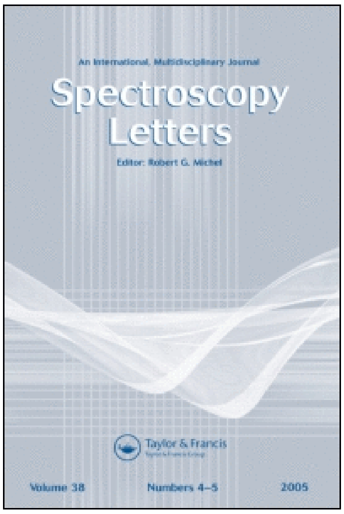

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Photodegradation Studies by Laser-Induced Fluorescence of the Reaction Product of 1,2-Indanedione And Glycine

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Abstract: Photodegradation of the reaction product of 1,2-indanedione with glycine in methanol at room temperature has been studied using laser-induced fluorescence. Samples were liquid solution and developed fingerprints on papers. Continuous laser excitation of fresh solution of 1,2-indanedione–glycine dissolved in methanol shows that the emission peak at 564 nm reached a quite stable low level after almost 1 hr of continuous excitation. For latent fingerprints on papers developed with 1,2-indanedione dissolved in methanol solution, the luminescence peak decreases for the first week and reached a stable level for almost 2 weeks. A long-term study is needed to reach a conclusion on the stability of the samples (liquid and developed fingerprints) at room temperature conditions.

Keywords: Fingerprints, fluorescence, 1,2-indanedione, laser, photodegradation

INTRODUCTION

1,2-Indanedione is a fingerprint reagent that develops latent fingerprints on porous surfaces much like ninhydrin[1,2] and ninhydrin analogues.[3,4] We

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started working with ethyl acetate solution of 1,2-indanedione and glycine, but because glycine does not dissolve well in ethyl acetate, we have switched to methanol, which is more polar. The reaction product of 1,2-indanedione with glycine in methanol, or ethyl acetate, glows yellow under blue-green laser light. This property is very useful in fingerprint development, because finger deposits contain among other things the amino acid glycine.

During the evaluation of the 1,2-indanedione compound,[5–7] it was shown that it is capable of visualizing latent prints as well as or even better than 1,8-diazaflouren-9-one (DFO).[8,9] Like DFO, the indanediones do not produce strongly colored initial print development (typically a pale-pink color), but they do produce strongly fluorescent detail when excited with blue-green laser light. In a previous work on the spectroscopic properties of the reaction product (products) of 1,2-indanedione with glycine in methanol,[10] we showed that it gives formation of two products in the solution with about 80% for the preponderant product and about 20% for the second product. In this paper, we will concentrate more on the photodegradation of the methanol solution of 1,2-indanedione and glycine (IG). We will also study the stability of fingerprints on papers developed with 1,2-indanedione solutions.

Ninhydrin-treated fingerprint reacts with europium chloride and terbium chloride[11,12] and shows strong emission enhancement of the lanthanide ion (Eu^{3+} or Tb^{3+}) via intramolecular energy transfer[13] from the Ruhemann's Purple[14] (RP) ligand to the lanthanide ion. RP is the reaction product of glycine with ninhydrin. It has been shown that 1,2-indanedione–treated fingerprints react also with europium and terbium chlorides.[10] However, no appreciable emission enhancement of the lanthanide ion under near-ultraviolet light was seen. Under blue laser light, the organic ligand, which glows yellow, also did not show any fluorescence enhancement. Methanol solution of IG reacts also with zinc chloride to form a yellow-orange complex and also reacts with indium chloride to form a pink-red complex. Preliminary results do not show any intermolecular energy transfer from the IG ligand to the metal ion (Zn^{2+}) or any intramolecular energy transfer to the rare earth ion (In^{3+}).

MATERIALS AND METHODS

1,2-Indanediones were received as research samples from a forensic laboratory. The other chemicals and solvent were purchased from Aldrich Chemical Company (St. Louis, MO, USA) and used without further purification. All the reactions took place under room light at room temperature.

Solution of 5×10^{-3} M 1,2-indanedione in methanol was prepared as follows: 0.0584 g 1,2-indanedione was dissolved in 80 mL methanol at room temperature. This volume was divided into two parts: solution A ($V_A = 40$ mL) and solution B ($V_B = 40$ mL). Solution A was reacted with an excess of glycine and was left at room temperature for 1 day for the reaction to take place completely, because of the low solubility of glycine in methanol. Heat may accelerate the reaction. The final concentration in the reaction is 5×10^{-3} M due to the 1–1 stochiometry. The reaction product's color is pale-yellow depending on the concentration: it reaches dark-yellow if the concentration reaches 10^{-2} M. Solution B was kept intact and was used for developing latent fingerprints on papers, while solution A (glycine-reacted solution) was used for spectroscopic measurements.

RESULTS

Emission Measurements in Solution

Emission spectra were recorded using typical spectroscopy equipment. The source of excitation was a CW argon ion laser (Coherent INNOVA 90, Laser Innovations, Santa Paula, CA, USA). The laser beam passes through a converging lens to hit the maximum of the sample. The diameter at the opening of the laser was 0.1 mm. The emission monochromator was a 3-m scanning monochromator (McPherson Inst., Chelmsford, MA, USA). The monochromator slit opening was 1 nm. The scanned wavelengths were in the 520–660 nm range because we were interested in a the 564-nm emission peak. Liquid samples in a quartz cuvette (4 cm^3 silica quartz cuvette, UV-visible spectrometry 200 nm and up) were irradiated with argon ion laser line 488 nm for 2 hr continuously. Laser power (1 W) was kept constant for the entire period of measurements for comparison purposes.

Laser induced emission spectra were recorded each 10 min with 5 min between each measurement (9 emission spectra were taken during the 120-min period). The results are shown in Fig. 1. We were interested mainly on the maximum emission peak (564 nm), and we have recorded its evolution as a function of time. The results are reported in Fig. 2, which shows that the emission maximum decreases for the first hour and reached a plateau for the rest of the measurements. If we assume an exponential decay for the peak, the photobleaching time constant τ_S for the IG solution is about 109 min. This means that 1,2-indanedione–glycine methanol solution is quite stable, for a short-term, at room temperature. More work is needed to give a conclusion for long-term stability of the IG solution in methanol.

Emission Measurements for Developed Fingerprints on Paper

Treated latent fingerprints on papers (office papers mainly) with solution B were also excited with the same wavelengths, but not continuously. The same irradiation conditions were used for the solution phase and the

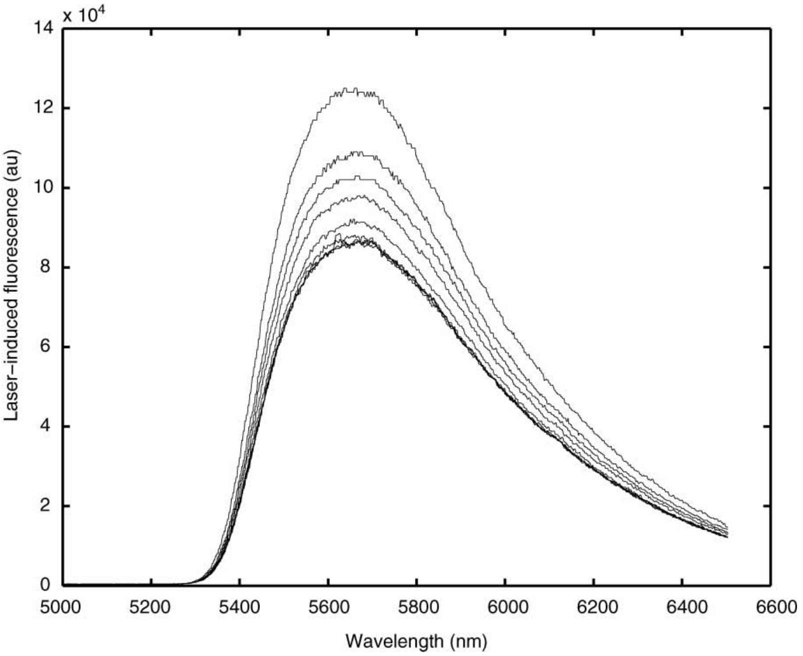

Figure 1. Laser-induced fluorescence of 1,2-indanedione with glycine in methanol solution. The laser excitation is the blue-green argon ion line with a high-pass optical filter. The top curve is the first measurement, and at the bottom there are few overlapped curves.

fingerprints, except for the period of the experiment. For the solution, the irradiation experiment lasted for a continuous 2 hrs, whereas the fingerprint irradiation experiment was noncontinuous and lasted for 17 days (almost 5 min per day). It is done in this way because we know from previous experiences with ninhydrin that RP solution degrades quicker than latent fingerprints on papers developed with ninhydrin.

The response of the fingerprints samples to the argon laser excitation was a yellow broad emission with a maximum around 564 nm. An orange filter (High-pass, OG 550, Ocean Optics, Dunedin, FL, USA) was used for visual and qualitative observation. Quantitative measurements were done with the same spectroscopic set as above. The paper samples were put in a solid holder to make them easy to manipulate and rotate to get the signal on the monochromator slit. The first measurement took place after the completion of the reaction and then the samples were left to degrade in the laboratory at room temperature. Measurement of the intensity of the peak emission was done every day for 17 days. Background fluorescence of the paper itself has been measured. It is well-known that office paper fluoresces under UV light. Here in our experiment, we were not using UV laser; the 488-nm

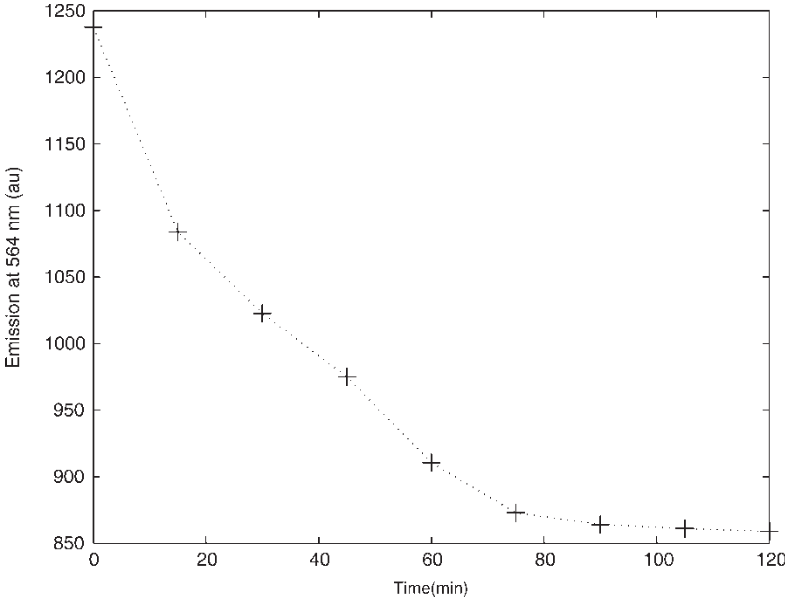

Figure 2. Evolution of the peak of emission (564 nm) of the reaction product of 1,2-indanedione with glycine in methanol solution.

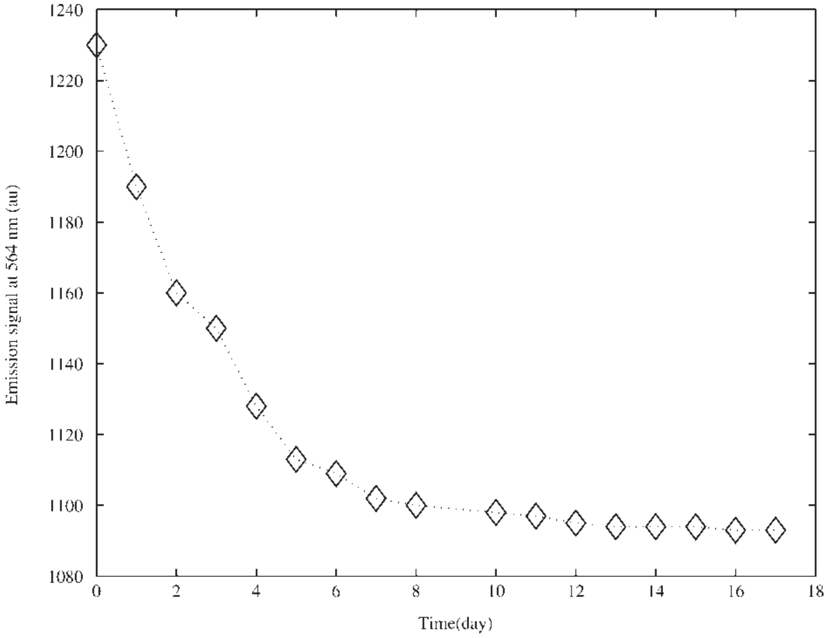

Figure 3. Evolution of the peak of emission (564 nm) of fingerprints on paper treated with 1,2-indanedione methanol solution at room temperature.

line of the argon laser was used as excitation. Still, there was background fluorescence from the paper, which we have taken care of by subtraction and by looking only at the 564-nm emission peak of our samples.

For fingerprints, we were more interested in long-term stability of the laser-induced fluorescence of the samples. The results are shown in Fig. 3. The plateau was almost reached after 6 days, because there was no continuous laser irradiation for the fingerprints on paper. If we assume also, as in the solution case, an exponential decay for the peak, the photobleaching time constant τ_F for the 1,2-indanedione developed fingerprints is about 30 days. Our preliminary results show that the emission will degrade slowly with time due to the environmental condition and the degradation of the samples.

CONCLUSIONS

Continuous laser excitation of fresh solution of IG shows that the emission peak at 564 nm reached a plateau after almost 1 hr of continuous excitation and degrades very slowly at room temperature conditions. For the 1,2-indanedione fingerprints developed on papers and left at room temperature environment, the luminescence peak decreases for the first week and reached a plateau after almost 6 days. In this preliminary study, we were interested in the photodegradation of the 1,2-indanedione–glycine solution and 1,2-indanedione–developed fingerprints. A more detailed work should take into account the photobleaching quantum efficiency; this will be done in a future work. A long-term study is needed to reach a conclusion about the sample's stability. The samples on paper are kept in a folder for further studies.

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