Article

Single-Metal Deposition: Optimization of this Fingermark Enhancement Technique

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Abstract: Following the introduction of single-metal deposition (SMD), a simplified fingermark detection technique based on multi-metal deposition, optimization studies were conducted. The different parameters of the original formula were tested and the results were evaluated based on the contrast and overall aspect of the enhanced fingermarks. The new formula for SMD was found based on the most optimized parameters. Interestingly, it was found that important variations from the base parameters did not significantly affect the outcome of the enhancement, thus demonstrating that SMD is a very robust technique. Finally, a comparison of the optimized SMD with multi-metal deposition (MMD) was carried out on different surfaces. It was demonstrated that SMD produces comparable results to MMD, thus validating this technique.

Introduction

In a short communication published in 2007, we presented a new fingermark detection technique called single-metal deposition (SMD) [1]. Based on the same principles as multimetal deposition (MMD), SMD is characterized by a reduced number of steps and simpler and less expensive reagents. Thus, SMD constitutes a viable alternative to MMD.

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The first (preliminary) results obtained with SMD showed a comparable efficiency to that of MMD in enhancing fingermarks. These results were promising, even though the parameters used in the preparation of the reagents and in the application of SMD were not optimized. Thus, the objective of this paper is two-fold:

- To study the effects of the different parameters of SMD on the enhancement of fingermarks, in order to determine the optimized set of parameters.
- To evaluate SMD by comparing its efficiency with MMD on different surfaces.

MMD was introduced by Saunders in 1989 [2] and optimized by Schnetz and Margot in 2001 [3]. It is based on a two-step metallic deposition. First, gold colloids (nanoparticles) are deposited onto the fingermark residues and silver is precipitated on the colloids. This second step substantially grows the nanoparticles, resulting in a visible dark grey to black fingermark. In the SMD procedure, the silver-based enhancement step is replaced by a gold-based one: Gold colloids are grown through gold reduction on their surface, as illustrated in Figure 1 (original formula shown).

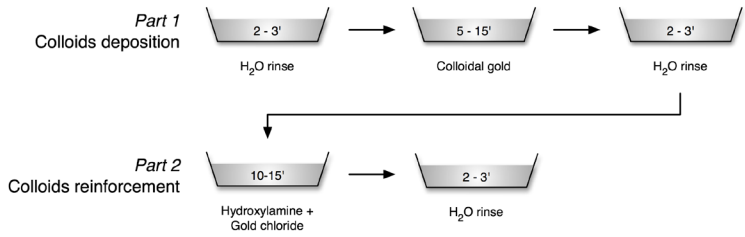

Figure 1

Original SMD two-step procedure.

Because the first part of the application of MMD remains unaltered in SMD, the deposition of the gold colloids on the fingermark deposits will not be discussed here. With regard to the second part of MMD, the optimized formula calls for a physical developer based on a silver acetate–hydroquinone couple (which requires two consecutive immersions) [3]. In SMD, this couple is replaced by a gold chloride–hydroxylamine couple, similar to the silver-based developer, but for which one immersion suffices. As a result, this new physical developer reduces the number of steps necessary to perform the enhancement, the number of reagents, and the cost.

Gold Chloride–Hydroxylamine Physical Developer

With SMD, the gold colloid growth is carried out by precipitating gold on the colloids through a redox reaction between tetrachloroauric acid ($HAuCl_4$) and hydroxylamine (NH_2OH). Because this reaction is highly accelerated by the gold surface, an enlargement of the existing gold nanoparticles takes place rather than the production of new gold nanoparticles, as shown in Figure 2 [4]. Conversely, in the absence of a catalyst gold surface, the redox reaction occurs at an extremely slow rate.

The gold-based physical developer uses the same tetrachloroauric acid solution necessary to prepare the gold colloids. The final solution is easily prepared by dilution. Finally, it uses hydroxylamine, also easily prepared by dilution, and stable at room temperature for a long period of time.

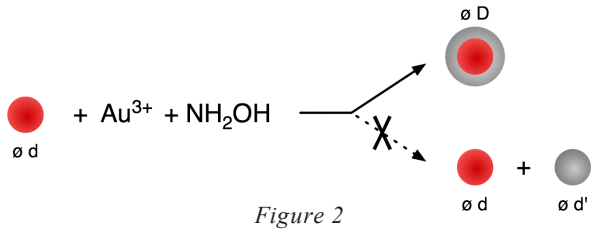

Figure 2

Redox reaction between tetrachloroauric acid ($HAuCl_4$) and hydroxylamine (NH_2OH) when in presence of a gold surface, which acts as a catalyst. Gold colloid (shown in red on the left) has a small diameter (ød). The catalyzed path favors the creation of a larger colloid (øD) rather than a second colloid (ød').

Materials and Methods

General Considerations

All chemicals used in the study were purchased from Sigma-Aldrich or Merck with a high purity grade and used without any further purification. The reagents and steps carried out in the first part of the gold colloids deposition were prepared and carried out according to Schnetz and Margot [3]. In the SMD versus MMD comparison study, the silver-based physical developer was also prepared and applied according to Schnetz and Margot [3]. All glassware used with reagents was siliconized and the water used to prepare solutions was bidistilled. The samples were rinsed using deionized water. When applicable, the stirring was carried out using a rotating platform shaker (model KL2, Edmund Bühler, Germany).

After enhancement, the resulting fingermarks were digitally acquired by scanning the surface at 1,600 dpi with a 24-bit depth. The overall contrast of each portion was independently enhanced using the Adobe Photoshop software (brightness, white balance, and contrast). This was done in order to obtain the best result for each image and to determine the most efficient enhancement based on the final output as in a real case.

SMD Optimization

In the first part of this study, only one type of surface, a low-density polyethylene transparent film, was chosen in order to concentrate on the influence of the parametric variations rather than on an influence due to variable surface characteristics. Fingermarks from two different donors were collected using the same specific protocol as described in the preliminary work done on SMD [1]. Prior to depositing fingermarks, fingers were rubbed through the person's hair and on the face in order to be loaded with sebaceous as well as the normal eccrine secretions. Fingermarks were then deposited as shown in Figure 3.

Two fingermarks with the same quality in terms of secretion deposition cannot be obtained or controlled, therefore fingermarks are cut in half and each half is treated with the respective technique in order to validly compare them. Thus, after the first part of the enhancement (gold colloid deposition), the fingermarks were cut according to Figure 3 and the left and right support portions were developed with the newly tested parameters, and the center support portion was developed with the base (original) conditions. The fingermarks were stored for 2 to

3 months in a dark and dry place prior to development, because SMD, like MMD, is a technique particularly useful to develop aged fingermarks. Four different variables, each with different values, were tested as shown in Table 1.

Variables	Values			
Immersion time (minutes)	**10**	**15**	20	30
Stirring speed (rpm)	0	30	70	
Gold/hydroxylamine ratio (mol:mol)	1:1	**1:2**	1:4	
Gold concentration (mol/l)	1.5×10^{-4}	**3×10^{-4}**	6×10^{-4}	15×10^{-4}

Table 1

The different variables tested along with the values. Original values used in [1] are shown in bold.

Each variable was tested in succession, following the order shown in Table 1. In this fashion, base values from the original experiments were held constant with the stirring configuration set to 30 rpm, the gold/hydroxylamine ratio to 1:2, and the gold concentration to 3×10^{-4} mol/l in order to test the immersion time variable. Once the optimal value was found for a given variable, this value was subsequently used to test each further variable in turn while base values on untested variables were held constant to the values applied in the original experiments.

The temperature of the bath was not evaluated, because an increase in temperature simply results in an increase in reaction kinetics, which was not pertinent in this case. Thus, all immersions were performed at room temperature.

MMD versus SMD Comparison

In the second part of this study, different surfaces were selected to test the optimized parameters of SMD in comparison to MMD. These surfaces were bleached and unbleached white paper, glass, painting tape (both adhesive and nonadhesive sides), styrofoam (polystyrene foam), and latex (gloves).

Fingermarks were collected similarly to the procedure described earlier. Both half-fingermarks were developed using the same baths for the first part of the enhancement (gold colloid deposits) and then separated for the physical developer part. One half-fingermark was developed with SMD using the newly optimized parameters and the other half with MMD, following Schnetz and Margot's conditions [3].

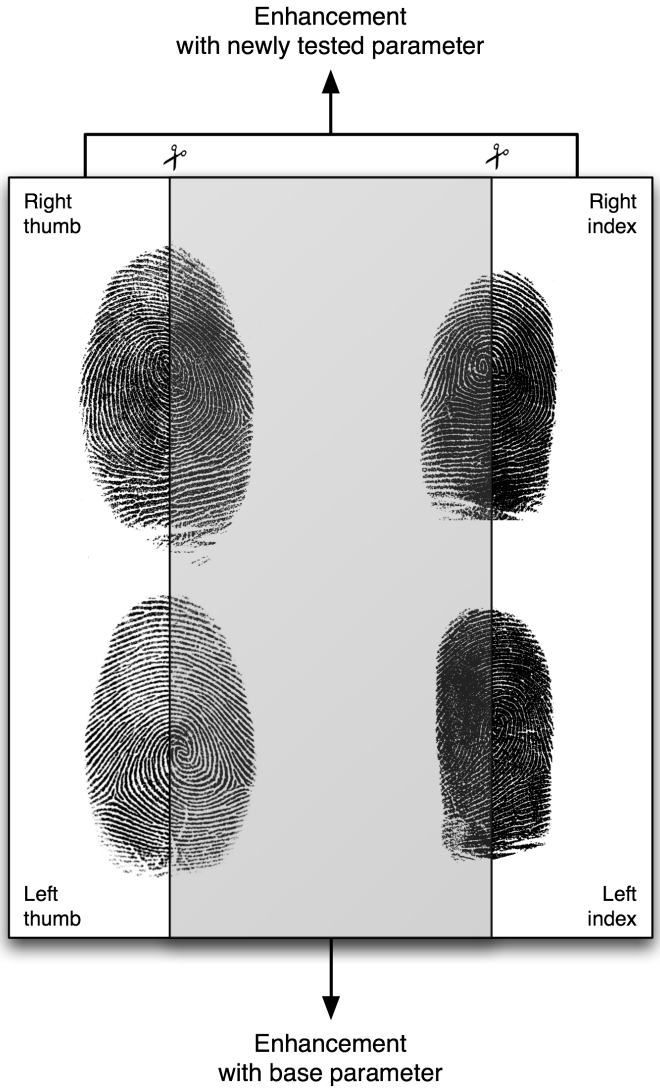

Figure 3

Setup used to collect fingermark and to prepare half-fingermarks for enhancement.

Results and Discussion

Immersion Time

A 10-minute immersion time leads to inhomogeneous ridges, particularly on the edge of the marks. In general, the contrast is excellent, even without digital image treatment. However, a 15-minute immersion time leads to a homogeneous fingermark with regularly enhanced ridges, a significant advantage. This was particularly advantageous because no increase of the background noise was observed. A slightly longer immersion time (20 minutes) resulted in an increase of the fingermark contrast with no noticeable increase of the background noise. One great advantage of SMD is that it is possible to control the development of the fingermark in real time, so that the examiner can directly determine when the optimal contrast is reached. The stability of the solution gold chloride–hydroxylamine allows this flexibility. An immersion time longer than 20 minutes did not substantially improve the contrast. The different results are illustrated in Figure 4.

Overdevelopment of the fingermark was also tested, because this is known to occur quite often with MMD. Figure 5 shows some fingermarks that were immersed for 60 and 90 minutes, respectively. No noticeable overdevelopment took place, demonstrating that SMD is quite a safe technique to use. Consequently, a 20-minute immersion time, considered optimal, was subsequently used.

Stirring Speed

Stirring has a significant influence on the development of fingermarks. When no stirring was used, the marks were very inhomogeneous, and the ridges exhibited irregular densities throughout the marks. This may create serious problems, particularly in the borders of the marks. As soon as stirring was applied, ridges became more homogeneous and the quality of the developed prints was highly improved, as demonstrated in Figure 6. However, stirring also increased background noise, although this increase did not significantly counteract the improvement of the mark quality. To limit the background noise development, it was crucial to thoroughly rinse the surface after gold colloid deposition. The upper limit in stirring was reached by the mechanical limitation of the recipient. Too much stirring led to splashes and did not produce more homogeneous fingermarks.

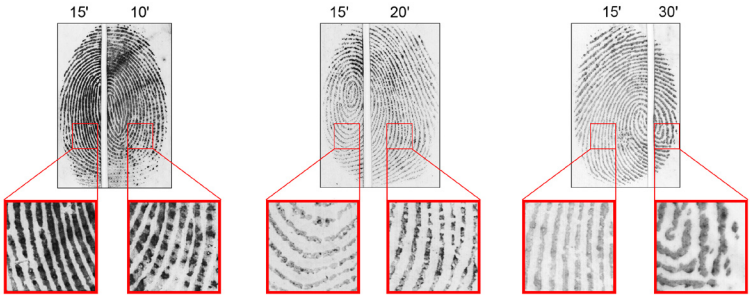

Figure 4

Influence of the immersion time to the fingermark development.

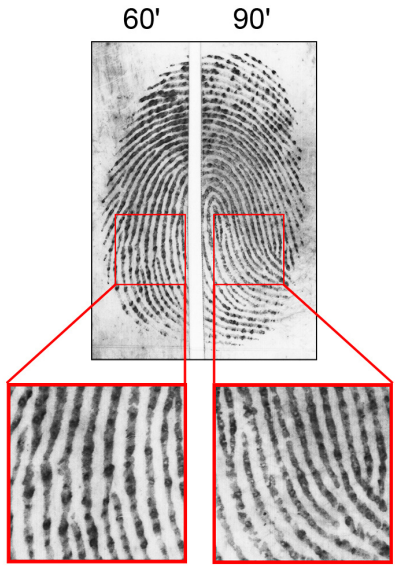

Figure 5

Attempt to overdevelop the fingermark with long immersion times.

As a consequence, 70 rpm, which corresponds to a high-intensity stirring, was considered to be the optimal stirring configuration and was subsequently used.

Gold/Hydroxylamine Ratio

No significant differences were observed between the three different ratios, as evidenced in Figure 7.

These results can be understood by the stoichiometry of the reaction, which called for one mole of hydroxylamine per mole of gold chloride. As such, increasing the concentration of the reducing agent only guaranteed a complete reaction of the gold. This could have increased the kinetics of the reaction, but given the speed of the reaction, it would not have been significant. Additionally, a greater reaction speed would not favor particularly the catalytic precipitation of gold on already existing gold nanoparticles [5]. This would only result in an increase of background noise. As a consequence, a 1:1 gold/hydroxylamine ratio was considered optimal and was subsequently used. It should also be noted that a greater concentration of gold compared to hydroxylamine was not tested, as this would simply decrease the amount of gold available for reduction on the existing nanoparticles.

Gold Concentration

When the gold concentration was varied, the concentration of hydroxylamine was varied accordingly, to respect the 1:1 ratio. In general, a concentration of 1.5×10^{-4} M was too weak and resulted in inhomogeneous ridges, as shown in Figure 8. A concentration of 3×10^{-4} M provided a good contrast, with little background noise. With an increased concentration, the background noise increased accordingly. As a consequence, 3×10^{-4} M was considered the optimal concentration.

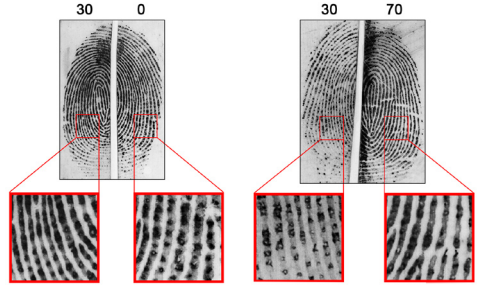

Figure 6

Influence of the stirring speed to the fingermark development. Values are in rpm.

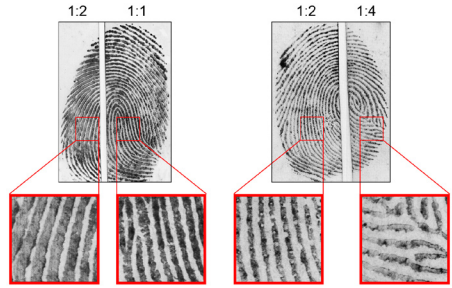

Figure 7

Influence of the gold chloride/hydroxylamine ratio to the fingermark development.

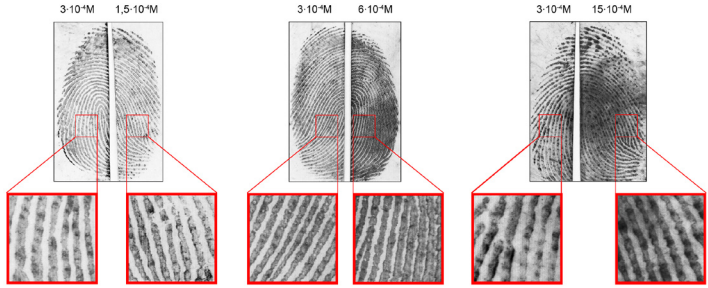

Figure 8

Influence of the gold concentration to the fingermark development.

Summary of Retained Optimal Parameter

The optimal parameters to conduct SMD were determined to be:

Immersion time	20 min
Stirring speed	70 rpm (intense)
Gold/hydroxylamine ratio	1:1 mol/mol
Gold concentration	3×10^{-4} M

These optimized parameters are very close to those first proposed by Stauffer et al. [1] No major modifications were made. However, these results also demonstrated that SMD is a very efficient and robust technique, because even important changes in its operational parameters (such as doubling the gold concentration) did not significantly affect the development of the fingermarks. This is definitely a critical quality, because the examiner does not need to be completely accurate in the reagent's preparation and technique application during the second part of the development. However, this does not apply to the first part of the development (gold colloid attachment), which may strongly suffer from small deviations from its established parameters, particularly in the pH of the solution. The complete procedure to conduct SMD is presented in appendices 1 to 3.

Surface Testing and Comparison with MMD

Seven different surfaces were tested and showed very similar results between SMD and MMD, as illustrated in Figure 9. No significant differences were observed on glass; even though MMD produced a slightly better contrast, the SMD contrast can be enhanced using digital image treatment. On styrofoam, the results were identical between the two techniques. Although the results obtained on unbleached paper were more random, there were no significant differences between MMD and SMD. Similarly, on bleached paper, both MMD and SMD provided mostly no difference. This problem has been the subject of other studies [6]. SMD did not produce as good a result as MMD with the nonadhesive side of masking tape; however, after digital image treatment, it was still possible to clearly observe the fingermark and its ridges. With regard to the adhesive side of masking tape, both techniques offered the same contrast; however, MMD had the tendency to overdevelop the substrate (due to an increased background darkening), whereas SMD did not suffer from this problem. Finally, on the latex surface, fingermarks enhanced

with SMD were slightly better when compared to MMD, even though the overall results were similarly poor. It should be noted that latex is a very difficult surface to recover fingermarks from using classical as well as advanced techniques. Finally, with MMD, the silver from the physical developer precipitated all over the surface, which was not the case with the gold-based physical developer used in SMD.

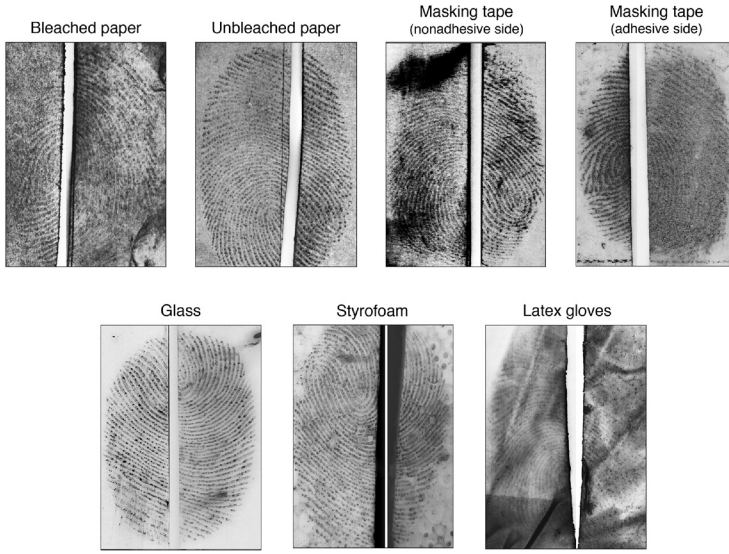

Figure 9

SMD to MMD comparison on different substrates. For each substrate, the left half-fingermark was enhanced with SMD and the right part with MMD.

Conclusion

Although SMD still suffers from the same disadvantages as MMD – a lack of contrast on dark and patterned surface and cumbersome application – it offers much easier laboratory constraints and decreased costs. Additionally, it offers the same sensitivity, because it relies on the same principles of gold colloid attachment on fingermark secretions. SMD works on a wide variety of surfaces, both porous and nonporous, though it exhibits some difficulties on surfaces that have a basic pH.

The optimized parameters for SMD varied very little compared to the original parameters used while the technique was being discovered. This indicates the robustness of the physical developer process in SMD, which resists well to varying application conditions. Consequently, relatively large changes during the second part of the development were shown not to influence the final results in any significant manner.

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Appendix 1

Preparation of the stock solution of gold nanoparticles according to Schnetz and Margot [3]:

Reagents

Solution A **10% tetrachloroauric acid solution in bidistilled water (0.29M)**
This solution must be kept refrigerated and is stable for several months.

Solution B **1% sodium citrate in bidistilled water**
This solution is stable at room temperature for a couple of months.

Solution C **0.1M citric acid in bidistilled water**
This solution is stable at room temperature for a couple of months.

Solution D **1% EM grade tannic acid in bidistilled water**
This solution must be kept refrigerated and is stable for a couple of months.

Procedure

Note: A volume of maximum 500 mL of gold colloid solution should be prepared at once.

1. In a beaker, mix 500 µl of solution A with approximately 400 mL of bidistilled water.

2. In another beaker, mix 20 mL of solution B and 100 µl of solution C with 75 mL of bidistilled water.

3. Heat both beakers separately to 60 °C. Once this temperature is reached, rapidly pour the second solution into the first one under heavy stirring. Bring the final solution to its boiling point at which point the solution turns ruby red.

4. Let the solution cool down to room temperature and add bidistilled water to reach the exact volume of 500 mL. This solution is stable for several months when kept in polypropylene bottles and under refrigeration.

Appendix 2

Reagent's preparation and procedure for gold colloids deposition used in the first step of single-metal deposition [3]:

Reagent

Colloidal Gold Working Solution

1. Mix 500 µL of Tween 20 to the 500-mL solution of gold colloids made according to Appendix 1 under constant stirring.
2. Adjust the pH of the solution to 2.5 to 2.8 (2.65 being optimal) by gentle addition of solution C under constant stirring.

Procedure

1. Rinse the sample with deionized water for a few minutes under stirring.
2. Immerse the sample in the colloidal gold solution for 5 to 15 minutes under gentle stirring.
3. Rinse intensively the sample with deionized water for a few minutes.

Appendix 3

Reagents' preparation and procedure for the gold-based physical developer used in the second step of single-metal deposition:

Reagents

Solution A **10% tetrachloroauric acid solution in bidistilled water (0.29M)**
Note that this solution is the same solution A used in the preparation of gold colloids according to Schnetz and Margot [3]. This solution must be kept refrigerated and is stable for several months.

Solution H **2050 mg hydroxylamine hydrochloride in 100 mL bidistilled water**
This solution is stable at room temperature for several months.

Procedure

1. Mix 200 µl of solution A with 200 mL of bidistilled water in an appropriate beaker.

2. Right before developing the sample, under an intense stir, add 200 µL of solution H. Then, transfer the solution to the recipient used for the immersion.

3. Immerse the sample for at least 20 minutes under an intense shaking speed (~ 70 rpm). Additional time can be used if necessary.

4. Rinse the sample with deionized water for a few minutes.

5. Hang the sample to dry at room temperature.