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Fluorescence from Colours Used for Japanese Painting under N_2 Laser Excitation

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The fluorescence spectra have been measured for various colours used for Japanese painting in order to identify the pigments in paintings. Fluorescence was observed in various natural and synthetic colours. The fluorescence intensities of these colours are generally weaker than those of oil colours.

KEYWORDS: laser-induced fluorescence, Japanese painting, nondestructive identification, pigment, dye, glue

§1. Introduction

The identification of pigments in paintings has been investigated in the field of conservation and restoration. X-ray fluorescence analyses and X-ray diffraction analyses are useful nondestructive methods for inorganic pigments. However, these methods cannot be applied to organic dyes. Optical reflection spectra have been reported as a nondestructive method for both organic dyes and inorganic pigments.1) However, this method is inferior to destructive methods regarding accuracy. Other nondestructive methods are desired since a combination of these methods can accomplish a more accurate identification of pigments.

In previous papers,2,3) the author has reported that fluorescence spectra are observed in oil colours and that an identification of pigments is possible using a laser-induced fluorescence method. The same method may be applicable to colours used for Japanese painting. In this study, the author investigated the fluorescence spectra of natural and synthetic colours used for Japanese paintings.

§2. Experimental Procedure

The natural colours used for Japanese paintings are listed in Table I. The colours used in this experiment were mainly obtained from Nakagawa Co., Ltd. They are listed in Tables I and II. The author has not been able to obtain the colours mentioned within parentheses. Most natural colours (Iwa-enogu) are made from ores, and synthetic colours (Shin iwa-enogu) are made from metallic oxides and lead glass. The grain size of colours is about 10 μm (No. 10). Colours have been glued on Japanese paper in Japanese paintings. However, paper shows fluorescence. In the present experiment, colours were glued on Al plates instead of paper, since Al shows very weak fluorescence.

In Japanese painting, natural dyes are also used for colours. Typical dyes are enji, to-o and ai, as listed in Table III. Samples for fluorescence measurements of enji and ai were silk cloths dyed with these dyes using traditional Japanese techniques. Fluorescence from to-o was measured using a lump dye (without cloth).

The fluorescence spectra were measured at room temperature with the following apparatus (similar to that described in ref. 4). The excitation source was a pulsed N_2

laser (NDC JS-1000L; λ = 337.1 nm, pulse duration = 5 ns, repetition rate = 4 Hz). The laser beam was set at an angle of about 50^{o} off the normal incidence to the plane of a sample and was focused on a spot about 1 mm^2 in area by a quartz lens (focal length f = 150 mm). The peak intensity of the laser light on the sample was about 50 kW/cm^2. Fluorescence was observed at 90^{o} to the laser beam and was focused on the entrance slit of a monochromator (Oyo Bunko ASI-50S) by a glass lens (f = 70mm). A glass filter (Toshiba L-39) was used to eliminate any scattered light from the laser beam. The fluorescence spectra were measured with a monochromator, a photomultiplier (Hamamatsu R955), a boxcar integrator (homemade) and a recorder.

§3. Results and Discussion

Figure 1 shows the fluorescence spectra of natural colours. Fluorescence is observed in colours except for suihi-taisha. However, glue shows intense fluorescence band at about 430 nm in Fig. 1(b). Colours without glue were also measured. Fluorescence is not observed in meno-matsu, midori-meno, matsuba-rokusho and iwa-gunjo without glue. The bands around 440 nm are not observed in shinsha and kincha without glue. Thus, the fluorescence bands at about 440 nm shown in Fig. 1 are attributable to glue. On the contrary, the 440 nm band in gofun was observed without glue. Fluorescence is observed without glue for the colours shown in Fig. 4.

Fluorescence for meno-matsu, midori-meno, matsuba-rokusho and iwa-gunjo in Fig. 1 is attributable to glue. While the spectral shapes for meno-matsu and midori-meno are almost the same as that of glue, the shapes for matsuba-rokusho and iwa-gunjo are slightly different from that of glue. This result indicates that the fluorescence from glue is partly absorbed by pigments of matsuba-rokusho and iwa-gunjo. This absorption effect may cause a change in spectral shape of the fluorescence from glue. The absorption effect may be relatively small for meno-matsu and midori-meno.

The fluorescence intensity of glue becomes weak in the presence of colours. For example, the intensity of the 440 nm band for kincha in Fig. 1(a) is about 1/100 of that of glue in Fig. 1(b). This result can be explained by the absorption effect: fluorescence from glue is absorbed by pigments of colours, as described above. Moreover, the excitation light from the laser is also absorbed by the colours. Both absorption effects weaken the fluorescence from glue.

The main ingredient of shinsha is the same as that of vermillion of oil colours. Vennillion shows a fluorescence band at 600 nm.2) On the other hand, shinsha shows a fluorescence band at 630 nm. Moreover, the fluorescence intensity for shinsha is about 1/40 of that for vermillion. This long-wavelength shift and quenching of fluorescence may be due to impurities in shinsha, since shinsha is considered to have a high concentration of impurities.

Other natural colours are used for Japanese painting. They are listed in Table I (within parentheses). Since the main ingredient of o-do is similar to that of suihi-taisha, fluorescence from o-do may not be observed. The main ingredient of enpaku is the same as that of lead white of oil colours. Since lead white shows no fluorescence,2) en-paku may not show fluorescence.

Fluorescence from dyes is shown in Fig. 2. Enji shows a fluorescence band near 640 nm. The fluorescence band at about 410 nm is attributable to silk fibres.4) To-o shows a fluorescence band at about 580 nm. On the other hand, fluorescence from ai is not observed.

Fluorescence from natural colours, except for white colours, has not been observed under Hg-lamp excitation.5) On the contrary, fluorescence from some natural colours was observed under N_2 laser excitation. This result indicates that the laser-induced fluorescence method is more sensitive than the ordinary fluorescence method.

Figure 3 shows the fluorescence spectra of synthetic colours. Fluorescence from glue (the 440 nm band) is not observed in beni-shinsha. This result can be explained by the absorption effect: fluorescence from glue is absorbed by the pigment of beni-shinsha. Furthermore, fluorescence from glue may be masked by the relatively intense fluorescence from beni-shinsha.

Figure 4 shows the intensity ratios of fluorescence from some synthetic (solid circles) and natural (open circles) colours. Fluorescence from other colours is attributed to glue; therefore, their intensities are not shown in Fig. 4. The fluorescence intensities of glue and cadmium red are shown in Fig. 4, since cadmium red is a standard oil colour for fluorescence intensity in oil colours.2) In general, the fluorescence intensities of colours used for Japanese painting are weaker than those of oil colours reported in ref.

2.

Fluorescence from glue affects the fluorescence spectra of some colours. Since glue is an organic compound, fluorescence from glue may change with long-time storage. The fluorescence spectrum was measured for a glue film on an Al plate stored for 3 years in the dark at room temperature. A noticeable change in the fluorescence spectra was not observed in the stored glue film.

Fluorescence spectra were measured for a Japanese painting, which may have been painted about 200 years ago. Figure 5 shows the fluorescence spectra of red, yellow and white parts of the painting. Fluorescence bands are observed at 640 nm for the red part, at 590 nm for the yellow part and at 550 nm for the white part. The 640 nm band is similar to that of shinsha in Fig. 1(a), and the 590 nm band is similar to that of to-o in Fig. 2. Although the colours actually used by the artist are not known, this spectrum suggests that the identification of pigments may be possible for Japanese painting.

The 440 nm band of glue is not observed in Fig. 5. This result can be explained in terms of glue degradation. The chemical composition of glue is considered to change with long-time (about 200 years) storage; thus, peak wavelength and intensity of fluorescence may also change. Moreover, the fluorescence from glue may be masked by the fluorescence from paper. The fluorescence spectrum of paper is similar to that of the white part of the painting.

In summary, the fluorescence spectra of colours were measured under N_2 laser excitation. Fluorescence was observed in various natural and synthetic colours. An identification of pigments may be possible for these colours.

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References

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Figure captions

Fig. 1. Fluorescence spectra of natural colours and glue. Peak intensities are normalized.

Fig. 2. Fluorescence spectra of natural dyes. Peak intensities are normalized.

Fig. 3. Fluorescence spectra of synthetic colours. Peak intensities are normalized.

Fig. 4. Intensity ratios of fluorescence from several colours. Wavelength of fluorescence band is denoted in parentheses. Open circles represent natural colours and solid circles represent synthetic colours.

Fig. 5. Fluorescence spectra of red, yellow and white parts of Japanese painting. Peak intensity ratios are as follows: 0.017 (red), 0.08 (yellow), 0.08 (white).

Table I. Natural colours for Japanese painting. Colours within parentheses were not used in this experiment.

Name	Main ingredient	Colour tone
Shinsha	HgS	red
Suihi-taisha	Fe_2O_3	red
(Entan)	Pb_3O_4	red
(0-do)	$Fe_2O_3 \cdot H_2O$	yellow
Kincha		yellow
Meno-matsu		yellow
Midori-meno		green
Matsuba-rokusho	$CuCO_3 \cdot Cu(OH)_2$	green
Iwa-gunjo	$2CuCO_3 \cdot Cu(OH)_2$	blue
Gofun	$CaCO_3$	white
(Hakudo)	$H_4Al_2SiO_7$	white
(Enpaku)	$2PbCO_3 \cdot Pb(OH)_2$	white
(Haku-unmo)	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	white

Table II. Synthetic colours used in this experiment.[1]

Name	Colour tone
Beni-shinsha	red
Kincha	yellow
Kiguchi-uraba	green
Matsuba-rokusho	green
Gunjo	blue

[1] Main ingredients of synthetic colours are metallic oxides and lead glass.

Table III. Natural dyes used in this experiment.

Name	Main ingredient	Colour tone
Enji	laccaic acid and erythrolaccin	red
To-o	gamboge (resin)	yellow
Ai	indigo	blue

Fig. 1(a)

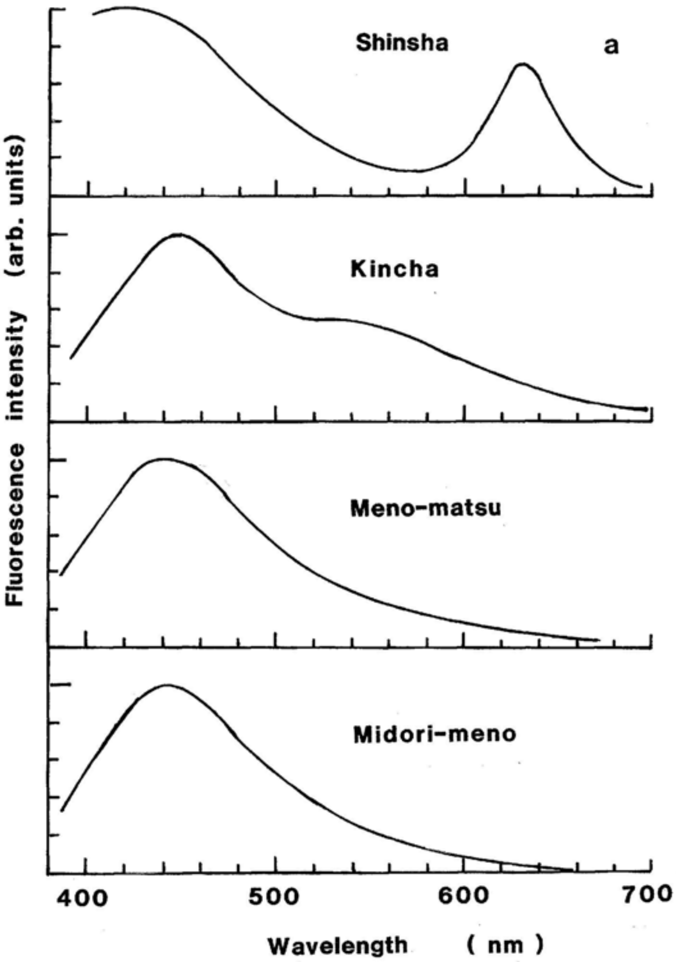

Shinsha
a
Kincha
Meno-matsu
Midori-meno
Fluorescence intensity (arb. units)
400
500
600
700
Wavelength (nm)

Fig. 1(b)

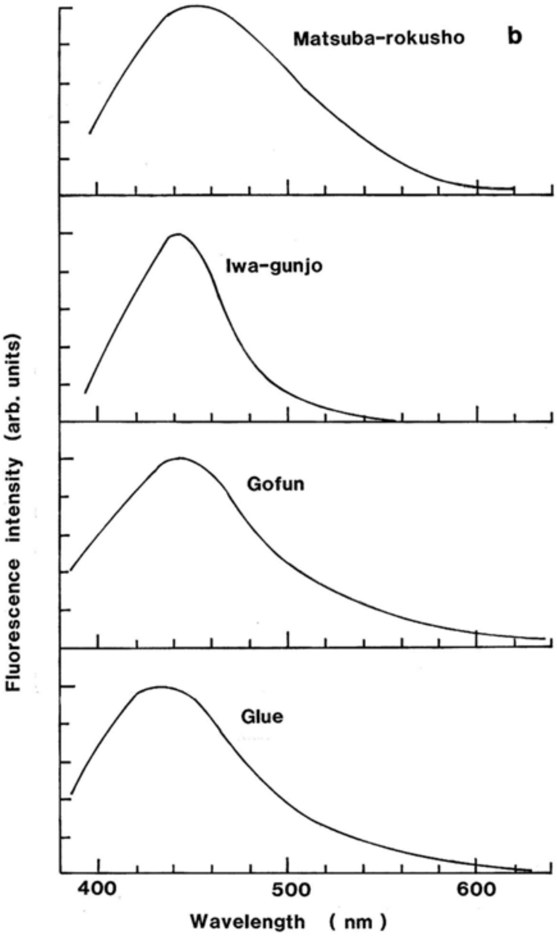

Matsuba-rokusho
b
Iwa-gunjo
Gofun
Glue
Fluorescence intensity (arb. units)
400
500
600
Wavelength (nm)

Fig. 2

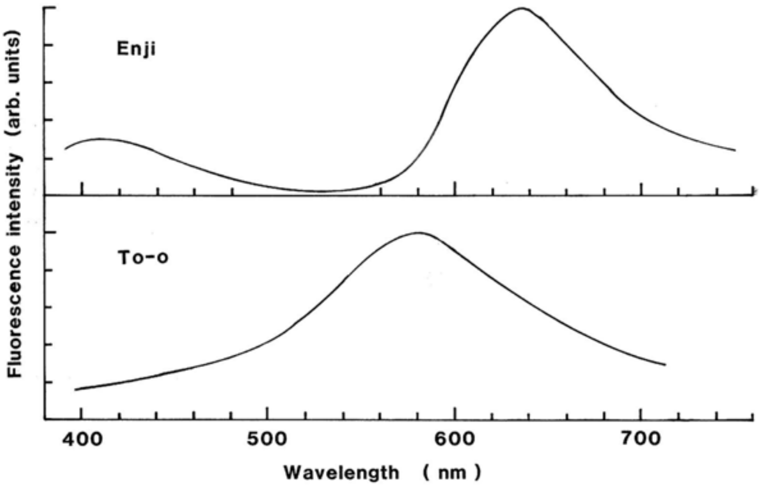

Enji
To-o
Fluorescence intensity (arb. units)
400
500
600
700
Wavelength (nm)

Fig. 3

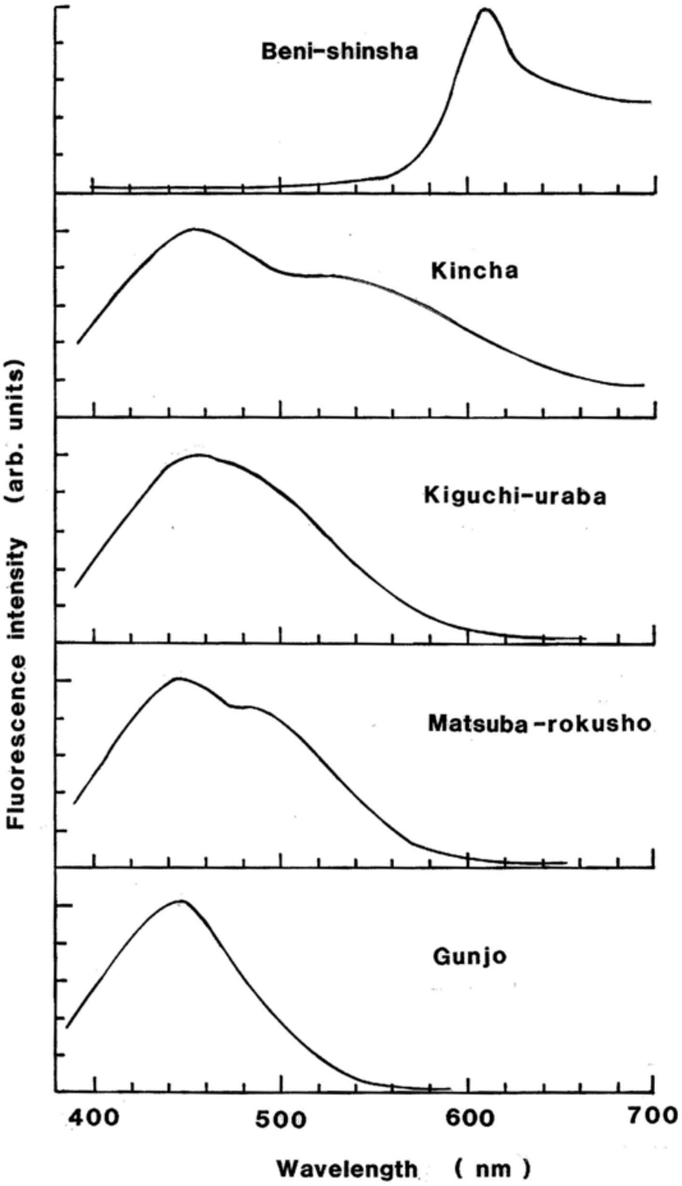

Beni-shinsha
Kincha
Kiguchi-uraba
Matsuba-rokusho
Gunjo
Fluorescence intensity (arb. units)
400
500
600
700
Wavelength (nm)

Fig. 4

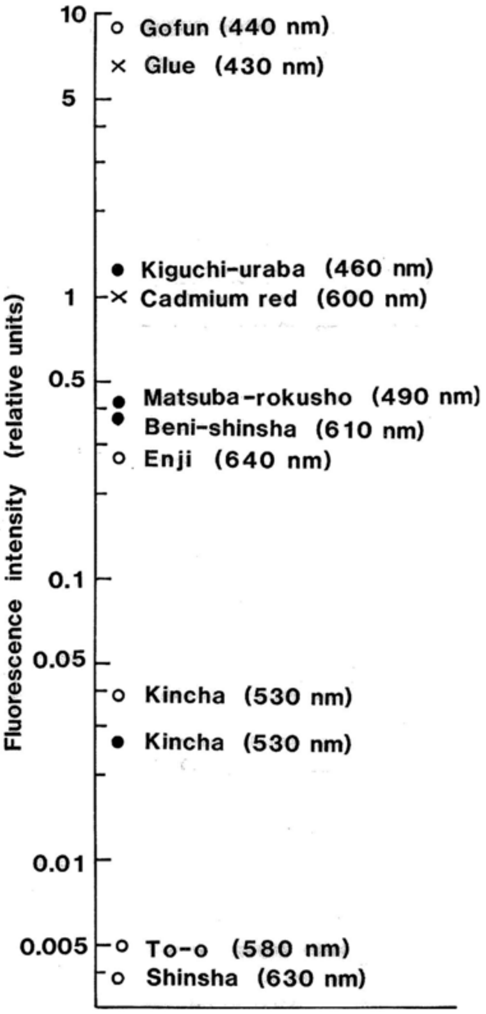
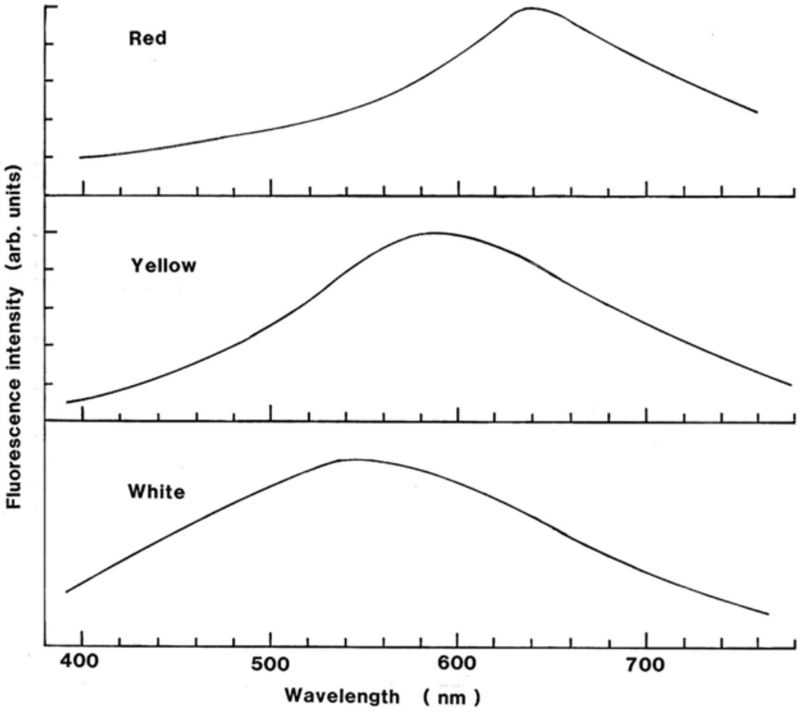

10
5
1
0.5
0.1
0.05
0.01
0.005
Fluorescence intensity (relative units)
○ Gofun (440 nm)
× Glue (430 nm)
● Kiguchi-uraba (460 nm)
× Cadmium red (600 nm)
● Matsuba-rokusho (490 nm)
● Beni-shinsha (610 nm)
○ Enji (640 nm)
○ Kincha (530 nm)
● Kincha (530 nm)
○ To-o (580 nm)
○ Shinsha (630 nm)

Fig. 5


Red
Yellow
White
Fluorescence intensity (arb. units)
400
500
600
700
Wavelength (nm)