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## Improved Enhancement of Ninhydrin Developed Fingerprints by Cadmium Complexation Using Low Temperature Photoluminescence Techniques

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**ABSTRACT:** Fingerprints developed with ninhydrin form stable, colored complexes when treated with various metal salts. Many of these colored complexes can be used to increase the sensitivity of detection of latent prints because of photoluminescent properties. The intensity of this photoluminescence is increased at low temperature (77K), and this is a common characteristic of each of the complexes formed with salts of the IIb group of the Periodic Table. Spectral characteristics of these Group IIb metal complexes and the influence of environmental factors on their formation are reported. These data have helped determine optimal conditions for the enhancement of ninhydrin developed fingerprints. Taking into account spectral characteristics, solubility, versatility, stability, and reproducibility, the use of the cadmium nitrate tetrahydrate complex is advocated for general use for fingerprint enhancement. The use of zinc nitrate is favored if toxicological considerations are paramount, but ninhydrin development has to be carefully controlled if optimal results are to be obtained. Limited applications for mercuric complexes are found when a red shift is desired to remove background effects.

**KEYWORDS:** forensic science, fingerprints, ninhydrin, luminescence, fingerprint enhancement, photoluminescence, IIb metal complexes, papers

Ninhydrin (2,2-dihydroxy-1,3-indanedione) is the most widely used chemical reagent for developing latent fingerprints on paper. It reacts with the amino acid component of the eccrine gland secretions to give a purple-colored product known as Ruhemann's purple [1].

When ninhydrin developed prints are treated with various metal salts the fingerprint color changes as a result of the formation of coordination complexes.

Recently, Herod and Menzel [2] reported that the colored complex formed with zinc chloride showed strong fluorescent properties following illumination from an argon ion laser ( $\lambda_{\text{ex}} = 488 \text{ nm}$ ). In this way, increased sensitivity and improved fingerprint details was observed. Increased photoluminescence can be obtained by cooling the developed prints in liquid nitrogen (77K) and a more cost-effective method of illumination using a filtered xenon arc lamp [3] has been described. However, poor results were obtained on some surfaces such

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as newspaper and yellow postal envelopes. The present paper investigates other metal complexes in this role as fingerprint agent.

## Materials and Methods

### Reagents

All reagents were laboratory grades with ninhydrin obtained from Sigma Chemical Co. (USA);  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CdI}_2$ ,  $\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{HgBr}_2$ ,  $\text{HgI}_2$ ,  $\text{Hg}(\text{CH}_3\text{CO}_2)_2$ ,  $\text{ZnBr}_2$ ,  $\text{ZnI}_2$ ,  $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoBr}_2 \cdot \text{H}_2\text{O}$ , and  $\text{CuBr}_2$  from BDH (UK);  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{AgBr}$ ,  $\text{CaBr}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  from May & Baker (UK);  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , acetic acid, and solvents from Ajax Chemicals (Australia); 1,1,2-trichlorotrifluoroethane from ICI (Australia); and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  from Hopkins & Williams (UK). Pure Ruhemann's purple was produced by Mr. C. Lennard in our laboratory [4].

All latent fingerprints were treated with the nonflammable ninhydrin (NFN) formulation reported by Morris and Goode [5]. Preliminary results indicate that comparable prints are obtained using the more easily prepared "Ninhydrin: Plus Two" formulation reported by Tighe in 1984 [6].

Metal salts were dissolved in a minimal amount of an appropriate organic solvent (methanol or ethanol) and diluted in 1,1,2-trichlorotrifluoroethane in the presence of glacial acetic acid (2% v/v) (final concentration approximately  $3.25 \times 10^{-2} M$ ). (Note: 1 g  $\text{Cd}(\text{NO}_3)_2$  in EtOH (12 mL) diluted with acetic acid (2 mL) made up to 100 mL with 1,1,2-trichlorotrifluoroethane.)

### Samples

Fingerprints were deposited on four types of paper surfaces and allowed to dry for at least 24 h before ninhydrin treatment.

Three types of paper were selected because of their widespread use as well as their problematic effect on the detection of weak fingerprints developed with ninhydrin and enhanced with  $\text{ZnCl}_2$ .

They were

- (1) yellow postal envelopes (Croxley "Tuftare Kraft" DRG, Australia),
- (2) manila postal envelopes (Croxley "Manila Envelopes" DRG, Australia), and
- (3) newsprint paper (mechanical wood pulp with strong absorbency, Albury Papermill, Australia).

The fourth paper was selected because of its low photoluminescence background at experimental wavelengths and temperatures.

- (4) filter paper (Whatman No. 541, WSR, Balston Ltd., UK).

All photoluminescence spectra were studied on this type of paper.

### Ninhydrin Treatment

Samples were dipped briefly in the ninhydrin solution. One set of samples was air dried for 24 h in the dark at room temperature. The ninhydrin reaction was accelerated for a second set of samples. This was achieved by developing in a microwave oven containing a water-saturated cotton pad, operating at full power setting for 5 min and 80% of fan air circulation blocked. For a third set of samples, the ninhydrin reaction was accelerated by overheating the sample by contact with a hot iron.

### *Complexation*

Ninhydrin developed prints were dipped in a solution of the metal salt and air-dried. The reaction was rapid and the color change could be observed as soon as the solvent was evaporated. When the relative air humidity was low ( $\leq 50\%$ ), a brief exposure to a jet of steam was necessary for completion of the reaction. Microwave oven treated samples did not require further steaming provided the secondary treatment was carried out without delay.

### *Effect of Water on Complexation*

The effect of water on the complexation of Ruhemann's purple with zinc and cadmium salts was studied by treating pure Ruhemann's purple separately with zinc nitrate hexahydrate and cadmium nitrate tetrahydrate (equimolar concentrations). This was done in ethanol containing less than 3% water and in the presence of over 12.5% (v/v) water, respectively.

The absorption spectra of the resulting solutions were compared.

### *Instruments*

Photoluminescence spectra were recorded with a Perkin Elmer MPF-44B fluorescence spectrometer linked to a DC SU-2 correction unit. Various instrumental settings for wavelengths and sensitivity were calibrated essentially according to the manufacturer's manual. All measurements were done at liquid nitrogen temperature (77K).

Room temperature absorption spectra were made on a Cary 219 Spectrophotometer (Varian, USA) at a range setting of 1. A Rank Litton "Meal in One" microwave oven, model AU1065.0 (Litton Microwave Cooking Products, USA) was used for steam treatments. A Sunbeam iron (Sunbeam "Shot of Steam" iron, Australia) was used at full power setting (that is, "linen"), without steam.

Photographs were taken in the automode with an Olympus OM-2 camera (Japan) fitted with a 50-mm macro-lens and Kodak (Eastman Kodak, USA) technical Pan Films 2415 used at 64 ASA. Processing was done in a Kodak (Eastman Kodak, USA) HC-110 developer dilution "D" for 10 min followed by a stop bath and a fixer bath manufactured by Kodak (Australasia) Pty. Ltd., Australia according to manufacturer's specifications.

Visualization of luminescent fingerprints was done with a Xenon Arc Lamp (Ealing Stabilarc 250) fitted with a 150-W xenon tube together with appropriate filters and at liquid nitrogen (77K) temperature.

The filters for excitation were

1. A four-cavity interference filter with peak transmittance at 490 nm and a half bandwidth of 40 nm for zinc-RP complexes.
2. A four-cavity interference filter with peak transmittance at 510 nm and a half bandwidth of 40 nm for cadmium-RP complexes.
3. A four-cavity interference filter with peak transmittance at 550 nm and a half bandwidth of 40 nm for mercuric-RP complexes. The maximum excitation wavelength was obtained by tilting the filter to shift its peak transmittance at 525 nm. The specification for these filters are designed for normal incidence. As the angle of incidence is increased, the peak wavelength is shifted to shorter wavelengths. For angles below  $30^\circ$ , the shape of the band pass does not change appreciably except for a small reduction in transmission [7].

The barrier filters were all four-cavity interference filters with peak transmittance at 550 nm and a half bandwidth of 40 nm for zinc II-RP complexes, 585 nm and a half bandwidth of 40 nm for cadmium II-RP complexes, and 600 nm and a half bandwidth of 40 nm for mercuric-RP complexes.

The fingerprinted document was placed in a foam plastic tray, secured with pins, and covered with liquid nitrogen. The tray was covered with a hot air warmed glass plate to avoid water condensation.

## Results

### *Ninhydrin Development*

The development of fingerprints with ninhydrin at room temperature gave consistent and good results as long as sufficient relative humidity (60 to 80%) was present, but the process was slow. It has long been recognized that humidity plays an important role in the development and the speeding up of the reaction by steaming has been advocated [8]. Excess humidity is detrimental as amino acids are water soluble and a reduction in sharpness can be observed. It was found that uncontrolled steaming could lead to high background and a need to establish standardization of the steaming process has led to the development of the microwave oven technique (*loc cit*).

Prints obtained by room temperature or microwave development were each suitable for secondary treatment involving photoluminescence enhancement. In contrast, the overheated samples showed a high background and caused problems (*vide infra*).

### *Complexation*

Purple-colored ninhydrin developed prints were treated with metal salts to form orange-colored prints with zinc; red colored prints with cadmium, mercury, nickel, cobalt, calcium, iron, copper, and silver, and blue-colored prints with magnesium [9].

The presence of water ( $\geq 50\%$  relative humidity or microwave technique) was necessary for complexation to occur, whence the reaction was fast and the color change was visible soon after the carrier solvent evaporated off from the sample. Photoluminescence at low temperature (77K) was observed for many metal complexes, but only those based on metals of the IIb group of the Periodic Table (zinc, cadmium, and mercury) showed adequate intensity and spectral characteristics suitable for use in the enhancement of ninhydrin developed fingerprints.

The nature of the salt used for complexation, the presence of water, and the amount of RP were found to be critical.

### *Effect of Ninhydrin Overheating*

Overheating created a purple-colored background from the residual ninhydrin in the paper. Treatment of such prints with a metal complexing reagent and subsequent observation of the resultant photoluminescence did not improve the contrast between the print and the background. In the case of the zinc reagent, the usual orange-colored complex was replaced, in part, by a brownish-red complex which was nonluminescent; such areas appeared as black marks on the photographed print (see Fig. 1).

With cadmium or mercuric salts this problem was less acute as complexation still occurred and, although the background photoluminescence was increased, weak prints could still be observed in the photoluminescence mode (Fig. 2).

### *Effect of Water on Complex Formation and Its Stability in Solution*

As previously reported [3], some moisture is necessary for the formation of the complex between zinc and Ruhemann's purple. Normal atmospheric humidity was usually sufficient.

In solution, zinc salts produced immediately an orange-colored complex whereas cad-

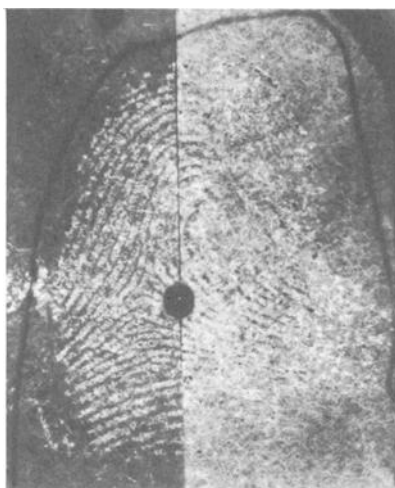


FIG. 1—Weak fingerprint developed with ninhydrin, enhanced by treatment with zinc nitrate and photoluminescent visualization ( $\lambda_{ex} = 490 \text{ nm}$  and  $\lambda_{em} = 550 \text{ nm}$ ). The ninhydrin development was accelerated by the microwave oven process on the left and by overheating with a dry iron on the right. Note the dark ridge segments and the high background luminescence created by the extreme conditions used on the right.



FIG. 2—Weak fingerprint developed by overheating the ninhydrin reaction. Left: enhanced with zinc nitrate. Right: enhanced with cadmium nitrate. (Photographic conditions ideal for zinc-RP and cadmium-RP complexes, respectively.)

mium salts and mercuric salts produced a red-colored complex. Their absorption spectra are shown in Fig. 3 together with the spectrum of Ruhemann's purple. Little water (up to 3%) did not modify the spectra significantly. With excess water (>12.5%), both cadmium and mercuric complexes spectra were unaltered, whereas the zinc complex changed and a peak caused by Ruhemann's purple at 580 nm appeared in the spectrum, with a simultaneous decrease of absorbance at 490 nm (maximum for RP-zinc complex) (Fig. 4). This indicated that zinc complex is not stable in the presence of significant amounts of water.

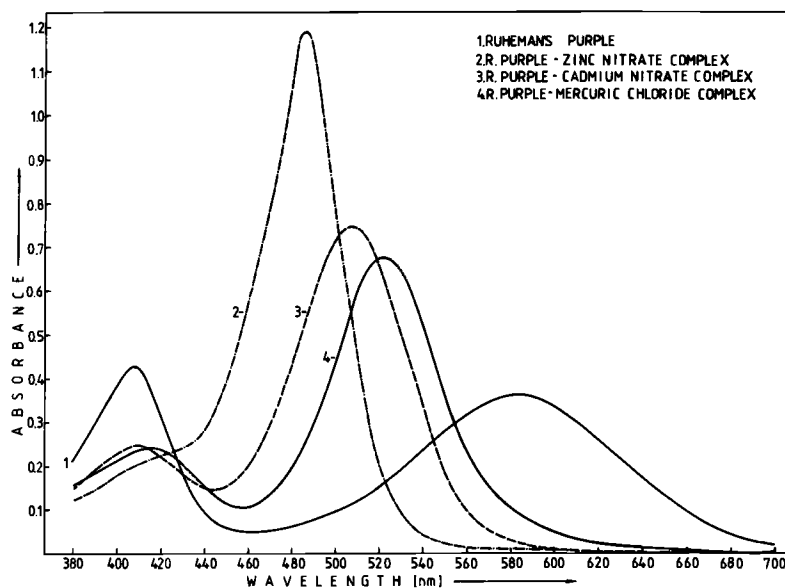


FIG. 3—Absorption spectra of Ruhemann's purple and its complexes with zinc II, cadmium II, and mercury II in absolute ethanol.

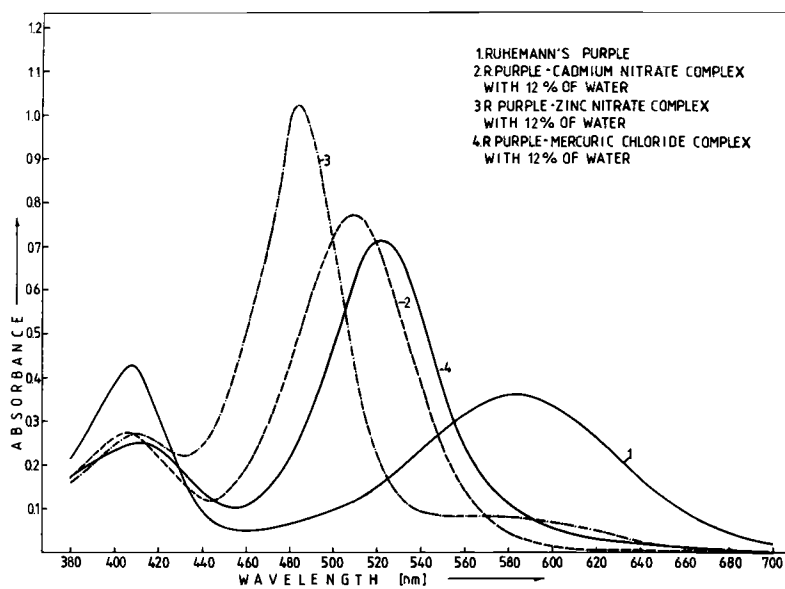


FIG. 4—Absorption spectra of Ruhemann's purple and its complexes with zinc II, cadmium II, and mercury II in absolute ethanol and 12.5% water.

Clearly, moisture has a marked effect on the stability of the Ruhemann's purple-zinc complex. This could explain the inconsistent results obtained with papers that have high absorbent properties, that is, contain absorbed water.

#### *Photoluminescence Spectra of Zinc, Cadmium, and Mercuric Complexes on Filter Paper*

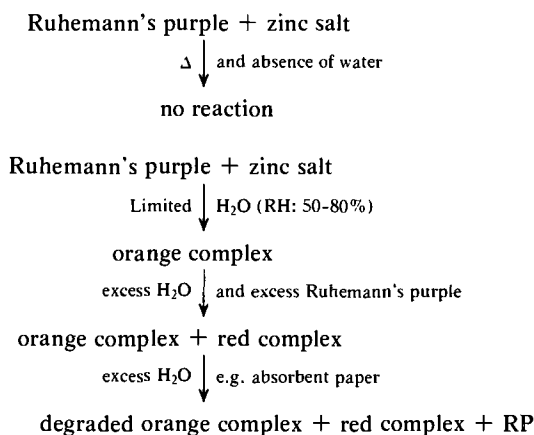
**Zinc Complexes**—Zinc complexes showed weak photoluminescence at room temperature which was best observed using high intensity excitation such as the 488-nm band of an argon ion laser [2]. The quantum yield was greatly increased at low temperature (77K) and removed the need for such a high power excitation source [3].

All the zinc salts examined showed very similar photoluminescence characteristics [ $\text{ZnBr}_2$ ,  $\text{ZnCl}_2$ ,  $\text{ZnI}_2$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ ]. The excitation spectrum showed two absorption bands (Fig. 5) with maxima at  $\lambda = 410$  nm and  $\lambda = 495$  nm, respectively ( $\epsilon \cong 12\,000$  and  $58\,000$  in solution [4]).

In an earlier paper [3], it was reported that weak and strong prints did not form a complex when the paper was thoroughly predried (in an oven at  $80^\circ\text{C}$ ). The prints would only develop the orange-colored complex in the presence of some moisture (atmospheric humidity  $> 50\%$ ; light steaming). Further steaming (excess) of strong prints created a red complex.

This orange-colored complex exhibited a single emission band (maximum at 540 nm) (Fig. 6), while the red-colored complex showed two sets of emission bands maxima at  $\lambda = 540$  nm and  $\lambda = 570$  nm (Fig. 6). It was further observed that when excited at  $\lambda = 495$  nm it did not favor either of the two emission bands, whereas excitation at  $\lambda = 410$  nm favored the red-shifted band emission (Fig. 6).

This suggested that the following reaction sequence as follows occurs between Ruhemann's purple and zinc salts:



This proposal indicates why the conditions for production of the zinc complex were difficult to control and moisture had a marked influence. These variations influence the quality of the final results in the development of fingerprints as shown in Fig. 9.

#### *Complexes Made With Cadmium Salts*

Complexes made with cadmium salts did not show any room temperature photoluminescence, even when excited with an argon ion laser operating in the powerful all lines lasing mode or specific wavelengths (488 or 514.5 nm) at energies up to 2 W. At liquid nitrogen

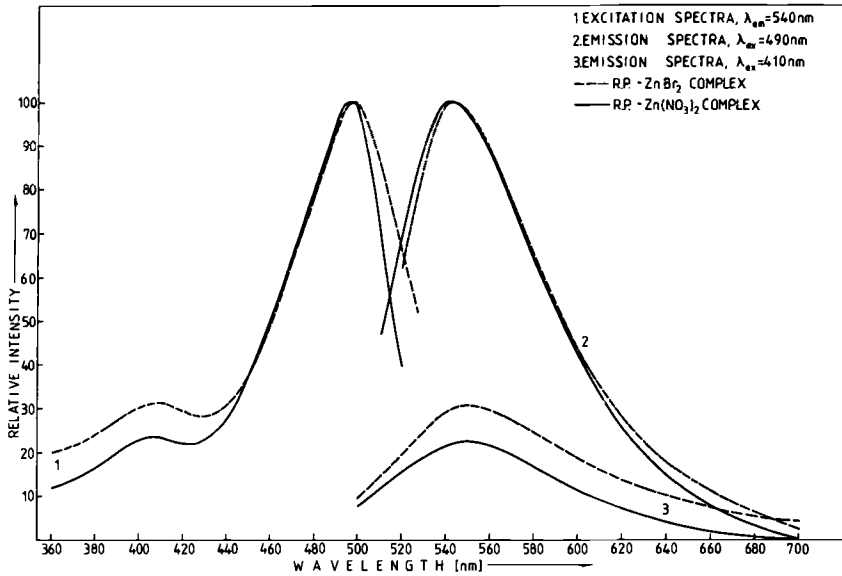


FIG. 5—Photoluminescence spectra of Ruhemann's purple complexes with zinc nitrate and zinc bromide on filter paper at 77K.

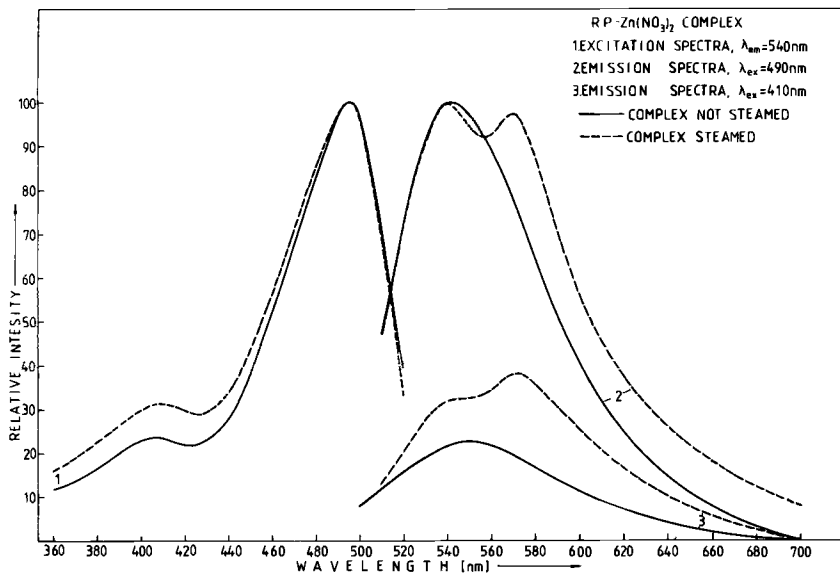


FIG. 6—Photoluminescence spectra of Ruhemann's purple complex with zinc nitrate tetrahydrate on filter paper at 77K, unsteamed and after steaming showing the emergence of a second photoluminescence peak at  $\lambda = 570 nm$ .



temperature (77K), intense luminescence was observed using the 488-nm line or the xenon arc lamp (510-nm filter).

Ruhemann's purple-cadmium complexes formed from  $\text{CdBr}_2$ ,  $\text{CdCl}_2$ ,  $\text{CdI}_2$ ,  $\text{Cd}(\text{CH}_3\text{CO}_2)_2$ , and  $\text{Cd}(\text{NO}_3)_2$  all showed similar photoluminescence characteristics which were not greatly influenced by development conditions.

Ruhemann's purple-cadmium complexes showed an excitation spectrum consisting of two absorption bands (Fig. 7) with maxima at  $\lambda = 410$  nm and  $\lambda = 510$  nm ( $\epsilon \cong 12\,000$  and  $40\,000$  solution [4]).

The emission spectrum produced by excitation at 510 nm was comprised of a single band, maximum  $\lambda = 585$  nm. No change in the position of this maximum was observed after steaming, but the band narrowed slightly (Fig. 8). Excitation at  $\lambda = 410$  nm broadened the emission spectrum of Ruhemann's purple-cadmium complexes.

It was found that steaming was not necessary for complex formation with cadmium salts except in dry conditions ( $\leq 50\%$  relative humidity) when it helped complexation. Although some water was found to be necessary for complex formation [4], experimental conditions were far less critical than with zinc. Even in the presence of excess water, the photoluminescence of the cadmium complex remained the same, and results were dramatically improved when compared with those obtained by zinc enhancement, on highly absorbent surfaces. This is illustrated in Fig. 9 in which cadmium nitrate was used for complexation. The increased separation between excitation and emission wavelengths, as well as the general red shift obtained with the cadmium complex, increased photoluminescence contrast on yellow paper surfaces. This revealed fingerprints which were not visible in similar zinc complexes. This was a dramatic improvement over zinc enhancement and is illustrated in Fig. 10.

#### Complexes Made With Mercuric Salts

Most mercuric salts were poorly soluble in the experimental conditions. Only mercuric chloride, bromide, and, to a lesser extent, acetate were suitable.

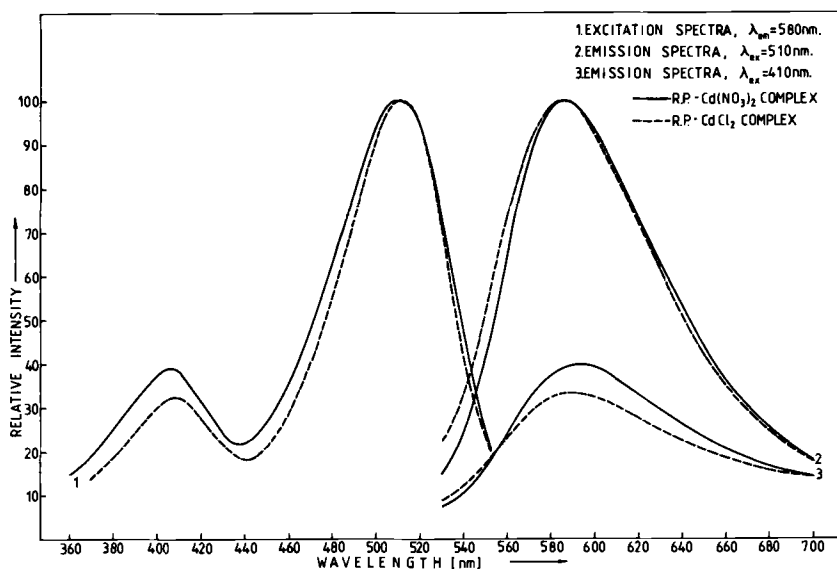


FIG. 7—Photoluminescence spectra of Ruhemann's purple complexes with cadmium II salts on filter paper at 77K.

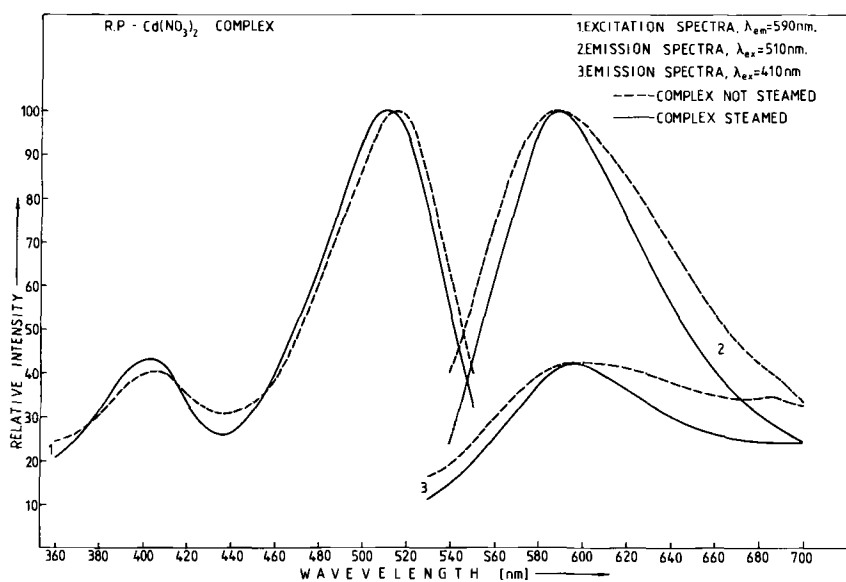


FIG. 8—Photoluminescence spectra of Ruhemann's purple complex with cadmium nitrate on filter paper at 77K and the effect of steaming during complex formation.



FIG. 9—Fingerprint on newspaper developed with ninhydrin and the microwave oven technique (a) in white light, subsequently treated with zinc nitrate (left) and cadmium nitrate tetrahydrate (right); (b) in high relative humidity conditions (> 80%); and (c) after drying for 30 min at 60°C. Photographic conditions optimal for RP-Zn complex on the left and RP-Cd complex on the right (see text).

These mercuric complexes did not show any room temperature photoluminescence; however, at low temperature (77K), they were highly photoluminescent.

The absorption spectrum showed two excitation bands with maxima at  $\lambda = 410$  nm and  $\lambda = 525$  nm (Fig. 11) ( $\epsilon \cong 11\,000$  and  $37\,000$ , respectively, in solution [4]).

The photoluminescence of Ruhemann's purple-mercury complexes was influenced both by humidity and the anion of the salt. Unsteamed  $\text{HgCl}_2$  and  $\text{HgBr}_2$  showed two photoluminescence emission bands with maxima at  $\lambda = 585$  nm and  $\lambda = 620$  nm. The longer wavelength band was dominant in both cases (Fig. 11). Steaming reduced almost completely the second band for  $\text{HgCl}_2$ , whereas, it combined these two bands to form a single broader band with a maximum at  $\lambda = 600$  nm for  $\text{HgBr}_2$  (Fig. 12). In dry conditions (relative humidity < 50%), complexation was helped by brief steaming.



FIG. 10—Fingerprint on yellow envelope paper developed with ninhydrin and enhanced with zinc nitrate on the left and cadmium nitrate on the right. Photograph taken under optimal excitation/emission conditions for zinc complex photoluminescence and under optimal conditions for cadmium complex photoluminescence, respectively.

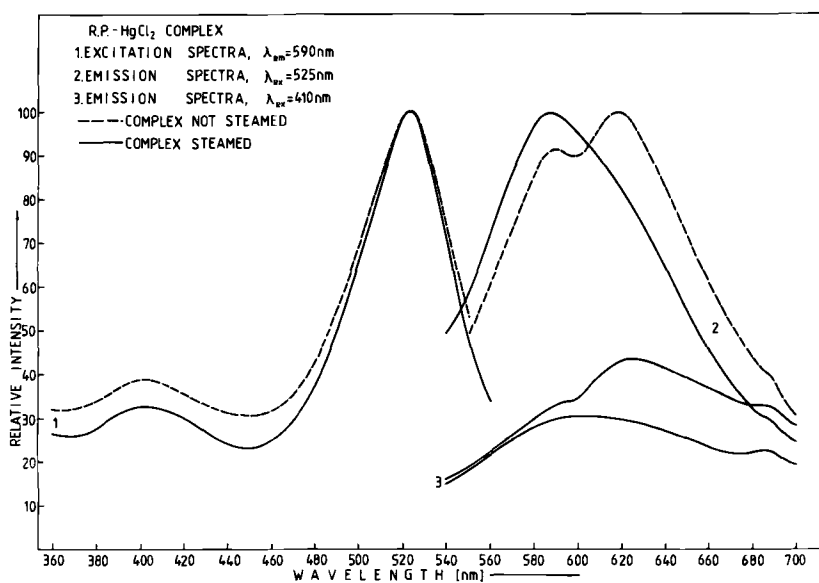


FIG. 11—Photoluminescence spectrum of Ruhemann's purple complex with mercuric chloride on filter paper at 77K and the effect of steaming during complex formation.

## Discussion

Numerous metal salts produce colored complexes with Ruhemann's purple. They have been used as toning reagents to improve the contrast of fingerprints developed with ninhydrin on highly colored surfaces [9]. Among these complexes, those produced with zinc are reported to display photoluminescence [2] at room temperature which could be enhanced by cooling [3].

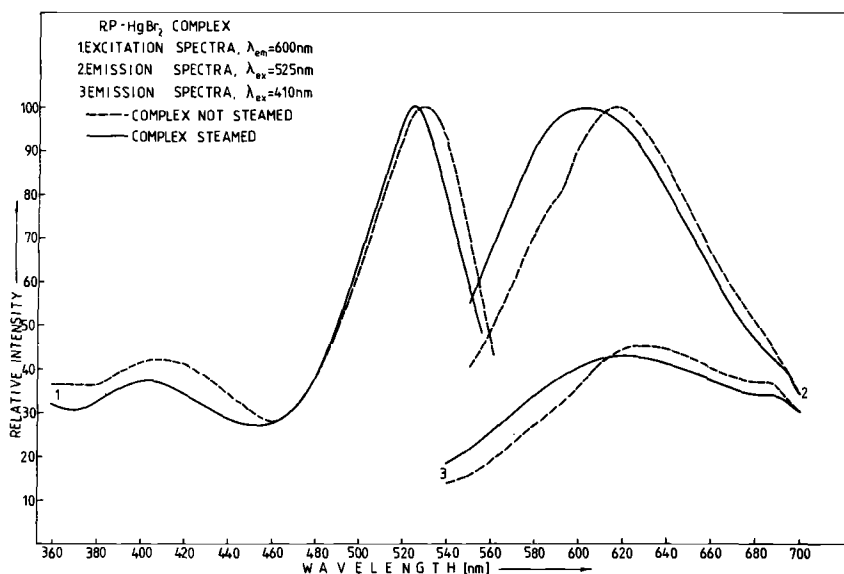


FIG. 12—Photoluminescence spectrum of Ruhemann's purple complex with mercuric bromide on filter paper at 77K and the effect of steaming during complex formation.

Complexes formed with metal salts of the IIb group of the Periodic Table (zinc, cadmium, and mercury) were found to be highly photoluminescent after cooling to liquid nitrogen temperature. This prompted their evaluation in the enhancement of weak ninhydrin developed fingerprints as reproducibility problems had been encountered with ZnCl<sub>2</sub> depending on the technique used to develop the ninhydrin print and the presence or absence of moisture. Detection problems were also encountered on surfaces such as yellow postal envelopes, manila envelopes, brown cardboard, and newspaper which reduced its potential for case work studies. Problems were encountered in several case studies and three factors were seen to influence the outcome of the fingerprint enhancement.

In two cases, the ninhydrin development had been speeded up by heating with a hot iron in direct contact with the print. Poor or no photoluminescence was observed after complexation with zinc chloride. In one other case, fingerprints on newspaper had been developed with ninhydrin in the presence of excess environmental water. Secondary treatment with zinc chloride failed to reveal good photoluminescence. This was found to be a common problem on most highly porous papers, especially under conditions of high relative humidity. Secondary treatment could be achieved, but only after drying the sample, when good photoluminescence was observed.

The third problem was the high background luminescence of some papers at the wavelengths used for photoluminescence enhancements. This led to the investigation of factors influencing the development and observation of a photoluminescent fingerprint after complexation.

It was found, and it is worth repeating, that the ninhydrin development technique was critical for fingerprint detection and subsequent enhancement, especially in the ZnCl<sub>2</sub> process. The development should preferably be done at room temperature and with a relative humidity of 60 to 80% for 24 to 48 h. Any speeding up is likely to increase the background and decrease the chances of an identification, but when speed is of utmost importance, it should be done under carefully controlled conditions such as the microwave oven technique.

Secondary treatment or enhancement by complexation with zinc salts gave excellent

results on numerous common paper surfaces (bond paper, nonabsorbent paper, and so forth). The treatment is safe because of the low toxicity of zinc salts. Nevertheless, it suffered the drawbacks that the enhancement technique had to be carefully controlled if reproducible results were to be obtained. It has been demonstrated that the use of heat and the presence of excess moisture, especially on highly absorbing surfaces, greatly influenced the quality of the enhancement as well as the reproducibility of the development. The separation between excitation and emission wavelength of the zinc complex was also relatively small (45 nm) and this created a technical problem: the need for filters that did not overlap for excitation and detection, which, at the same time, showed a high transmittance. These are difficult and expensive to manufacture. The use of the 488-nm laser line did not suffer from this limitation because it allowed the use of a barrier filter with less stringent design features, and, in addition, it could be effected at room temperature. Notwithstanding, the high cost of a laser precludes its use in many laboratories.

Cadmium complexes showed definite technical advantages over zinc complexes. They suffered less from ninhydrin development conditions and gave reproducible and stable results under extreme conditions of heat and moisture (as illustrated in Figs. 1 and 2). The separation between excitation and emission wavelengths was extended to 75 nm (compared to 45 nm for zinc complexes) which facilitated the selection of filters with qualities suitable for the purpose of fingerprint enhancement (no overlap and high sensitivity). This feature made the use of cadmium salts attractive. It also proved very successful on difficult surfaces such as newsprint, manila, and yellow papers which were at the source of the problems encountered when zinc enhancement was attempted (Figs. 1, 2, 9, and 10). Two disadvantages of the cadmium treatment were the toxicity of cadmium salts which are dangerous when ingested and after long-term exposure. The small concentrations used, the low volatility, and their stability make the danger minimal when good laboratory practices are enforced. The other drawback was the need to cool the fingerprint in order to make it photoluminescent, but then, results were extremely rewarding as illustrated in Figs. 2 and 10.

Mercuric salts also showed good properties for fingerprint enhancement. They formed complexes which had a separation between excitation and emission wavelengths of between 60 and 95 nm depending on the anion of the salt and the amount of moisture present. The nature of the anion and the treatment conditions had to be controlled for reproducible complexation. These salts could be used in cases where a high background photoluminescence is present between 550 and 590 nm to remove background interference. Mercuric salts suffer nevertheless major drawbacks owing to their high acute toxicity, relative volatility, and light sensitivity. They are not recommended for general use.

One other major consideration in criminal investigations is the need to use reagents that alter as little as possible the evidence under consideration. Written or printed contents of documents should ideally remain unaltered. Alcohols can create ink running [5] and have to be kept down to a minimum in fingerprint reagents, when they cannot be altogether eliminated. Zinc bromide, cadmium nitrate tetrahydrate, and zinc nitrate hexahydrate were all readily soluble in ethanol and remained in solution when diluted with 1,1,2-trichlorotrifluoroethane. The exact concentration of salt was not critical and concentrations of between 10 and 20mM were suitable; in addition, the solution contained less than 10% v/v ethanol in fluorisol and this was an advantage in regard to potential ink running.

## Conclusion

Salts of metals of the IIb group of elements produced complexes with Ruhemann's purple which were highly photoluminescent at low temperature (77K).

This feature has found applications in the enhancement of weak fingerprints detected with ninhydrin on papers.

Cadmium nitrate has been shown to be a superior reagent to zinc chloride for the enhance-

ment of weak fingerprints. Taking into account spectral characteristics, solubility, versatility, and reproducibility (as well as the less critical ninhydrin development procedure), the use of cadmium nitrate tetrahydrate is advocated at a concentration of approximately 20mM in a 10% alcoholic 1,1,2-trichlorotrifluoroethane solution in the presence of acetic acid (1 to 2%). The red-colored complex formed is illuminated with the xenon arc lamp through a four-cavity filter at  $\lambda = (505 \pm 3)$  nm with a half bandwidth of  $(37 \pm 4)$  nm, and observations are made through a filter with a transmission maximum at  $\lambda = (590 \pm 3)$  nm with a half bandwidth of  $(37 \pm 4)$  nm and conducted at 77K.

Zinc nitrate hexahydrate is favored when toxicological considerations are paramount, provided that the ninhydrin development has been carefully controlled and the moisture present during the secondary treatment is kept within narrow limits (50 to 80% relative humidity with a dried sample) for subsequent photoluminescent observations. Mercuric bromide is advocated for limited applications when a red shift is necessary ( $\lambda_{\text{ex}} = 525$  nm;  $\lambda_{\text{em}} = 600$  nm). Moisture also has to be controlled and great caution has to be exercised when mercuric salts are being used because of their high toxicity.

#### Acknowledgments

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