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Development and empirical optimization of an electrochemical analysis cell for the visualization of latent fingerprints and their chemical adhesives

Tommy Bergmann[1],Sebastian Gottschall[2],Enrico Fuchs[2],Oliver Berlipp[1], Dirk Labudde[1,3]

Abstract:

Fingerprint analysis played a major role in the investigation of criminal offences for the past 100 years and is often the sole means of criminal identification [YA04]. Electrochemical analysis can yield important additional evidence like fingerprint age, biological age and gender of its creator as well as chemical adhesives [GRW12]. Additional gained characteristics through electrochemical analysis can supplement latent or incomplete fingerprints. In previous work a ruthenium-complex based solution was used as illuminant. Since luminol is readily available and is used in many forensic applications, the presented paper will focus on luminol as an alternative chemical for the ECL-aided visualization of fingerprints. Experiments were conducted by creating an electrochemical reaction inside a purpose build analysis cell. Eccrine, sebaceous glandlike and vaseline contaminated fingerprints were created on a stainless-steel plate placed inside the cell and investigated while applying direct current. Aim of this research was to investigate which kind of fingerprints can be visualized and which quality of the resulting images can be reached using luminol as illuminant. The used laboratory power supply created a strong light reaction at the start of each experiment revealing potential for further enhancement of the image quality. Eccrine dactyloscopic evidence showed no visible results. For sebaceous glandlike fingerprints age was discovered to significantly influence image quality.

Keywords: latent fingerprints (LFP), electrochemoluminescence (ECL), luminol, chemical adhesives (substances), gender determination, age determination, information of fingerprints, forensic science.

1 Introduction

1.1 Background

The use of forensic dactyloscopy for suspect indentification is as old as criminalistic itself. References to this can be seen in ”System und Praxis der Daktyloskopie” from *Heindl*. Also, *Heindl* clearly describes the historical development of dactyloscopy, which has already undergone several innovations in the course of its development [He22]. Today, fingerprints are even considered more valuable evidence than deoxyribonucleic acid (DNA)

[1] University of Applied Sciences, Computer-and Biosciences, Technikumpl. 17, 09648 Mittweida, Deutschland, Email: {*firstname.name*}@hs-mittweida.de
[2] Fraunhofer-Institut für Verfahrenstechnik und Verpackung IVV, Institutsteil Verarbeitungstechnik, Heidelberger Straße 20, 01189 Dresden, Deutschland, Email: {*firstname.name*}@ivv-dd.fraunhofer.de
[3] Fraunhofer-Institut für Sichere Informationstechnology SIT, Rheinstrasse 75, 64295 Darmstadt, Deutschland

[HS07]. A new approach for the visualization of latent fingerprints is the use of electrochemical luminescence (ECL) reactions. In ECL reactions the luminescence is generated electrochemically by applying an electrical potential e.g. to a luminol, ruthenium, or rubrene solution. The resulting intermediates are subjected to an immense exergonic reaction in order to reach an energetically higher state. In the further course of the process, the relaxation leads to a transition to the energetically lower state, whereby the energy difference can be observed in the form of light. ECL reactions are already proven in analytical applications because they are highly sensitive and can be used selectively by applying a potential [GA13, FBK09, Va16, PS74]. For example, *Beresford et al.* describe visualization by spatially selective deposition of an electrochromic polymer (polyaniline). The electrochemical process is inhibited by the fingerprint and a negative image is created. The advantages of their method is an increase in contrast by varying the applied electric potential. Also, the electrochromic coating results in a longevity of the evidence [BH10]. In the work of *Jasuja et al.* an aqueous electrolyte solution was used, which made it possible to visualize latent fingerprints on deformed surfaces (aluminum foil) [Ja15]. Additional examples are provided in the review‘s of *Su et al.* [Su16] and *Yamashita et al.* [YF11].

The work of *Xu et al.* shows that the combination of electrochemistry and forensic dactyloscopy has a considerable advantage. For example, explosive residues can be detected [Ad11, LZJ06]. Due to the difference in brightness on the electrode caused by this reaction and the fingerprint residue lying thereon and blocking the electron exchange a contrast is generated which results in high-resolution images of the fingerprint.

[a] [b]

Fig. 1: [a] Experimental setup with recommended chemicals published by *Xu et al.*; Reproduced by our research group [b] high-contrast and high-resolution images of fingerprints based on the method described by *Xu et al.*

Furthermore, electrochemical scanning methods are used to detect spatial differences in the electrochemical reactivity and surface exit work of fingerprints. It is of special interest to reach a resolution which makes pores visible as demonstrated by *Xu et al.* [Xu12]. We could reproduce this high quality images using their recommended chemicals (tris(2,2’-bipyridyl) ruthenium(II) ([Ru(bpy)3]2+) and tri-n-propylamine (TPrA) as illustrated in Fig. 1. All minutiae (islands, inclusions, branches, bridges, etc.), even sweat pores within the papillary ridges, are clearly visible. However the high price and poor availability of the used ruthenium-solution leads to the demand for alternatives. The use of luminol to make blood evidence visible with the help of a catalyst has been a common practice since 1937 [Sp37]. It is also used in immunoassays as a part of an antibody reaction [Ji13]. Due to

its wide usage in forensics using luminol for ECL-reactions is a cost efficient and obvious approach. Therefore the presented research will focus on the development of luminol as an alternative chemical for the ECL-aided visualization of fingerprints.

2 Materials and Methods

Development of an electrochemical analysis cell An analysis cell with a two electrode system was constructed out of available stainless steel components, a petri dish and completed by a purpose built part 3 D printed from polyethylene terephthalate (PETG). A plate electrically connected through a screw forming the base electrode was placed at the bottom of the petri dish. The insulation distance of 1 mm between both electrodes was realized with the 3 D printed part enclosing the second electrode as well as restricting the cells active area to a circular diameter of 28 mm while reducing the necessary liquid volume to 2.4 ml. Fig. 2 illustrates the construction of the cell.

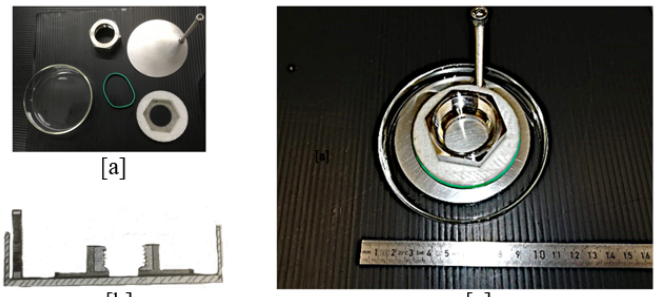


Fig. 2: [a] Overview of the components, [b] construction sketch cross-section and [c] structured analysis cell. The construction as seen in the picture consists of a petri-Dish, they contain two electrodes (stainless steel -plate, -nut), separated by a plastic insulator.

Both electrodes were connected using crocodile clip equipped wires. While the wire to the stainless steel nut was constantly connected to a laboratory power supply the second electrode was switched by plugging and unplugging it. The influence of ambient light fluctuation was eliminated by conducting all experiments in a darkroom and using a camera for observation. Additionally, two ultra violet (UV) lamps [see Tab.1] illuminating the fingerprints at 45 degree angle were positioned left and right of the camera.

Materials	Manufacturer
Laboratory power supply unit: ”PPS-11360”	VOLTCRAFT
Fine balance: ”New Classic MF”	METTLER TOLEDO
Camera: ”VCXU-51C”	BAUMER
Lens: TV ZOOM Lens S6x11 11.5-69 mm	SPACECOM
Drying cabinet ”VC 0020”	Vötsch Industrietechnik
UV lamp: Synergy 21 LED Prometheus UV V2	ALLNET GmbH

Tab. 1: laboratory equipment

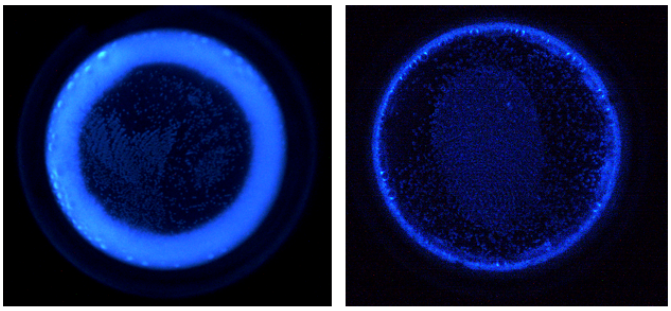
Luminol Solution In the experiments undiluted (0.025 mol/ l) and diluted luminol solution was tested. For the preparation of the solution, 0.44 g luminol was dissolved in 3 ml hydrogen peroxide (NaOH) with a purity of 50 % [Ea11]. Subsequently, 97 ml deionized water was added. For the further experiments, this luminol solution was used as the basis for the undiluted version or, with the addition of 100 ml deionized water, for the diluted version.

Preparation of the fingerprints For the following experiments the fingerprints (thumb and index finger) of a single person were used. Before the application of the fingerprints, the person was instructed to wash their hands with soap and then rinse them with lukewarm water. Drying was done by air. For the transfer of eccrine fingerprints, powder-free rubber gloves were worn for 10 minutes to stimulate sweat production. To get sebum with fingerprints, the person touched the forehead, the lateral nostrils, and the areas behind the ears with their fingers. Finally, to produce vaseline-containing fingerprints, contact was made with commercially available vaseline, which was wiped off on external surfaces before the fingerprint was transferred. All images of fingerprints listed in chapter 3 were transferred to a stainless steel plate, which then was included in the electrochemical analysis cell. For the transfer, the contact time was about one minute.

Fingerprint visualization The analysis cell was aligned so that the fingerprint was in the centre of the stainless steel nut and a reference picture was taken under UV exposure. Then 5 ml of the luminol solution was added to the fingerprint. Furthermore 0.25 ml of the hydrogen peroxide solution was added and a current of 2 amperes (A) was applied and a picture was taken. The voltage was between 8 V and 10 V in all experiments. This resulted in emission of light that occured everywhere in the solution, except at the adhesion (fingerprint) itself.

3 Results

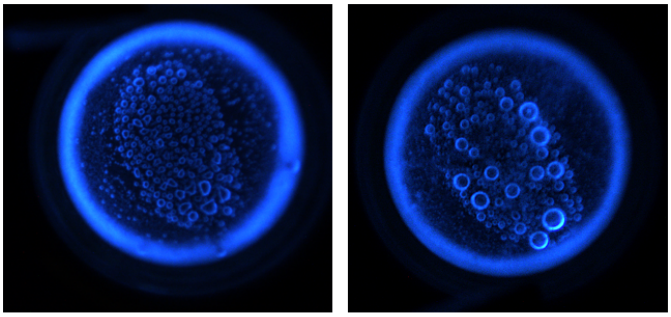
In the experiments light emission could be observed everywhere in the solution except for the adhesion or the sebaceous fingerprint. The intensity of the emitted light shortly peaked at the start of each experiment when the power supply was connected. The ECL reaction resulted in a useful contrast only when the fingerprint was placed onto the anode.
Fig. 3 shows a comparison of the visibility of the characteristics of differently aged sebaceous fingerprints. In Fig. 3 [a] a partial impression of the fresh fingerprint with characteristic values and optical anomaly (scar) is shown. In Fig 3 [b] a 16 h aged fingerprint is visible, including more detailed anatomic features. The Comparison of the visibility of the anatomic features of the fresh and the aged sebaceous fingerprint revealed that the aged fingerprint created better optical results. The picture in Fig. 3 [a] was taken several seconds delayed to the application of the electrical current resulting in a vivid reaction growing form the outside inwards.



[a] [b]

Fig. 3: Images created with ECL of two sebaceous fingerprints [a] fresh and [b] aged

As with *Xu et al.*, it could be experimentally confirmed in Fig. 4 [a], [b] that vaseline adhesion can also block signals. Details of the anatomic features were not visible, only the outline of the fingerprint. All areas of the fingerprint coated with vaseline showed a specific reaction (a bubble-like pattern). Fig. 4 demonstrates the results of fingerprints covered with vaseline. The experiment was carried out as described in chapter 2. The undiluted luminol solution [see 2 Luminol Solution] was used for this purpose.



[a] [b]

Fig. 4: Images created with ECL of fingerprints with vaseline adhesion.

The visualization of the eccrine fingerprints was not possible with our method. In subsequent processes, it is necessary to either pre-treat the eccrine impression fingerprint or to implement a different methodology in the prototype specifically for this evidence.

4 Discussion and future work

The observed peak in intensity right at the start of each experiment was caused by the output capacity of the used power supply creating a short burst in current. Utilizing this effect in the millisecond range requires an optimal timing between applying the current and image acquisition.
In summary, the visualization of sebaceous fingerprints and fingerprints with adhesions was possible with the presented method. The vaseline adhesion complicated the visibility

of anatomic features and also caused a bubble-like pattern which could be specific for this kind of adhesion and should be further investigated. The solubility of eccrine fingerprints prevented a successful visualization. It can be assumed that fresh fingerprints are better soluble in water than old ones. The ridges of the old trace are optically smaller than by the fresh one. As a result, it's easier to see the anatomic features. Our presented method therefore works better with traces that already dried up. Furthermore, fingerprints with other adhesions are to be investigated, preferably with criminally relevant background. Subsequent image processing may be one way to improve the results.
It should also be noted that there is a need to add hydrogen peroxide to the luminol solution, as it acts as a catalyst, even though it increases the formation of bubbles and should therefore be kept to a minimum.
The current approach is limited to smooth conductive surfaces. In future work transfering fingerprints from various surfaces to the ECL analysis cell should be tested. Future work should focus on the visualization of fingerprint adhesions. Forensic relevant information like gender and age can be determined from the ratio of different amino acids and fatty acids. Those adhesions can also serve as a hint for the usage of drugs or fire accelerators [AIA12, Du17, Gi16]. In summary, it is desirable to gain more information of a fingerprint than the anatomic features. ECL approves to be a good approach to reach this goal. Those information can be used to increase the succes rate of identification. The linkage between dactyloscopy and ECL can change forensic casework in terms of duration and quality, but needs further scientific analysis to develop its full potential.

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