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TECHNICAL NOTE

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Laser-Assisted Thin-Layer Chromatography and Luminescence of Fingerprints: An Approach to Fingerprint Age Determination

In an earlier paper [*1*] we described a new method for the detection of latent fingerprints that involved illuminating an exhibit with high-intensity argon-laser light and viewing the resulting yellow-green inherent fingerprint luminescence. The range of utility of the method could be extended, when needed, by treatment of the exhibit under scrutiny with fluorescent materials.[2]

It was also stated that old fingerprints, as viewed by the laser method, differed in color from fresh prints, exhibiting an orange rather than a yellow-green luminescence. This difference must have arisen from chemical transformations of luminescent components in the latent print. It appears possible that spectroscopic analysis coupled with a knowledge of the stability of the luminescent components of palmar sweat might allow the determination of the age of the fingerprint. This would be of great importance to forensic science.

The implementation of this concept requires two main areas of research. First, it must be demonstrated that spectroscopic measurements on a single fingerprint are feasible. In this paper we demonstrate that this is indeed the case. Second, it is necessary to identify the luminescent components of fingerprint residue and to elucidate the nature and rate of chemical transformations as a function of time and environmental conditions. We describe a thin-layer chromatographic (TLC) study of fingerprint residue, which, coupled with laser luminescence investigation, allows one to isolate the luminescent components of palmar sweat.

Although our work in this aspect has necessarily been qualitative and incomplete, it is hoped that it will provide those more experienced in the field of analysis of biological compounds with the necessary ground work to permit identification of the compounds responsible for fingerprint luminescence.

Experimental Procedures

Thin-Layer Chromatography

Fingerprint material was collected by wiping fingers and palms (of one person for each chromatogram) with a cotton swab soaked in diethyl ether and extracting the residue into

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[2]E. R. Menzel and J. M. Duff, "Laser Detection of Latent Fingerprints—Staining with Fluorescers," unpublished report.

ether solution. The solution was concentrated to about 1 ml and was streaked onto a 20 by 20 by 0.025-cm commercial precoated TLC plate (Macherey-Nagel silica gel G, without ultraviolet indicator, available from Brinkmann, Inc.). The chromatogram was developed in room light in diethyl ether or acetone solvent for 11 to 13 cm by using tank saturation.

No bands were discernible under normal room light. However, when a chromatogram was illuminated by argon-laser light (4 W, all lines) and viewed through laser safety goggles (Fisher 11-409-50A), six luminescent bands were seen. These bands, shown in Fig. 1*A* and

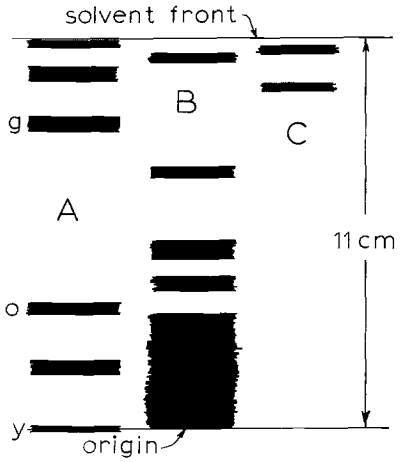

FIG. 1—*Diagram illustrating components of fingerprint residue separated by TLC (ether development) on silica gel;* (A) *bands detected by laser;* (B) *new bands detected by laser following UV irradiation; and* (C) *bands detected by iodine vapor. (Code:* y = *yellow,* o = *orange, and* g = *green).*

outlined in Table 1, consisted of a strong yellow band at the origin, an orange band at R_f = 0.31, a strong green band at R_f = 0.78, and three relatively weak green bands at R_f = 0.16, 0.91, and 0.98. Inspection of the chromatography plates under short (254 nm) or long (365 nm) ultraviolet (UV) light showed no bands in most cases. However, in one case where a very heavy deposit of residue was chromatographed, UV illumination revealed three extremely weak luminescent bands corresponding to the strongest bands detected by laser illumination (Components 1, 3, and 4 of Table 1).

Exposure for about 1 min of a developed plate to UV light from a low-pressure mercury lamp (Oriel C-13-61) caused new, luminescing, green bands to become visible on subse-

TABLE 1—*Luminescent components of fingerprint residue detected by laser following TLC separation.*

Component	R_f Value		Color	Relative Intensity
	Ether	Acetone		
1	0	0	yellow	strong
1a	0	0.06	green	weak
1b	0	0.17	green	medium
2	0.16	...	green	weak
3	0.31	0.81	orange	medium
4	0.78	0.87	green	strong
5	0.91	...	green	weak
6	0.98	...	green	weak

quent laser examination. These five new bands (one a long, tailing band indicative of decomposition on the plate) are shown in Fig. 1*B*.

Treatment of the TLC plate with iodine vapor revealed two bands, shown in Fig. 1*C*, of high R_f values (0.87 and 0.98), which are attributable to lipid substances. Spraying with ninhydrin reagent (0.1% in isopropyl alcohol) and heating to 150°C revealed no bands.

Development of the TLC in the more polar solvent, acetone, eluted two new green luminescent bands from the polar yellow band. With acetone the original orange and strong green bands (Components 3 and 4 of Table 1) were observed at much higher R_f values.

Emission Spectroscopy

The luminescence spectrum of a single fingerprint, deposited on a glass slide, was measured. The light from an argon-laser (4 W, all lines), chopped with a mechanical light chopper, illuminated the fingerprint. The fingerprint luminescence, prefiltered with a laser safety goggle filter, passed through a monochromator and was incident on an EMI 9785B photomultiplier tube. The photomultiplier signal was processed with a lock-in amplifier and recorded on a strip chart recorder. Background subtraction was performed by illuminating bare glass and subtracting the resulting signal from the fingerprint luminescent bands from the polar yellow band. With acetone the original orange and strong green bands (Components 3 and 4 of Table 1) were observed at much higher R_f values.

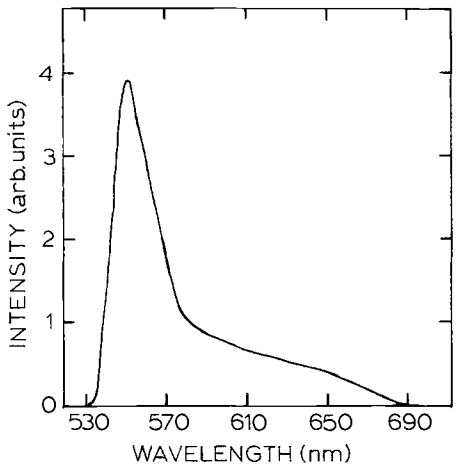

FIG. 2—*Emission spectrum of a single fingerprint deposited on glass.*

A similar procedure was employed to measure the emission from the three strongest bands (Components 1, 3, and 4 of Table 1) on the ether-developed TLC plate. Additionally, the material corresponding to Bands 3 and 4 was eluted from the silica gel with methanol. The resultant solutions were examined with a Perkin-Elmer MPF-4 fluorescence spectrophotometer. The results of these spectroscopic studies are summarized in Table 2.

Discussion

Fingerprint Spectroscopy

Figure 2 illustrates the luminescence characteristics of a fresh fingerprint as seen through a laser goggle filter. The emission is dominated by a relatively intense peak at 550 nm (we

TABLE 2—*Luminescence characteristics of some components in fingerprint residue.*

Component	Medium	Emission Maxima, nm	Excitation Maxima, nm
1	silica gel[a]	535,565	...
3	silica gel,[a] methanol	580	...
		550	530
4	silica gel,[a] methanol	500 (broad)	...
		470,500	370, 420, 450

[a]Excitation by laser.

note, however, that this peak is affected by the transmittance of the filter) which accounts for the greenish-yellow hue of the laser-induced luminescence from fresh prints. Also significant is the broad weak band that tails into the red. It is tempting to suggest that decomposition of the component(s) responsible for the strong green emission and concomitant predominance of the yellow to red emission (from stable compounds) accounts for the change in observed color of old fingerprints. However, given the very complex mixture of luminescent material involved, this may be too simple an explanation.

The most important point regarding Fig. 2 is that the spectrum was obtained with instrument settings far from ultimate detection sensitivity. It might be possible to approach the aging problem in an empirical manner by performing spectroscopic measurements on fingerprints, on a variety of substrates and under several ambient conditions, as a function of time.

Identification of Luminescent Components

The observed profusion of laser-detected TLC-separated components in fingerprint residue indicates a greater diversity of luminescent constituents than was suspected on the basis of our initial spectroscopic study [*1*]. At least eight luminescent bands (Table 1) and five potentially luminescent components (Fig. 1*B*) are present. Compounding the problem are (1) a marked instability of many biologicals to light, solvent, and silica gel; (2) the diversity of chemical modifications of known fluorescers, such as riboflavin and pyridoxine, which would result in a number of TLC bands for the same luminescent entity; and (3) the fact that our method of perspiration collection (swabbing with ether) may have eluted extraneous materials from the epiderm. A major aim of the present study was to pinpoint the key luminescent components in fingerprint residue in order that they may be identified by others more skilled in the field. These are, in our estimate, the strong green band (4), the orange band (3), and the strong yellow band (1) of Table 1. The luminescence characteristics of the former two are described in Table 2. We note that the emission spectrum of Component 4 in methanol solution shows peaks at 470 and 500 nm, in good correspondence with bands reported earlier for unseparated fingerprint residue [*1*]. Respective excitation peaks were found at 370, 420, and 450 nm. These agree with peaks in the riboflavin absorption spectrum [*2*]. Thus there is a distinct likelihood that Component 4 of Table 1 and perhaps a number of the other observed green-luminescing bands may be due to riboflavin derivatives. In this context we also suspect that the new bands appearing on UV irradiation might be attributable to lumiflavine, a strongly luminescent material derived from the photodecomposition of riboflavin [*3*]. We have not identified the orange luminescing band (3 of Table 1) but note that its solution emission maximum at 550 nm and excitation maximum at 530 nm correspond closely with our earlier results on unseparated fingerprint residue [*1*].

The luminescence spectrum of Component 1 on the TLC plates developed with ether

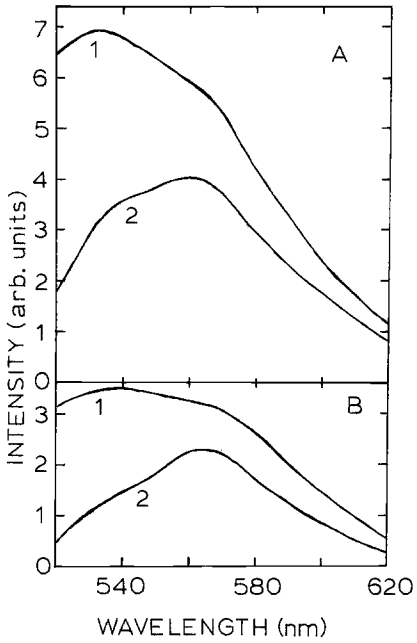

FIG. 3—*Emission spectra of* (A) *B-vitamin tablet with* (1) *488-nm laser excitation and* (2) *514.5-nm laser excitation and* (B) *the polar yellow strong component of fingerprint residue with corresponding excitation wavelengths.*

was obtained by direct illumination of the plate with the argon-laser, using 488- and 514.5-nm excitation wavelengths. Luminescence peaks, which change relative intensities with change of excitation, were found at 535 and 565 nm. The spectra are shown in Fig. 3*B*. Figure 3*A* shows the luminescence spectra of a B-vitamin tablet, containing vitamins B_1, B_2 (riboflavin), B_6 (pyridoxine), nicotinamide, and calcium *d*-pantothenate, obtained under corresponding excitation conditions. The obvious similarity between the two sets of spectra suggests that the predominant luminescence from the yellow TLC band is also due to a B-vitamin. However, we do not know which component(s) of the B-vitamin tablet gives rise to the observed luminescence.

It has not escaped our attention that UV irradiation might represent a means of augmenting the laser-induced fingerprint luminescence. However, no discernible increase of observed fingerprint luminescence was found for UV preirradiated latent fingerprints. It may be that the photochemistry of the TLC-isolated components differs from that in latent fingerprints. Still, a suitable latent fingerprint treatment procedure coupled with UV irradiation, and followed by laser illumination, may allow fingerprint luminescence enhancement.

Laser-Induced Luminescence

Our results indicate that laser illumination represents a sensitive TLC detection method for suitable luminescent materials. The action of UV light, which converted invisible components to luminescing species, constitutes a useful extension of the procedure. We also found that urine and saliva showed a number of strong green to orange luminescent components when developed chromatograms were examined under laser light. Thus the method might be of general utility in the analysis of exocrine fluids and other areas of analytical biochemistry. The sensitivity of the method has yet to be compared to that of alternative

chemical detection methods [*4*] and to commercially available TLC scanners. Nonetheless, as the present study has shown, the method is convenient and was superior to the limited number of alternative procedures tried. Furthermore, it should be possible, by using different laser wavelengths, to extend the technique to a greater range of materials.

Acknowledgment

We thank Mr. B. G. Dalrymple of the Ontario Provincial Police for acquainting us with current fingerprint detection methods and problems associated with them.

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