Clay E. Allred,[1] *B.S.; Tao Lin,*[1] *M.S.; and E. Roland Menzel,*[1] *Ph.D.*

Lipid-Specific Latent Fingerprint Detection: Fingerprints on Currency*

REFERENCE: Allred CE, Lin T, Menzel ER. Lipid-Specific latent fingerprint detection: fingerprints on currency. J Forensic Sci 1997;42(6):997–1003.

ABSTRACT: We describe a lipid-specific lanthanide-based method of latent fingerprint detection, specifically its application to fingerprints on currency. In the counterfeiting context, the method allows one to distinguish between fingerprints placed on the paper before and after the ink deposition.

KEYWORDS: forensic science, criminalistics, latent fingerprints, lipids, lanthanides, currency, counterfeiting

The emission of light by the lanthanides, a subset of the rare earth elements, has been of interest for a long time in many scientific/technical fields. Examples are biochemical probes, fiber-optic communication and the construction of lasers (e.g., Nd and Er based lasers). Lanthanide-based methods of latent fingerprint detection are intended to allow processing of surfaces that display intense background fluorescence. The lanthanides exhibit long luminescence lifetimes (of millisecond order) because parity-forbidden f–f transitions, which, moreover, involve states of differing spin-multiplicities, pertain. Accordingly, we refer to lanthanide luminescence as phosphorescence rather than fluorescence. We will at times use the general term photoluminescence. The long lanthanide luminescence lifetimes permit one to suppress background fluorescence via time-resolved imaging. This was suggested already in 1976 (1) and was first demonstrated in 1979 (2) with a dusting powder that, incidentally, contained a terbium compound as the phosphorescent ingredient. From an instrumentation perspective, the methodology was at the time not mature, but this has changed since (3). The lanthanide of choice is usually europium, not so much because of time-resolved prospects but because of the large color discrepancy between the ultraviolet excitation and the red luminescence, which in most instances permits facile optical filtering for background fluorescence suppression. Lanthanide luminescences are spectrally sharp in comparison with typical organic luminescences. This is generally not an important feature in fingerprint work but it is of interest in the examination of fingerprints on counterfeit currency, as we shall see.

[1]Students and professor, respectively, Departments of Chemistry and Physics, and Center for Forensic Studies, Texas Tech University, Lubbock, TX.

*This research was supported in part by the Agency Contracts Group through the U.S. Secret Service (Contract 94-P194000-000).

Received 5 Aug. 1996; and in revised form 9 Dec. 1996, 26 Feb. 1997, 11 April 1997; accepted 14 April 1997.

Current Lanthanide-Based Fingerprint Treatments

The trivalent lanthanide ions can emit with high quantum efficiency because the 4f valence electrons are shielded by outer full-shell electrons. Luminescence intensities are low, however, because of very poor absorption, hence poor luminescence excitation. This problem can be overcome by chelation with organic ligands that absorb well and intramolecularly transfer the excitation energy to the lanthanide ion of the complex. The recognition that lanthanide luminescence can thus be enhanced dates back to 1942 (4). For fingerprint detection, a number of smooth surfaces are amenable to dye staining, typically after cyanoacrylate fuming. This approach is very effective with photoluminescence-based procedures and can be implemented using lanthanide complexes (5–7). Porous surfaces such as paper are customarily dealt with via reagents that attack amino acids of fingerprint residue. Ninhydrin (or a ninhydrin analog) is the workhorse of this type of fingerprint detection. Fluorescence fingerprint detection often utilizes a post-ninhydrin treatment with zinc chloride (8). Lanthanide salts can be employed similarly (9–11), but we note that the photophysical mechanism involved in the zinc chloride treatment is not the intramolecular energy transfer that pertains to the lanthanide context. The ninhydrin-based amino acid/lanthanide approach is not yet mature.

Lipid-Specific Lanthanide-Based Fingerprint Detection

Amino acid solubility results in many instances in loss of fingerprint detail, with articles that are readily wetted by polar solvents. Lipid-sensitive procedures, such as physical developer (generally used for detection of fingerprints on articles exposed to water), can be employed in such situations. They generally rely on (relatively weak) physical processes of preferential adherence to fingerprint residue. We have recently developed a *chemical* lipid-specific lanthanide-based method that is very widely applicable, hence potentially universal in character (12,13). It involves the formation of mixed ligand chelates. The chemistry is quite flexible. Its optimization, in terms of chelating ligands, lanthanide ion, solvents and reaction conditions, has not yet been undertaken in detail, but even at the present stage the method is quite amply sensitive. The basic chemical scheme is depicted in Fig. 1. The (non-luminescent) conjugating complex serves the specificity to latent prints and the sensitizing ligands provide the intense lanthanide luminescence via energy transfer. To date, we have mainly utilized europium as the lanthanide, ethylenediaminetetraacetic acid (EDTA) as the conjugating ligand and thenoyltrifluoroacetone (TTA) and orthophenanthroline (OP) as sensitizing ligands. The details of the chemistry and procedures are given in refs. 12 and 13. In this article, we describe the utilization of the method for detection of latent fingerprints on currency. A talk on a europium method for lipid

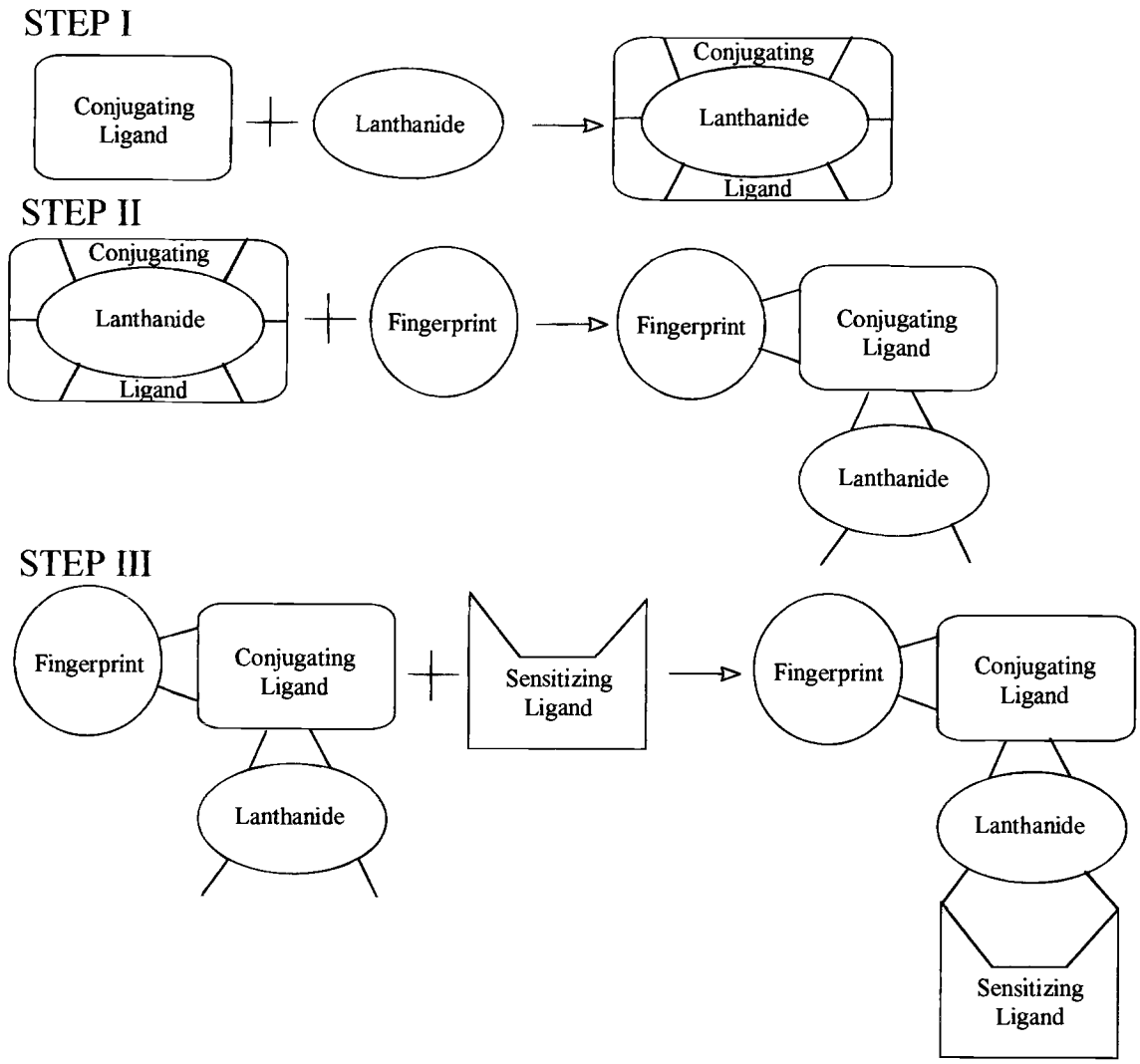

FIG. 1—*Basic scheme for lipid-specific fingerprint detection.*

prints was given at the fingerprint detection and identification symposium held in 1995 in Ne'urim, Israel (14). The described approach involves staining, akin to what is reported in ref. 6.

For review, the salient results (12) that persuade us that chemical lipid-specific fingerprint detection is pertinent are briefly outlined. Lipid (margarine) spots were deposited on paper and processed by the below-described procedure. For light deposits, nicely luminescent spots were obtained. Heavy deposits, however, are more revealing. Here, no development is obtained in the central region of the spot, not surprisingly, because the polar solvent delivery system does not wet the non-polar spot. The interesting region is the periphery of the spot, namely the interface between it and bare paper. The paper is readily wetted by the delivery solvent system, with considerable migration of solvent and reagent molecules via surface tension and capillarity effects associated with the paper fibers. To some extent, the solvent system also solubilizes lipid molecules, such that there is the needed contact for chemical reaction to occur. We find, as is shown in Fig. 2, a very brightly luminescent ring around the periphery of the heavy lipid spot, with considerable bleeding evident. In the third region of interest, namely the bare paper region removed from the lipid spot, some background luminescence develops (a sensitizing ligand is, after all, used), but it is faint in comparison with the luminescent ring. Amino acid, protein and salt spots similarly processed gave no result. Fingers dipped liberally in margarine and then pressed against paper were nicely developed with amply crisp ridge detail, i.e., the treatment was not so aggressive as to obliterate ridge detail. We argue that the outlined results are unambiguous in showing that (a) lipids are being attacked and that (b) the attack is chemical. A preferential adherence-type mechanism, as in dye staining, is not commensurate with the inherent incompatibility between polar and non-polar media. The brightly luminescent ring, as compared to the bare paper background, indicates that lipid-specific chemistry is taking place. We do not as yet know just what kind of lipid is being probed. We note, however, that latent fingerprint composition is quite variable in terms of lipid content, for instance when prints of children and adults are compared (15). The chemistry descibed in the present article may be probing lipids different from those to which physical developer, for instance, is sensitive. Further work is likely needed to match the chemistry to typical fingerprint lipids.

Fingerprints on Currency (16)

In the procedure used by us until now, the non-luminescent EDTA:Eu complex is prepared in a 4:1 mixture of methanol:acetone, 100 mL, by dissolving about 75 mg of $EuCl_3 \cdot 6H_2O$ and an

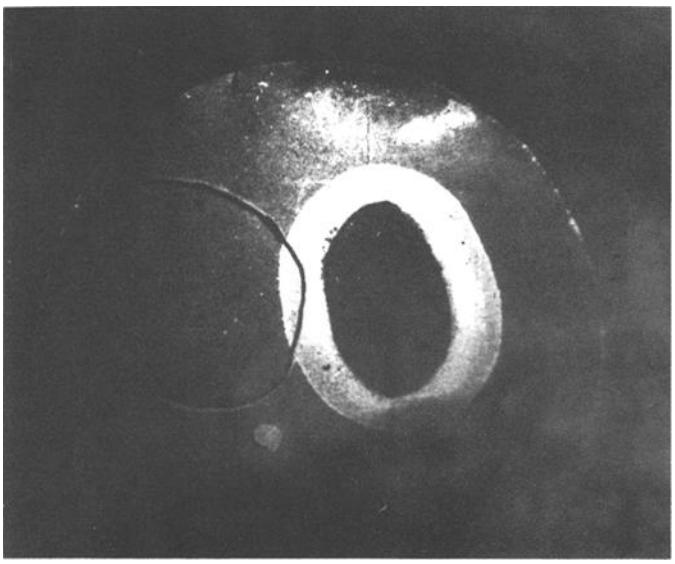

FIG. 2—*Margarine spot developed by the scheme of Fig. 1. See text for discussion. Photographs often suffer considerable loss of fidelity on reproduction from the original.*

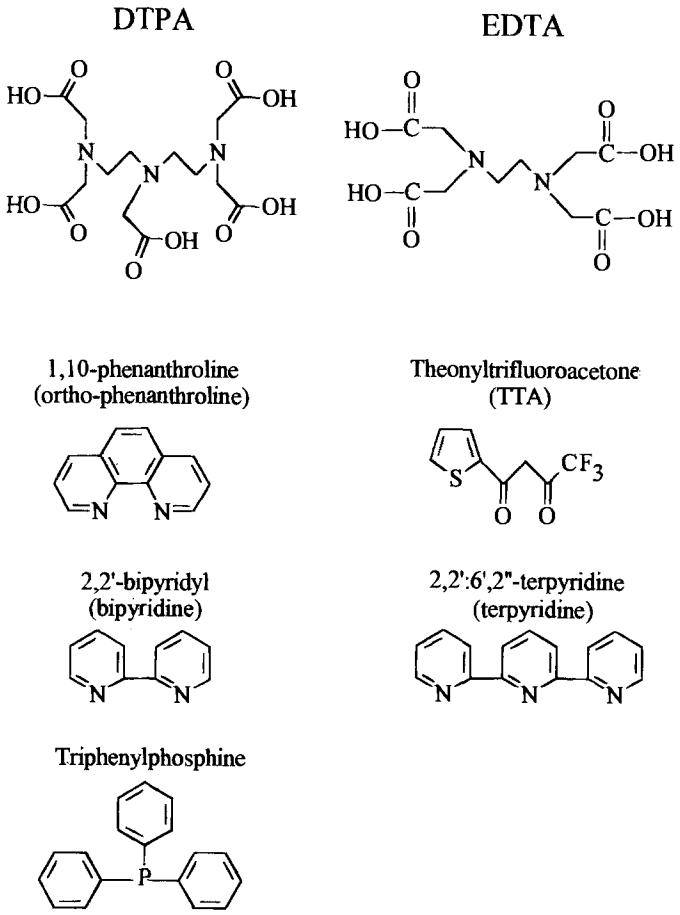

FIG. 3—*Ligands useful for lipid-specific lanthanide-based fingerprint detection.*

excess (to saturation, roughly 0.5 g) of EDTA. The solution is decanted and sprayed (using a chromatographic sprayer) onto the article under examination. Next, about 75 mg of OP is dissolved in the same 100 mL solvent system and, a minute or two later, sprayed onto the article. Finally, about 45 mg of TTA is dissolved in the solvent system and applied, as the third spraying, again within minutes after the second spraying. Reagent concentrations are not critical. The luminescent fingerprints develop fully within a few minutes after the third spraying. When background lanthanide luminescence, arising from complex formation of Eu with ligands that have not reacted with fingerprint residue, is severe, a very vigorous water wash can be done to reduce the background. Often, fingerprint detail improves in the process as well (12,13). On currency, U.S. currency in particular, the procedure does not work well because the TTA ligand not only reacts with the europium, but with constituents of the paper also, so that the post-treatment wash cannot significantly reduce the background europium luminescence. Accordingly, a modified procedure is employed. In this case, the TTA spraying step is deleted altogether. Reduction in fingerprint luminescence intensity results, but contrast is greatly improved. Diethylenetriaminepentaacetic acid (DTPA) can generally substitute for EDTA as the conjugating ligand. Ortho-phenanthroline as the sensitizing ligand is not the only option either. We have successfully used other ligands also. Examples are shown in Fig. 3. Finally, the above-cited solvent system can be varied also. For instance, a 1:1 water:acetone mixture generally works well. We mention these variations to point to the flexibility of the lipid specific lanthanide chemistry. Figure 4 shows the comparison of fingerprint detection on U.S. currency with Eu: DTPA/OP and Eu: DTPA/OP/TTA. The photograph Fig. 4a shows fingerprints developed by $EuCl_3 \cdot 6H_2O$/DTPA spraying followed by OP spraying. Figure 4b shows the same sample after subsequent TTA spraying followed by water washing. The background in Fig. 4b is so intense as to mask the right and middle fingerprints seen in Fig. 4a and the left print is actually seen as less luminescent than the background. As an aside, we note that the general lipid-specific treatment is compatible with cyanoacrylate pre-fuming of nonporous surfaces. Since ester groups occur in the polymer formed via the fuming, one might expect chemical reaction to be able to occur, if our concept of the pertinent chemistry (12) is correct. Indeed, developed fingerprints are very robust, as indicated by the vigor with which post-treatment water washing can be applied. However, we cannot distinguish between chemical reaction with the cyanoacrylate polymer and intercalated complex formation in which reaction with the polymer does not occur.

Fingerprints on Counterfeit Currency

The specific issue addressed here is whether the latent fingerprint was deposited on the paper before (FB) or after (FA) the inking step, an issue which determines whether the print was unambiguously placed by the counterfeiter (former instance) or not. We have previously investigated this issue using a variety of fingerprint treatments, including membrane transfer procedures, physical developer and analogous treatments, vapor procedures, and ninhydrin/zinc chloride-type chemistries (17). Fingerprint deposits ranged from "normal," with donors chosen at random, to heavy lipid and heavy amino acid deposits. Only the ninhydrin/zinc chloride approach showed any practical promise, and is based on the idea that the fingerprint fluorescence for prints located underneath the ink must pass through the ink and thus will suffer absorption by the ink, such that the fluorescence intensity vs. wavelength will differ from that of fingerprint fluorescence when the print is located over the ink. Samples involved offset printing, ink jet printing or color copying, using bond or copy paper. Stripes of various colors were printed to simulate counterfeiting. The procedural details have

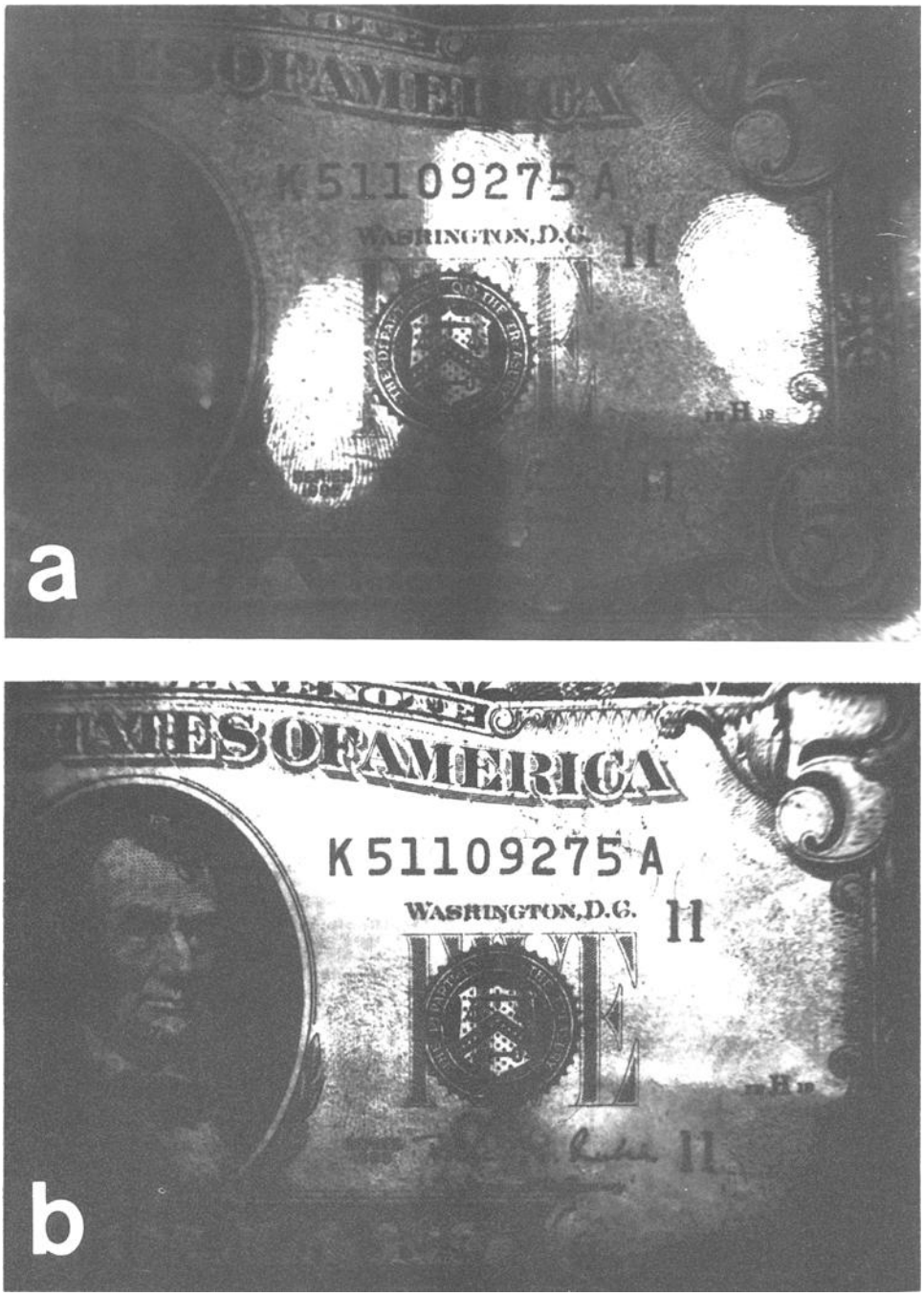

FIG. 4—*Photographs of fingerprints on U.S. currency developed by Eu:DTPA/OP (a) and Eu: DTPA/OP/TTA (b). See text.*

been reported earlier (17). Unfortunately, we found the spectral difference interpretation with ninhydrin/zinc chloride in the before vs. after instances difficult because fluorescence spectra are broad and featureless and because of the permeability of inks. Lipid-sensitive fingerprint detection partially solves the permeability problem and the sharpness of the europium luminescences (at about 579, 594 and 615 nm) facilitates the discrimination between the before and after situations, as long as the ink absorbance shows significant variations over the pertinent spectral range. This is dictated by the color of the ink. Basically, luminescence spectra are normalized at one of the luminescence wavelengths (e.g., 590 nm) and the differences at the other luminescence wavelengths provide an indicator of before vs. after fingerprint status.

An example (color copying) of the discrimination is given in Fig. 5. The europium luminescence at 579 nm was very weak in the shown example, indistinguishable from noise. Since the ink absorption spectrum is nearly constant over the spectral range 590–620 nm in the shown example, the difference in FA vs. FB intensities at 615 nm is small. To minimize problems associated with ink permeability, we used less aggressive solvent systems than those reported earlier, namely a roughly 10:1 water:acetone mixture for the Eu:DTPA step and a roughly 10:1 water:methanol mixture for the OP step. The acetone in the Eu:DTPA step serves the function of lipid solubilization so that the Eu:DTPA complex can chemically bind to the fingerprint residue. The methanol in the OP step serves as solvent for that reagent, with water in both

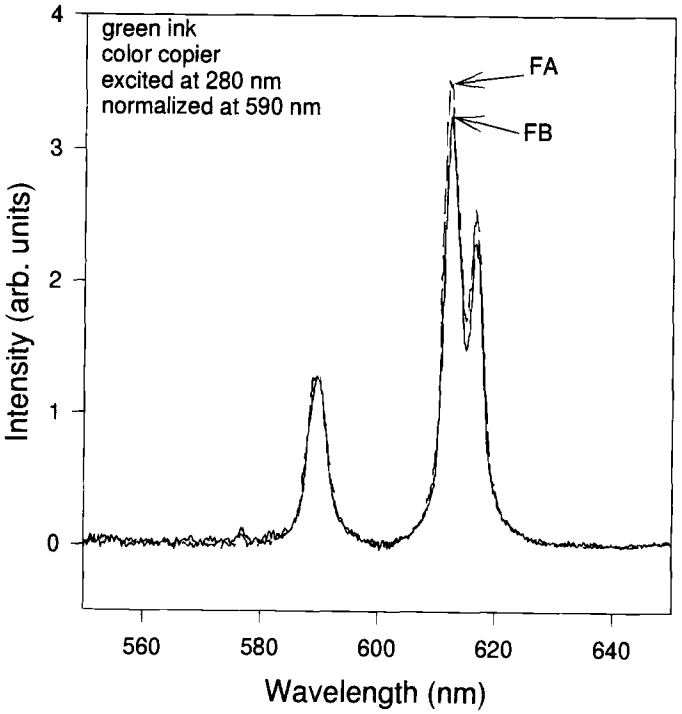

FIG. 5—*Normalized europium luminescence spectra of fingerprints before and after ink deposition by color copier.*

steps functioning as a carrier solvent which is not deleterious in terms of the relatively low permeability of the ink to fingerprint lipids. Substantial differences in overall intensities between portions of the fingerprints in uninked locations vs. inked locations can be seen in the before ink vs. after ink fingerprint deposition and are shown in Fig. 6. The samples had stripes of green, red, blue and black ink deposited by color copying. The ratios of fingerprint luminescence intensities, measured at 615 nm, between uninked and inked locales for the shown examples are 23 before and 8 after for green, 11 and 2, respectively, for red, and 21 and 9 for blue. For the black ink sample, the fingerprint luminescence intensities in the inked area were very low, so that precise ratios were not readily obtainable. We note in connection with the respective photograph that proper development in the inked area required long exposure, such that the uninked area is so grossly overexposed that no fingerprint detail is seen. The discrimination based on the intensity ratios is not always straight forward, given the wide variability in fingerprint residue composition and the amount of deposited material. We point out that the before vs. after differences seen in the photos of Fig. 6 result not only from ink absorption of fingerprint luminescence but also absorption by the ink of incident exciting light (before cases). Light scattering effects also play a role in the before as well as after cases. In instances in which the ink absorbance is essentially constant over the pertinent red spectral range, but varies in the green spectral range, the normalization approach can still be applied if europium is replaced by a lanthanide that emits in the green. Terbium is such a lanthanide. When used in a manner analogous to europium, sharp luminescences at about 490 and 540 nm are obtained, albeit with rather lower intensities than the red intensities obtained with europium. This intensity reduction is not a show-stopper in that the sensitivity of even garden-variety spectroscopic instrumentation is amply high. Fingerprint treatment using a mixture of europium and terbium salts in the first chemical step has potential applicability to

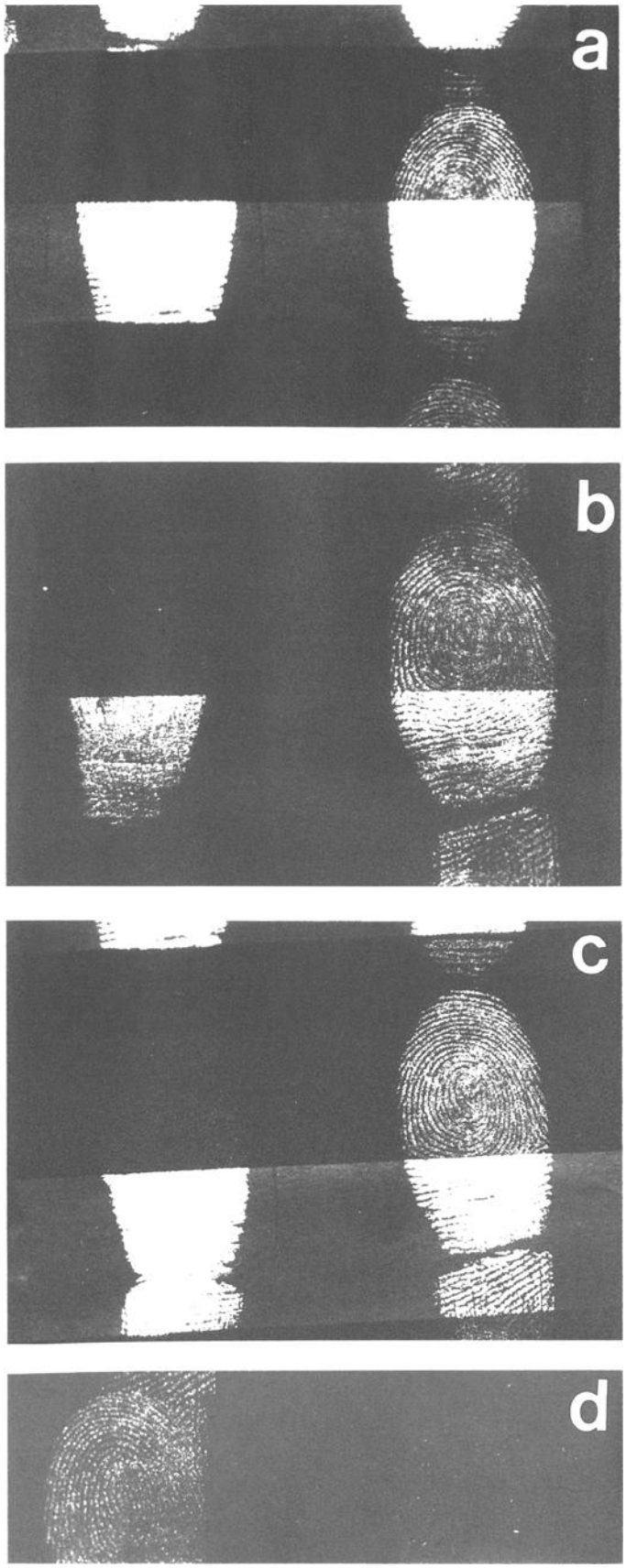

FIG. 6—*Photographs of fingerprints placed on paper before and after color copying ink deposition and developed by Eu: DTPA/OP. See text. a = FB, left and FA, right; green inked area, top of photo and uninked area, bottom of photo. b = same as a with red ink. c = same as a with blue ink. d = same as a with black ink, but FB is on the right and FA on the left.*

a wide range of ink colors, as is necessary for utility with currency in general. The absorbances of inks of various colors (from a color copier) are shown in Fig. 7. They present a guide to the lanthanide emissions best suited to discrimination via normalized emission spectra. We are presently investigating lanthanides other than europium and terbium, and sensitizing ligand options to tailor the chemistry to the employed lanthanide. Our work with counterfeiting simulation has to date been confined to fresh fingerprints because financial constraints precluded the protracted investigations necessary to study before vs. after fingerprint discrimination as a function of fingerprint age. For similar reasons, we have not extensively investigated counterfeiting by offset printing or other means. However, we have carried out some preliminary studies with fingerprints older than two or three days. We find that fingerprint detail smudges out and luminescence intensity decreases. We suspect that our chemistry probes mobile lipids that migrate into the paper with facility. Fatty acid oxidation may be occurring as well. This reduces the extent of chemical reaction, when reagents are applied by light spraying with volatile solvents, and causes obliteration of detail. We do not encounter this aging problem with fingerprints on smooth surfaces (without cyanoacrylate ester prefuming) or with fingerprints on the sticky side of adhesive tape.

Lanthanide Luminescence Excitation

The excitation of adequate lanthanide luminescence intensity generally requires ultraviolet light. In most cases, a hand-held UV lamp suffices. Occasions that demand time-resolved imaging (strong background fluorescence) can be handled with a modern argon ion laser (e.g., Coherent Innova 300 FReD). Such lasers are capable of near-UV and deep UV operation. We define deep UV as light of wavelength (approximately) in the 200–300 nm range (air absorbing at shorter wavelengths) and near-UV as covering the 300–450 nm range. When both TTA and OP are employed as sensitizing ligands, either near- or deep UV excitation can be used (near-UV excitation of the former and deep UV excitation of the latter), the former being more effective. With OP only, deep UV excitation is mandatory. We note here that the specifications of some UV lamps which have both deep and near UV operating features may be deceptive. For instance, we have compared the Model UVG-54 (Ultraviolet Products, Inc., San Gabriel, CA) and Model UVSL-25 (same manufacturer) lamps. In the former lamp, the light source as such in either the deep or near UV setting is a low pressure mercury lamp. The output at the two settings is merely a matter of the transmission characteristics of the used optical filters. The deep UV filter has a generally lower transmittance and passes relatively less light in the near UV in comparison with the deep UV. This, however, does not constitute a truly significant difference for our purposes in that the strong UV mercury lines occur at wavelengths of about 400 nm or less, where both filter transmissions are roughly comparable in relative transmission of deep and near UV. The lamp is compatible with either TTA or ortho-phenanthroline as sensitizing ligand. The Model UVSL-25 lamp is in a sense a more honest UV lamp. In its near UV setting, it emits a broad band between 300 and 400 nm, well matched to TTA, and no deep UV. The respective light source here is a low pressure mercury lamp internally coated with a luminescent material that absorbs the deep UV mercury output to convert it to near UV luminescence. In the deep UV setting, the lamp output is essentially that of the Model UVG-54 lamp operating in the deep UV setting. Thus, the Model UVSL-25 lamp in the near UV setting is not compatible with ortho-phenanthroline. The overall intensity of the Model UVSL-25 lamp is considerably lower than that of the Model UVG-54 lamp, incidentally.

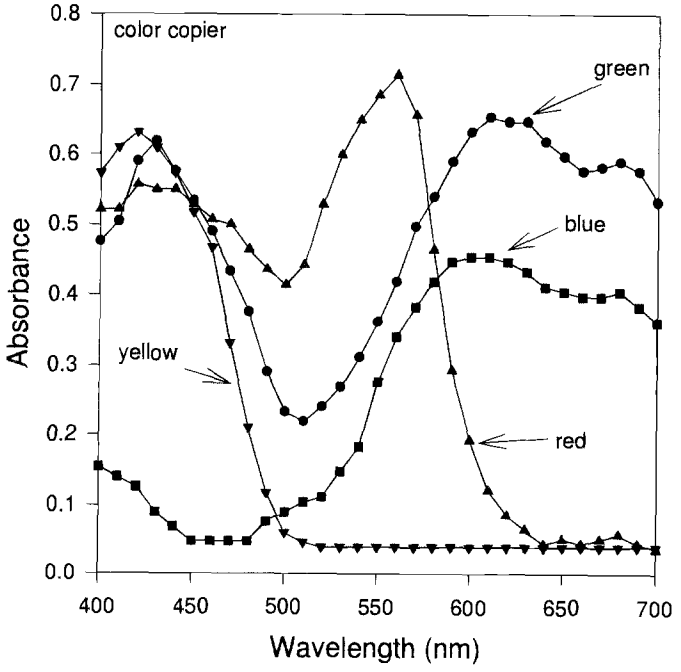

FIG. 7—*Absorption spectra of color copying inks on paper.*

Discussion

We emphasize that the described chemical methodology has yet to reach the maturity, with older latent prints in particular, for routine case work. It is nonetheless promising and worth further pursuit in that the general lanthanide strategy is universal in character. Fingerprint staining has been demonstrated (5–7,14), we have prepared viable dusting powders based on the TTA/OP mixed ligand complex, and we have obtained rather promising results on a chemical track parallel to what is described in this article, namely amino acid-specific detection, not with ninhydrin-type chemistry, but with phthaldialdehyde and similar reagents (18).

Acknowledgment

We are indebted to Dr. A. A. Cantu of the Secret Service for bringing the counterfeiting issue to our attention.

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Additional information and reprint requests:
E. Roland Menzel, Ph.D.
Center for Forensic Studies
Texas Tech University
Lubbock, TX 79409-1051