinematographic films, chromogenic films, is the fading of colours, the only solution for which is represented by digital restoration. In fact, the original dyes cannot be chemically restored, but their knowledge can nevertheless be significant for this process. In chromogenic films, colour is produced through the so-called subtractive synthesis, based on the combination of cyan, magenta and yellow dyes. These substances are formed during the development process following the reaction between the couplers, which are divided into the three different layers of the emulsion, and the oxidized developer. The chemical nature of these compounds, whose molecules are extremely complex, is not disclosed by the manufacturers, thus posing a difficult challenge for their identification by chemical methods of instrumental analysis.

Only a few examples have already been reported in the literature for the characterization of chromogenic dyes, based on the use of surface-enhanced Raman spectroscopy (Longoni *et al.*, 2022), Raman and Fourier-transform infrared (FTIR) spectroscopy (Di Pietro, 2007; Silva *et al.*, 2022) and high-performance liquid chromatography – mass spectrometry (HPLC-MS) (Silva *et al.*, 2022). In all cases however one or the other of the above techniques was applied to a limited choice of film samples, and only two of the reported papers refer strictly to movie films (Di Pietro, 2007; Longoni *et al.*, 2022).

In the present work, four portions of chromogenic 35-mm positive films of different brands were studied by vibrational spectroscopic and chromatographic techniques, aiming at the characterization of the corresponding dyes. In detail, the materials examined were: three Eastman Kodak films, two dated back respectively to 1990 and 1993, for which no code was available and a 2383 film (the date of the movie was not available, but the film was produced from 1999 to 2003); and a Fujicolor Eterna cp 3513D film (2006) (preliminary studied in Longoni *et al.* 2022).

Methods

The polymeric supports of the films were identified by attenuated total reflectance (ATR) FTIR spectroscopy, using a Jasco FTIR-470 spectrometer, and a zinc selenide ATR single reflection crystal with 45° angle of incidence. Each spectrum was obtained with resolution 4 cm⁻¹, as the sum of 256 accumulations in the range 4000-700 cm⁻¹. All films were analysed non invasively by simply putting a part of them in strict contact with the crystal.

For the analysis of the dyes, samples of the emulsion were taken from black lateral areas of the films with the aid of a scalpel under a stereomicroscope. For the chromatographic separations of the dyes, the emulsion was used as a whole after extraction with ethanol:water (3:1), while for the Raman analysis the layers corresponding to the different colors were selectively scraped and a further selection was made with the aid of a needle, always under the microscope.

Raman measurements were performed by a Bruker BRAVO handheld spectrometer, using two excitation wavelengths (850 nm from 300 to 2000 cm^{-1} and 785 nm from 2000 to 3200 cm^{-1}) and resolution around 11 cm^{-1} . The acquisition time ranged from 500 ms to 2 s and the number of accumulations from 5 to 300.

Details about the thin-layer chromatography (TLC) separation of the dyes and the surface-enhanced Raman analysis are reported in (Longoni *et al.*, 2022). Briefly, a suspension of silver nanostars was used as SERS-active substrate and the spectra were acquired with a 532-nm excitation wavelength using a JASCO RMP 100 portable Raman micro-probe.

HPLC-MS analyses were performed using a Thermo Fisher LCQ Fleet ion trap mass spectrometer equipped with the UltiMate™ 3000 UPLC system with ESI source and UV detector (λ 546, 650 and 438 nm) and a C18 column (3.5 μm , 4.6 x 150 mm). The eluents were (A) H_2O milliQ + 0.01% HCOOH and (B) MeOH and the following gradient was used: 0'-2', 70% A - 30% B; 20'-33', 100% B; 35'-45', 70% A - 30% B.

Results and discussion

Based on ATR-FTIR spectra (Fig. 1), for the two older Eastman Kodak films the support was recognized as cellulose acetate (Nunes *et al.*, 2020), while for the Kodak 2383 film and the Fujicolor film polyethylene terephthalate (PET) was identified as expected (Pereira dos Santos *et al.*, 2017).

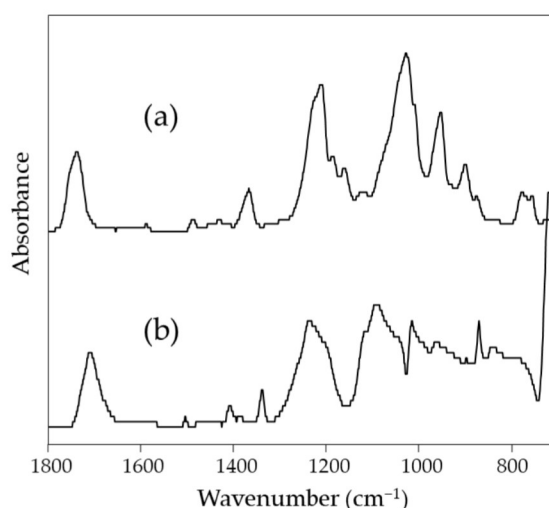


Fig. 1 – Examples of the ATR-FTIR spectra obtained on the polymer side of the films examined: (a) Eastman Kodak 1990; (b) Fujicolor 2006.

As regards the dyes, for the magenta colour in all four films the same dye formed from a coupler belonging to the family of pyrazolones could be detected, based on the Raman and SERS spectra (Fig. 2) (Longoni *et al.*, 2022) and on the HPLC-MS data (same retention time and m/z value). For the cyan colour, Raman and HPLC-MS analyses indicated that three different dyes were used, two for the older cellulose acetate films and the third for the two more recent PET films, but the SERS spectra indicated, at least for the Eastman Kodak 1993 film, that they derived from couplers

belonging to the same molecular class of naphthols (Longoni *et al.*, 2022). As concerns the yellow colour, HPLC-MS data could be acquired just for the two PET Kodak and Fujicolor films, demonstrating the presence of a common dye, with the addition of a second one only in the Kodak film. Probably due to the low concentration of the dye, no SERS signals could be acquired for the films with the exception of the spectrum already reported for the Fujicolor one, but Raman spectra resulted quite similar for the two PET films and for the Kodak Eastman film dated to 1993, again suggesting that a coupler belonging to the family of benzoyl acetanilides was used in all cases.

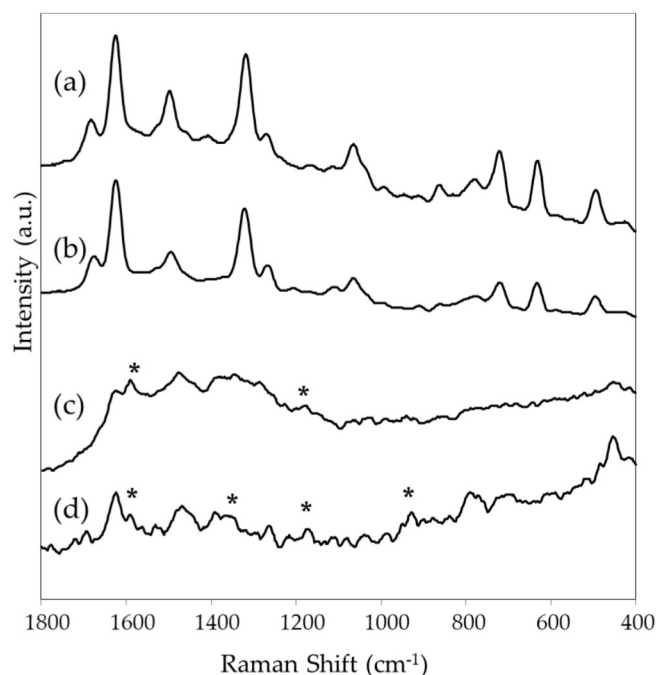


Fig. 2 – Examples of the SERS spectra (λ_{exc} 532 nm) obtained on the dyes extracted from the emulsion of the films examined: (a) magenta dye from Eastman Kodak 1993; (b) magenta dye from Fujicolor 2006; (c) cyan dye from Eastman Kodak 1993; (d) cyan dye from Fujicolor 2006. Legend: * = spurious bands due to the silver colloid.

Conclusions

The present work represents an effort in the direction of the chemical investigation of chromogenic dyes in movie films. Even if, similarly to previously reported papers, a univocal identification of the dyes has not been obtained, an assignment to molecular classes could be hypothesized. Moreover, this is a first attempt to build a database of spectroscopic and chromatographic data on these dyes. Looking ahead, this database, if sufficiently expanded, could be useful for comparing different films, especially in those cases where detailed information about the film itself is lacking and therefore spectral density curves for the three colours are not available.

References

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