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Fingermarks Development Using Dry Powder Alizarin Red Lake (1,2-Dihydroxyanthraquinone) and Its Nanosecond Transient Absorption Measurement in Isopropyl Alcohol

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Abstract

Alizarin red lake (1,2-dihydroxyanthraquinone) was utilized to develop latent fingermarks and palm marks on porous substrates. In addition, nanosecond transient absorption spectroscopy was employed to investigate its excited-state dynamics in isopropyl alcohol. Alizarin was used in its solid form (via the powdering method), marking it the first time dry powder alizarin that has been reported for fingermarks development. The palm marks and fingermarks exhibited distinctive, visible friction ridges under the light sources used in this study. In daylight and under yellow-filtered LED (395 - 405 nm) light, the marks were apparent. However, under unfiltered LED, they appear blurry, perhaps due to LED interference with the mark's background. Three substrates were used, including printmaking papers, event tickets, and thermal papers. The marks on printmaking paper (commonly used in the arts) were visible in daylight and under yellow-filtered LED. Under unfiltered LED light, the visibility of the friction ridges appears blurry. Similar visibility was observed with the event tickets and thermal papers, where the friction ridges under unfiltered light showed reduced visibility, whereas they were clearly visible in daylight and under yellow filtered LED. The transient absorption spectra revealed the formation of excited-state species upon nanosecond laser excitation, providing insights into the photophysical properties of the dye. Kinetic analysis indicated a rapid decay of the excited-state absorption, suggesting efficient non-radiative relaxation pathways. The findings demonstrate the suitability of Alizarin red lake for enhancing fingermarks visualization under visible light, attributed to its distinct transient absorption characteristics and solvent interactions. This study contributes to the optimization of dye-based forensic techniques, thereby improving latent fingermarks detection on various substrates. The fast decay dynamics of the dye suggest possible picosecond decay dynamics.

Keywords

Alizarin Red Lake, Dry Powder, Fingermarks and Palm Mark Development, Transient Absorption Spectroscopy

1. Introduction

Latent fingermarks development on porous surfaces, such as paper and cardboard, traditionally relies on reagents like ninhydrin and 1,8-diazafluoren-9-one (DFO) [1]. These reagents work by reacting with amino acids present in fingermarks residues, producing colored or fluorescent impressions. Ninhydrin produces purple-colored marks (Ruhemann's purple) under ambient conditions, while DFO fluoresces under UV light [1]. Despite their efficacy, these methods have limitations, including reagent instability, fading over time, and the need for specialized light sources for visualization [2]-[6]. In addition, the solvents used in their formulation are environmentally unfriendly [1].

Recently, alternative reagents derived from anthraquinone dyes have garnered attention for their stability, ease of use, and color contrast under visible light [7] [8]. Alizarin red lake or Alizarin (1,2-dihydroxyanthraquinone) and its derivatives, commonly used in histological staining and calcium detection, have demonstrated potential for forensic applications due to their ability to react with amino acids and other residues found in latent fingermarks [2] [7] [9]-[11].

In the recent application to the fingermarks development [8], Alizarin red lake was formulated in ethyl acetate/HFE 7100 (v/v) solution. However, that solution may not be environmentally friendly [1].

Alizarin red lake was previously characterized by gas chromatography, high-performance liquid chromatography, mass spectrometry, UV-vis spectrophotometry, Thin-Layer Chromatography, 12 NMR [12]-[14], and femtosecond transient absorption spectroscopy [15].

In this study, we report the development of fingermarks and palm marks on porous substrates using dry powder alizarin red lake, powdering method, and its nanosecond transient absorption spectroscopy (ns-TAS) measurement in isopropyl alcohol. The powdering method is the most commonly used approach in fingermarks development [16], and to our knowledge, this is the first report of dry powder alizarin red lake being used in the development of latent fingermarks and palm marks.

Highlights

- Fingermarks and palm marks development on porous substrates, including printmaking papers, event tickets, and thermal papers, were described.

- Alizarin red lake (1,2-dihydroxyanthraquinone) was used in the development of the marks.
- Solventless and solid alizarin (powdering method) was used for the first time to develop the marks.
- Nanosecond transient absorption measurements of alizarin in isopropyl alcohol were acquired.

2. Materials and Methods

a) Materials:

Alizarin red lake (Art Supply Warehouse, Westminster, CA, USA), isopropyl alcohol (ScholAR Chemistry, West Henrietta, NY, USA), Arnhem 1618 Printmaking paper warm white 245 gsm 22 × 30 (Plazaart, Nashville, TN, USA), borosilicate glass vial (Uline, Pleasant Prairie, WI, USA), 395 - 405 nm LED Flashlight 502B UV (UltraFire, Amazon, Seattle, WA, USA), Event tickets (Yellow) (Staples, Framingham, MA, USA), Thermal paper (Uline, Pleasant Prairie, WI, USA), Yellow filter glasses (Sirchie, Youngsville, NC, USA), Long handle brush (Sirchie, Youngsville, NC, USA), iPhone 11, iOS 18.4.1 (Cupertino, CA, USA), Diode pump solid state Nd:YAG laser (Magnitude Instruments, State College, PA, USA).

b) Methods:

Alizarin Red Lake for Palm Marks and Fingermarks Development

Alizarin powder was used as purchased without further formulation. Alizarin, 50 mg, was poured into a container (weight boat) and used to dust off the latent fingermarks and palm marks using a long-handled brush. The porous substrates—Arnhem 1618 Printmaking paper warm white 245 gsm, event ticket, and thermal paper—were cut (with scissors) into finger and palm-sized pieces for fingermarks and palm mark impressions. The latent impressions were carefully made with sebum-coated palms and fingers. The LED (395 - 405 nm) flashlight illuminated the palm and fingermarks directly through a yellow filter glass before visualization. The marks were photographed using an iPhone 11. This development method was repeated several times over the length of six months.

Photography

The photographs were taken with an iPhone 11, iOS 18.4.1 in daylight and under LED (395 - 405 nm). Light filtration was achieved by passing the LED light through the yellow filter glass to illuminate the fingermarks.

Alizarin Red Lake Stock Solution Film Measurement.

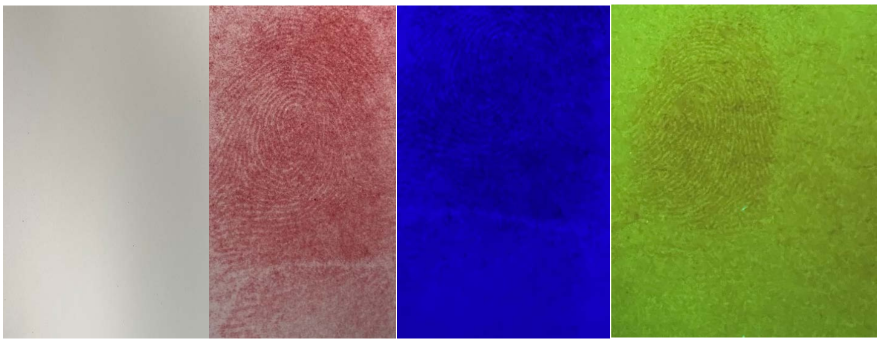
Alizarin red lake (40 mg) was dissolved in isopropyl alcohol (50 mL) contained in a volumetric flask (50 mL). The flask was placed in the Ultrasonic cleaner and sonicated for 10 minutes until complete dissolution, and constituted a stock solution. The resulting stock solution was aliquoted into 5 mL borosilicate glass vials for the collection of transient absorption spectra.

Nanosecond Setup for Film Measurements.

Transient absorption measurements were conducted with a Magnitude Instruments enVista system. The probe beam was an Xenon Lamp, while the pump source was an in-board diode-pumped solid state Nd:YAG laser outputting the third harmonic wavelength (355 nm) at 5000 Hz. The excited-state kinetics were obtained in 10 nm from 400 nm to 900 nm, with 1000 laser shots iterated for 2 times at each wavelength and a time window of 3,000 ns. A total of 2 kinetic sweeps over the range of 400 - 900 nm were averaged. The outputted pump beam had an area of 1 cm^2, and the excitation energy density was 90 μJcm^{-2}. The sample was rotated periodically throughout the measurements to minimize degradation.

3. Results

Fingermarks and palm marks were developed on porous substrates using alizarin red lake, visualized in daylight, under LED (395 - 405 nm), and photographed with an iPhone 11. The results are displayed in **Figures 1-4**. Alizarin red lake was used as purchased in solid (powder) form without additional formulation. Three porous substrates were utilized: printmaking paper customarily used in the arts, event tickets, and thermal papers. **Figures 1-2** illustrate the printmaking paper; **Figure 3** depicts the event ticket, and Figure 4 shows the thermal paper. Figure 1a displays fingermarks before the dusting off of alizarin and was visualized in daylight. **Figures 1(b)-(d)** show fingermarks after their treatment with alizarin, and were visualized in daylight (1b), under unfiltered LED (395 - 405 nm) (1c), and after passing the LED light through a yellow filter (1d). **Figure 1** revealed very distinctive fingermarks with visible friction ridges, except for 1c, which was blurry or not visible. **Figure 2** presents palm marks after their treatment with alizarin, and were visualized in daylight. It shows distinctive friction ridges in daylight.

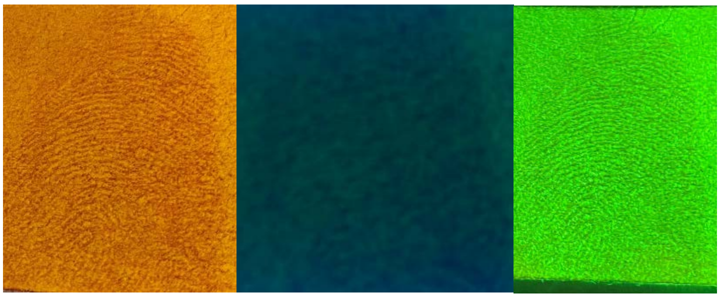


(a) (b) (c) (d)

Figure 1. Fingermarks on printmaking paper: (a) Before application of alizarin, (b) After application of alizarin and visualized in daylight, (c) After application of alizarin and visualized under LED, (d) After application of alizarin and visualized under LED through a yellow filter glass.

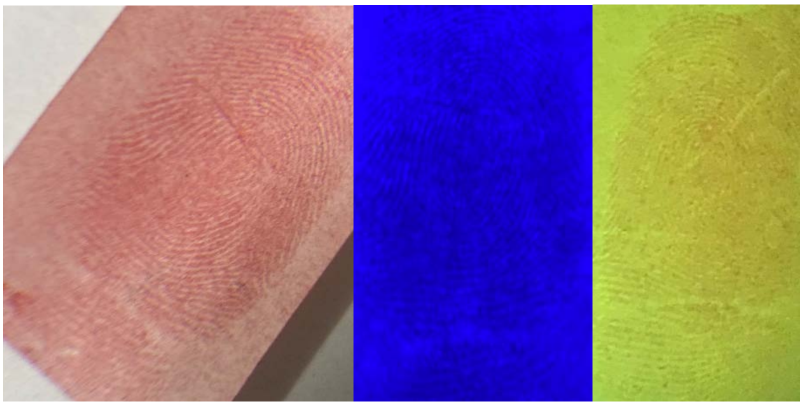
The marks on the event paper, **Figure 3**, demonstrate similar friction ridges visibility, in daylight (3(a)), under LED light-filtered (3(c)). However, the marks under unfiltered LED (3(b)) showed reduced visibility: A similar visibility was also observed with the thermal paper in **Figure 4**, where the friction ridges appeared visible in daylight (4(a)) and under yellow-filtered LED (4(c)) but blurry under unfiltered LED (4(b)).

Figure 2. Palm mark on Printmaking paper after application of alizarin and visualized in daylight.



(a) (b) (c)

Figure 3. Fingermarks on the event ticket after application of alizarin and visualized (a) in daylight, (b) under unfiltered LED, (c) filtered LED.



(a) (b) (c)

Figure 4. Fingermarks on Thermal paper: (a) after application of alizarin and visualized in daylight, (b) after application of alizarin and visualized under unfiltered LED, (c) after application of alizarin and visualized under yellow-filtered LED.

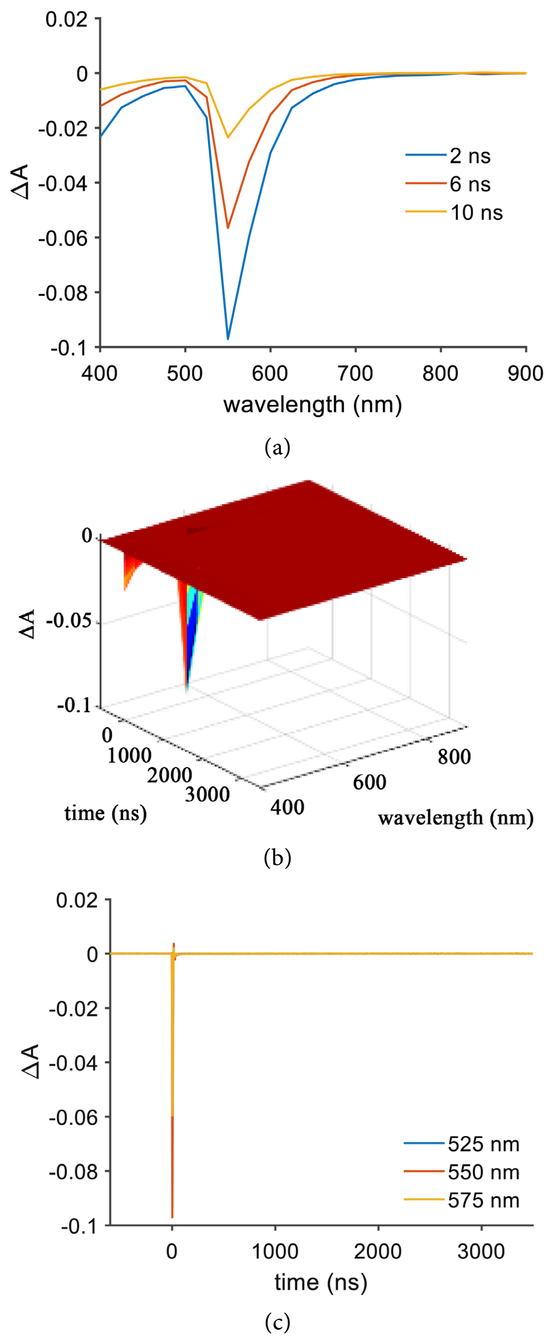


Figure 5. Transient Absorption Measurements of Alizarin: (a), (b), and (c) show the transient decay kinetics for Alizarin Red Lake.

The transient absorption spectra of the alizarin red lake were also acquired. The spectrum in Figure 5(a) shows a bleach around 550 nm that decays on a very fast nanosecond timescale, 10^2 ns. Decays of this magnitude are generally indicative that the dynamics are much faster than the ns timescales. Figure 5(b) shows an overlay of the bleach around 3 very close wavelengths 525, 550, and 575 nm. This plot shows little variation among the three separate wavelengths of decay. However, it does indicate that the bleach decays very rapidly after onset. Figure

5(c) shows a 3D graph of time, Change in Absorption and Wavelength. The 3D plot indicates that there is actually some decay at the wavelength close to the 355 nm pump wavelength.

4. Discussion

Alizarin red lake was used to develop fingermarks and palm marks on porous substrates and to acquire transient absorption spectra. Palm marks and fingermarks were obtained from one adult male donor with consent. No pretreatment of the porous substrates (cellulose-based papers) was undertaken to alter the adhesion of the Alizarin at the surface or to enhance the visualization. After coating the fingers and palms with sebum (enough to reveal marks), the fingermarks and palm marks were developed by dusting off alizarin powder from the impressions on porous substrates. The fingers' and palms' impressions were assessed visually in ambient conditions. The resulting fingermarks and palm marks were visible in daylight across all the substrates (printmaking paper, event ticket, and thermal paper) used in this study, producing detailed friction ridges.

Fingermarks on thermal paper, whose development was reported to be problematic due to solvents effect, showed clear contrast against the background in this solventless and heatless study [8].

The results with the LED showed consistency with the substrates used. When illuminated, the fingermarks on printmaking paper were blurry (**Figure 1(c)**) but became apparent under yellow-filtered LED (395 - 405 nm) (**Figure 1(d)**). The marks on event tickets were visible when illuminated with filtered and showed reduced visibility with unfiltered LED. The light interference appears to have contributed to the reduced visibility observed (**Figure 3(b)**). The marks on the thermal paper showed blurriness under unfiltered LED, a result also attributed to light interference.

This solventless method has reduced the drawbacks generally encountered in methods using solvents, such as background coloration of thermal paper, and has a lower environmental impact [1] [8].

The transient absorption measurement of alizarin red lake in isopropyl alcohol revealed key insights into its excited-state dynamics and potential utility in forensic applications. The transient decay kinetics illustrated in **Figures 5(a)-(c)** indicate a rapid bleaching at approximately 550 nm, with a decay rate occurring at the sub-nanosecond timescale. Such rapid decay suggests that the excited-state lifetime of alizarin red lake is exceptionally short, likely due to fast internal conversion or intersystem crossing processes. The presence of a bleach at this wavelength suggests that photoexcitation leads to a depletion of ground-state populations, which then rapidly return via non-radiative pathways. The overlay of transient kinetics at 525 nm, 550 nm, and 575 nm in **Figure 5(b)** further supports the conclusion that these rapid dynamics are consistent across multiple closely related wavelengths, reinforcing the notion that alizarin undergoes efficient excited-state quenching. Notably, the 3D transient absorption plot in Figure 5c provides additional confirmation that significant decay is also observed near the pump wavelength (355 nm), indicating complex relaxation dynamics occurring throughout the visible spectrum.

These findings have critical implications for the use of alizarin red lake as a forensic reagent for fingermarks development. The extremely short-lived excited states observed in this study suggest that alizarin red lake may be highly responsive to UV excitation, offering potential advantages for fluorescence-based detection. Given that conventional reagents such as ninhydrin and DFO rely on colorimetric changes or fluorescence for visualization, the ability of alizarin red lake to undergo rapid transient absorption changes upon excitation may provide a new approach for enhancing fingermarks contrast under specific lighting conditions. Furthermore, the resilience of alizarin to environmental factors such as humidity and light exposure, as previously documented, strengthens its candidacy for fingermarks development. The rapid kinetics observed in transient absorption measurements indicate that alizarin's photochemical behavior is highly dynamic, potentially offering novel opportunities for optimizing its use in forensic imaging techniques.

5. Conclusions

Latent fingermarks and palm marks were developed on a porous substrate using dry powder alizarin red lake, marking it the first report of this method in the fingermarks and palm marks study. The marks exhibited visible friction ridges when viewed in daylight and under yellow-filtered LED (395 - 405 nm). However, under unfiltered LED, they are blurry, possibly due to the light interference with the background of the marks.

The solventless, heatless, and dry powder method (powdering method) used for developing palm and fingermarks in this study not only reduces costs but also proves to be environmentally friendly. The nanosecond transient absorption spectra of alizarin red lake in isopropyl alcohol were obtained, illustrating its rapid excited-state dynamics, characterized by a significant bleach at 550 nm and a swift decay beyond the timescale of conventional ns-TAS measurements. These findings highlight the potential of alizarin-based systems in forensic science, especially for improving latent fingermarks visualization under controlled excitation conditions. Future research will aim to develop fingermarks on other substrates pertinent to criminal investigations using a higher-grade iPhone or camera for picture improvement, while comparing the sensitivity of alizarin red lake, ninhydrin, and DFO. Additionally, integrating alizarin red lake into hybrid detection methods, such as combining it with surface-enhanced Raman spectroscopy (SERS) or time-resolved fluorescence imaging, may improve its forensic performance.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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