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Further investigations into the single metal deposition (SMD II) technique for the detection of latent fingermarks

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Abstract

Single metal deposition (SMD II), a recently proposed method for the development of latent fingermarks, was investigated by systematically altering aspects of the procedure to assess their effect on the level of development and contrast achieved. Gold nanoparticle size, temperature of the deposition solution bath, and orbital shaking during detection were shown to affect the levels of development and contrast obtained. Gold nanoparticles of diameter 15-21 nm were found to be most effective for satisfactory visualisation of latent fingermarks, while solutions that were applied at room temperature were found to adequately balance the ratio between the contrast of the fingermark ridge detail and the level of background staining achieved. Finally, optimum levels of development and contrast were obtained through constant agitation of both solution baths at approximately 50 RPM throughout the submersion time. SMD II was also tested on a large variety of substrate types and shown to be effective on a range of porous, non-porous, and semi-porous surfaces; however, the detection quality can be significantly influenced by the substrate nature. This resulted in the production of dark grey, white, or gold coloured fingermarks on different surfaces, as well as reversed detection on certain types of plastic, similarly seen through the use of vacuum metal deposition.

Keywords

fingermark development; gold nanoparticles; nanotechnology; substrates

1. Introduction

Interest in nanoparticles for fingerprint detection has gained a lot of momentum since early 2000 due to the many potentially beneficial properties they exhibit (1-3). Nanoparticles are extremely small in diameter, generally 1000 – 10 000 times smaller than a fingerprint ridge width, ensuring excellent resolution upon detection (1, 4). The properties of nanoparticles can be modified easily by the addition of molecular chains or chemical functionalities on their outer surface (5-7), ensuring the specific targeting of fingerprint components (1, 4, 8). They can also exhibit various optical properties due to the presence of surface plasmons, and allow for the possibility of luminescence depending on the type of nanoparticle (1, 4, 8-10). This can effectively increase the sensitivity of detection techniques based on such materials (8, 11).

Single metal deposition (SMD II) is considered the latest improvement of the original multimetal deposition (MMD) technique, and uses gold for both the deposition and enhancement stages (12-16). This development technique involves the deposition of citrate-reduced gold nanoparticles onto fingerprint ridges in a colloidal gold solution bath, and then reduction of additional gold in a reinforcement solution bath for further contrast enhancement (Figure 1) (13-16).

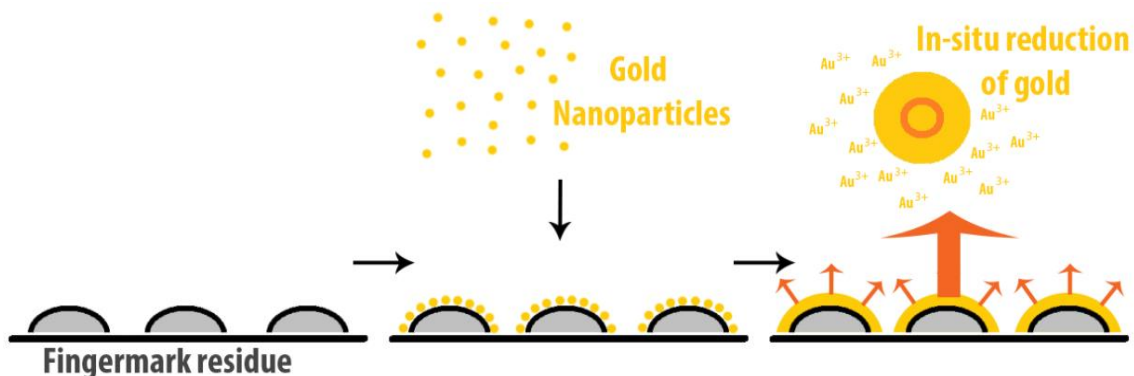


Figure 1: The development process of single metal deposition performed on latent fingerprint residue, involving a deposition step followed by a reduction step, adapted from Bécue, 2010 (17).

The colloidal gold deposition bath also contains a citric acid buffer, Tween 20 (surfactant) to prevent nanoparticle aggregation, and a small amount of L-aspartic acid, which is expected to replace a minor portion of the gold nanoparticle surface functionalisation to allow for efficacy of the method across a much wider pH range (12, 16).

This evolution of the technique was proven to be more efficient and robust than previous ones, allowing development of a larger number of samples in one solution bath with significantly less impact on the quality of the mark, and detecting 50 % more fingerprints (16). There is no need to monitor the pH of the working solutions as with other methods, and the synthetic protocol has been optimised to generate 2.5 L of solution, making it extremely suited to operational use (16). SMD II is believed to work on most surface types,

including adhesives, cartridge cases, and even wetted items, for latent fingerprints up to – and possibly older than – 2 years old (13, 16).

The standardisation and validation of newly proposed fingerprint detection methods is extremely important for strengthening fingerprint research and improving operational detection capabilities, therefore, the overall purpose of this study was to investigate the novel SMD II method for latent fingerprint detection with respect to the International Fingerprint Research Group (IFRG) Guidelines (18). The environmental conditions in which a fingerprint development procedure is performed can have a significant impact on its efficacy, such as in the case of 1,2-indanedione. Prolonged heating in low humidity conditions can result in the formation of non-fluorescent oligomeric by-products, while exposure to high humidity during the development or subsequent storage of samples can result in the degradation of Joulilié's Pink back to 1,2-indanedione or a hydrindantin derivative (19-21).

As it can be seen from the literature, most of the MMD/SMD optimisation studies were performed in Switzerland, the climate of which can be described as moderate, with no excessive heat, cold, or humidity (18, 22, 23). Climatic conditions in Western Australia vary from those of Switzerland in terms of both average temperature and humidity, with the south-west region in particular experiencing hot, dry summers and mild, wet winters (24, 25). For this reason, the procedure was firstly tested for its reliability and robustness under Western Australian conditions, and on a range of different substrates. The protocol was also subjected to systematic experimentation with several different parameters in accordance with Phase 2 of the IFRG Guidelines – 'Optimisation & Comparison' (18). This can provide knowledge as to which conditions are crucial for successful detection of latent fingerprints using a particular method, and assist forensic investigators in achieving optimum levels of development. The main areas of interest to be examined were the effect of nanoparticle size, temperature, and agitation of the solution baths.

2. Materials and Methods

Tetrachloroauric acid trihydrate, trisodium citrate dihydrate, sodium hydroxide, L-aspartic acid, Tween 20, citric acid monohydrate, and hydroxylamine hydrochloride were all sourced from Sigma-Aldrich, USA. Reagents were of analytical grade and used as received, and water utilised was deionised unless otherwise stated.

2.1 Fingerprint samples

Latent fingerprints were collected from five donors (three male and two female, all aged between 20-29 years) for each trial over the duration of the testing period. For each substrate considered in this study, the donors were asked to lightly touch the middle three fingers of each hand to leave 'uncharged' or natural fingerprint samples. They then rubbed the fingers of both hands over their faces and chests to 'charge' their fingers with sebum

before repeating the above deposition process. For substrate testing there were 23 substrates and 30 marks per substrate (3 charged and 3 uncharged marks from 5 donors) giving a total of 690 marks. For the studies into nanoparticle size, effect of temperature, and shaking there were 72 marks for each of the 3 studies (6 charged and 6 uncharged marks from 5 donors) giving a total of 180 marks. Each donor was allocated an anonymous alphanumeric code for recording purposes. Fingermarks were then stored in paper envelopes and placed in an office cupboard at room temperature for 1-2 weeks before treatment, unless otherwise stated. For comparison studies, all samples were cut in half down the middle finger immediately prior to their development to provide two alike samples. This 'split-mark' approach has been recommended by the IFRG, and in articles dealing with fingerprint deposition protocols for detection purposes (18, 26, 27).

2.2 Colloidal gold solution synthesis

The stock solutions for SMD II were prepared according to the method published by Moret and Bécue (16). Their contents were as follows:

Table 1: Stock solutions prepared for the SMD II development procedure.

Solution A	0.500 g tetrachloroauric acid trihydrate dissolved in 5 mL Milli-Q water
Solution B	1.70 g trisodium citrate dihydrate dissolved in 85 mL Milli-Q water
Solution C	0.120 g sodium hydroxide and 0.380 g L-aspartic acid dissolved in 25 mL Milli-Q water
Solution D	31.5 g citric acid monohydrate dissolved in 150 mL Milli-Q water
Solution E	1.00 g hydroxylamine hydrochloride dissolved in 50 mL Milli-Q water

Solution A was stored in a sample vial in a refrigerator at 4 °C to prolong its shelf-life, while solutions B-E were stored at room temperature in glass bottles in a cupboard away from light.

Colloidal gold was prepared as follows (17): solution A (1 mL) was added to deionised (DI) water (460 mL) and heated to boiling point under constant stirring (solution 1). In a separate beaker, solution B (42 mL) was combined with solution C (420 µL). When solution 1 reached its boiling point, the content of the beaker was quickly poured in. The solution continued to be heated under constant stirring until it turned a deep red colour, at which point it was diluted with DI water to reach a final volume of 2.5 L. Tween 20 (2.5 mL) was then added under stirring. The solution was stored in a polypropylene container in a refrigerator at 4 °C. For every application of SMD II, a red-coloured gold nanoparticle stock solution synthesised according to this method was used, unless otherwise stated.

Several versions of gold nanoparticle stock solution were synthesised that contained gold nanoparticles of different diameters, labelled stock #1 (original), and stocks #2 to #4 (derivatives). This was carried out by following the method outlined above, but altering the length of the boiling time of solution 1 prior to adding the reducing agents: under 1 minute of boiling time (stock #2), 5 or more minutes of boiling time (stock #3), and 1-2 minutes of boiling time (stock #4). The nanoparticle diameters within all these solutions were later measured using dynamic light scattering (DLS).

2.3 Nanoparticle characterisation

All gold nanoparticle stock solutions were analysed in 1 cm optical path cells and characterised using an Agilent Cary Series 4000 UV-Vis spectrophotometer across wavelengths of 400-800 nm. DI water was used as a blank reference sample. Data acquisition and processing was performed using Cary WinUV software (version 4.20).

DLS size analysis of all gold stock solutions was performed using the same standard operating procedure set at 20 °C, with the original stock solution #1 also being analysed at temperatures ranging from 10-30 °C. The measurements were performed using a Malvern Zetasizer Nano ZS (model ZEN3600) with a 1 cm optical path cell. A minimum 10 scans were performed per sample before producing a value. Malvern Zetasizer Nano software (version 7.11) was utilised for data acquisition.

2.4 Fingerprint detection

The detection of fingerprints was conducted as follows (17): gold nanoparticle stock solution (200 mL) was removed from the refrigerator and left to warm up to room temperature in a glass dish. 6 mL of solution D were then added under constant stirring to lower the pH of the solution (3 mL for every 100 mL of stock solution). Fingerprint samples were submersed in DI water for 2-3 minutes before being submersed in the gold nanoparticle solution bath for 20 minutes under constant orbital shaking on a PathTech Basic Orbital Mixer at approximately 50 RPM (Figure 2). Samples were then rinsed in DI water for 2-3 minutes. In another glass dish, solution A (200 µL) and solution E (200 µL) were added to DI water (200 mL) under intense stirring to form a reduction bath. Samples were then submersed in this reduction bath for 20 minutes under constant orbital shaking at approximately 50 RPM. They were then rinsed in DI water again for 2-3 minutes before being left to dry on paper towels at room temperature.

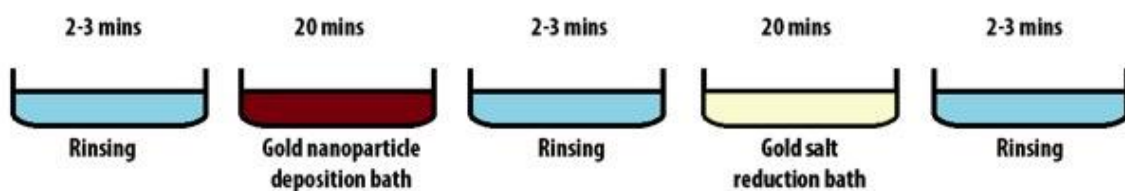


Figure 2: The solution baths required for latent fingerprint development using SMD II, adapted from Moret and Bécue, 2015 (16).

To investigate the effect of nanoparticle size on the development of latent fingerprints, several gold stock solutions that contained nanoparticles of different diameters (stocks #1 to #4) were applied to fingerprints using the SMD II procedure. Overlooking the size of the gold nanoparticles, these solutions were similar to the original gold nanoparticle stock solution, and were applied in the same way to split-mark samples (stock solution #1 vs #2, and #3 vs #4).

The effect of the temperature of the gold nanoparticle solution bath on the development of latent fingerprints was investigated through the application of portions of the best-suited gold stock solution to fingerprint samples at different temperatures; straight from the refrigerator at 4 °C, at a room temperature of 20 °C (RT), and heated to 30 °C immediately prior to the submersion of samples. These solutions were similar to each other in composition and appearance and, except for their temperature, were applied in the same way to split-mark samples (RT vs 4 °C, and RT vs 30 °C).

To investigate how agitation of the solution baths affects the development of latent fingerprints using SMD II, the method was carried out several times with the solution baths under different levels of agitation; constant agitation of both active solution baths for the entire submersion time, minimal agitation (30 second shake at the beginning, middle, and end of the submersion time for each bath), and no agitation at all. Trials were also done where only the gold nanoparticle solution bath was under constant agitation for the entire submersion time, while the reduction bath experienced no agitation at all. The agitation was kept steady throughout the procedure by using a PathTech Basic Orbital Mixer set at approximately 50 RPM. These nanoparticle solutions were all taken from one batch of the original gold nanoparticle stock solution (#4) and were therefore identical to each other. Excluding the level of agitation, these solutions were applied in exactly the same way to split mark samples (no agitation vs minimal agitation vs full agitation, and full procedure agitation vs only colloidal gold agitation).

2.5 Substrates

In order to assess the efficacy of the SMD II procedure on different surfaces, latent fingerprints were collected on 23 different substrates, as listed in Table 2.

Table 2: List of the substrates considered in this study.

Substrate	Type	Manufacturer/Product
Recycled white copy paper	Porous	OfficeMax® 50% recycled paper
Calcium carbonate-chalk / polyethylene blend paper	Porous	Nu World® Stone Paper
Transparent polypropylene document sleeve	Non-porous	Marbig®
White copy paper	Porous	Fuji Xerox® Business Digital Carbon Neutral
Glass microscope slide	Non-porous	Mikro® optical quality microscope slides
Aluminium foil (matte side)	Non-porous	Confoil® heavy duty
Aluminium can	Non-porous	Coke Zero®
Polycarbonate Compact Disk (recording side)	Non-porous	Lite-On®
Polyethylene bottle	Non-porous	Kartell® 500 mL laboratory bottle
Polyethylene terephthalate bottle	Non-porous	Cool Ridge® 600 mL water bottle
Polypropylene takeaway container	Non-porous	Unknown Manufacturer
Polymethyl methacrylate white car paint sample	Non-porous	Paint taken from a Holden VF GTS
White Post-It note	Porous	Post It®
Thick cardboard	Porous	Curtin University document wallet
Ruled graph paper	Porous	Gormack Graph Papers®
Glossy white paper	Semi-porous	International Association for Identification's "IDentification News" newsletter
Smooth white paper	Porous	American Academy of Forensic Sciences' "Academy News" newsletter
Lined thin white paper	Porous	Olympic® exercise book
Lined thick white paper	Porous	Spank Publishing® notebook
White matte photo paper	Semi-porous	HP® Photo Laser Paper 200 matte
Black cardboard	Porous	Optix® Jetz Black
Green copy paper	Porous	Optix® Veni Green
Patterned wrapping paper	Porous	Unknown manufacturer

All plastic substrates were characterised through attenuated total reflectance infrared (ATR-IR) analysis on a Thermo Scientific Nicolet iS50 Fourier transform infrared (FT-IR) spectrometer (see Supplementary Material Figures A1-6). The Nu World® Stone Paper was selected as the substrate for the majority of experimentation within this research, unless otherwise stated.

2.6 Recording and evaluation of results

Samples were photographed using a Nikon D300 camera, equipped with a 28 mm AF-S Micro-Nikon lens, mounted overhead on a Firenze Mini Repro stand and acquired on a computer using Nikon Camera Control Pro version 2.0.0. Samples photographed in reflectance mode were illuminated using dual incandescent light globes mounted on either side of the camera. Photographed samples were then stored in paper envelopes in a laboratory cupboard at room temperature. All images were later adjusted for brightness and contrast using Adobe Photoshop CS6 version 13.0, with any adjustments applied equally to all equivalent sample photographs.

All treated fingermarks were graded by a single evaluator based on the quality of friction ridge detail developed, and the contrast between the fingermark ridges and background of the sample. A 5-point system developed by the UK Home Office Centre for Applied Science and Technology (CAST) was used, as per Table 3 (28).

Table 3: UK Home Office grading system used to classify developed fingermarks (28).

Grade	Level of Development
0	No development
1	Signs of contact but less than 1/3 of continuous ridges, poor contrast
2	1/3 – 2/3 of continuous ridges, adequate contrast
3	More than 2/3 of continuous ridges but not quite a 'perfect' fingermark, good contrast
4	Full development; whole fingermark, continuous ridges, excellent contrast

These allocated grades should be considered as nonparametric class identities rather than continuous values. For this reason, the most frequently occurring fingermark grade (mode) was calculated for each trial and used as a means of comparison between samples. When trials resulted in equivalent modes, the central fingermark grade obtained (median) was also provided for a more detailed indication of the distribution of the grades (29).

3. Results and Discussion

3.1 Colloidal gold nanoparticle synthesis and characterisation

When synthesising gold nanoparticles for the SMD II stock solution according to the method published, it was found that the length of the boiling time of the gold salt in water had a significant effect on the size of the nanoparticles being produced, and therefore the colour of the solution. If the reducing agents were added immediately upon boiling (stock #2), nanoparticles with a larger diameter than intended were produced, resulting in a dark

purple coloured solution (Figure 3). If the reducing agents were added after a minute or two of boiling (original stock #1 and #4), nanoparticles of the intended size were produced, resulting in the desired red solution. If the reducing agents were added after approximately 5 or more minutes of boiling (stock #3), nanoparticles of a much smaller diameter were produced, resulting in a grey coloured solution.

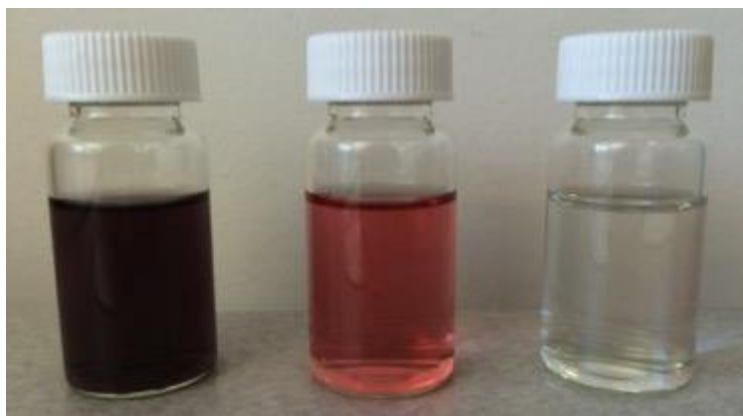


Figure 3: SMD II gold nanoparticle stock solutions #2 (left), #1 (middle), and #3 (right) containing different sized nanoparticles, with the length of the boiling time increased in samples from left to right.

The nanoparticle diameters were measured for the four different colloidal gold stock solutions using DLS after their dilution and the addition of Tween 20, with the results outlined in Table 4.

Table 4: Characterization of the different colloidal gold solutions in terms of colour and diameter size (measured by dynamic light scattering).

Gold Nanoparticle Stock Solution	Colour of Solution	Nanoparticle Diameter
Stock #3	Grey	6 nm
Stock #4	Red	17 nm
Stock #1 – "Reference"	Red	21 nm
Stock #2	Dark purple	34 nm

The reference solution (21 nm) that was synthesised by following the published method resulted in nanoparticles with a slightly larger diameter than those obtained by Bécue *et al.* (17 nm) (12, 16). For this reason stock solution #4 (17 nm) was utilised for all subsequent investigations. Exact boiling times utilised to produce these individual solutions could not be determined, as it was a varying parameter based on conditions such as the initial

temperature of the solutions and the quantity of solution being heated. Each individual gold nanoparticle stock solution was characterised by UV-visible spectroscopy (Figure 4).

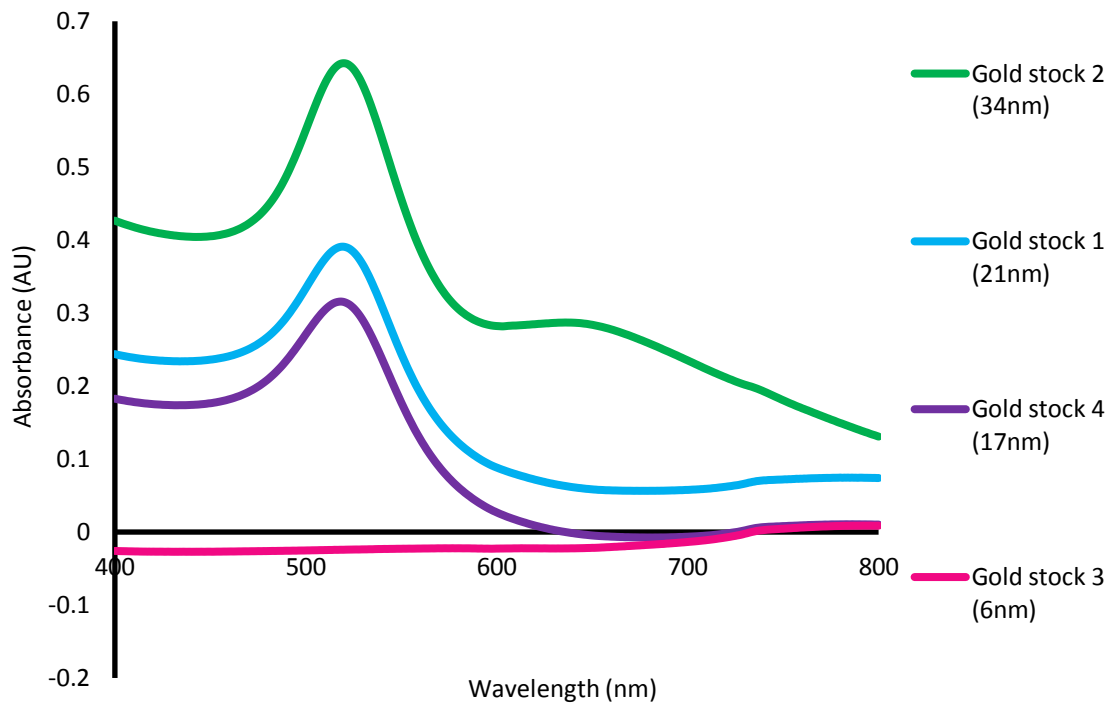


Figure 4: Absorbance spectra of the different colloidal gold solutions.

As the size of the gold nanoparticles increased, the absorbance peaks were broadened due to the increased scattering of light and variation in surface plasmon resonance (30-33). For nanoparticle diameters above 30 nm, another smaller, broader peak started to appear at longer wavelengths resulting in two absorbance maxima, caused by the presence of both transversal and longitudinal surface plasmon resonances (32, 33). The purple appearance of the solutions was produced by the additional absorption at these longer wavelengths of light. Gold nanoparticle solutions consisting of smaller diameter nanoparticles, such as stock #3 (containing 6 nm particles), can sometimes be too small to exhibit surface plasmon resonance, therefore resulting in no apparent absorbance of visible light (33). The spectrum produced by this solution above appeared to have negative values for its absorbance, which can most likely be attributed to an error in the background correction.

3.2 SMD II assessment guidelines

Guidelines for the assessment of fingerprint detection techniques have been proposed by the IFRG that outline methods for the development and evaluation of new fingerprint treatments (18). To ensure assessment of the naturally occurring variation in fingerprint composition, these guidelines state that pilot studies of novel fingerprint treatments should entail the use of samples from at least 3 donors (18). While previous publications have focussed on an actual assessment of the efficiency of the SMD and MMD development techniques, the emphasis of this study was put on the effect of the different parameters on

the detection quality of the published SMD II protocol. For this reason, the required number of donors was consequently less important than in a sensitivity or efficiency study.

There will always be a degree of variability throughout samples; although conditions have been kept as constant as possible throughout the experiments. All donors gave samples under similar conditions within 24 hours of each other, all samples were stored in similar environmental conditions (unless otherwise stated), and the same donors were used in each trial to allow for direct comparison. As it is unlikely that fingerprints at a crime scene will be processed while still fresh, fingerprint samples were stored for at least 1 week prior to treatment, unless stated otherwise. Furthermore, both natural fingerprints as well as fingerprints 'charged' with sebaceous material from the face were used throughout this research. This was done in order to replicate the use of the fingerprint treatment under operational conditions, while also obtaining some form of consistency throughout samples.

3.2 Effect of the nanoparticle size

Gold nanoparticle stock solutions containing different sized nanoparticles were applied to latent fingerprints using the SMD II procedure, and resulted in varying levels of development and contrast, as evident in Figure 5.

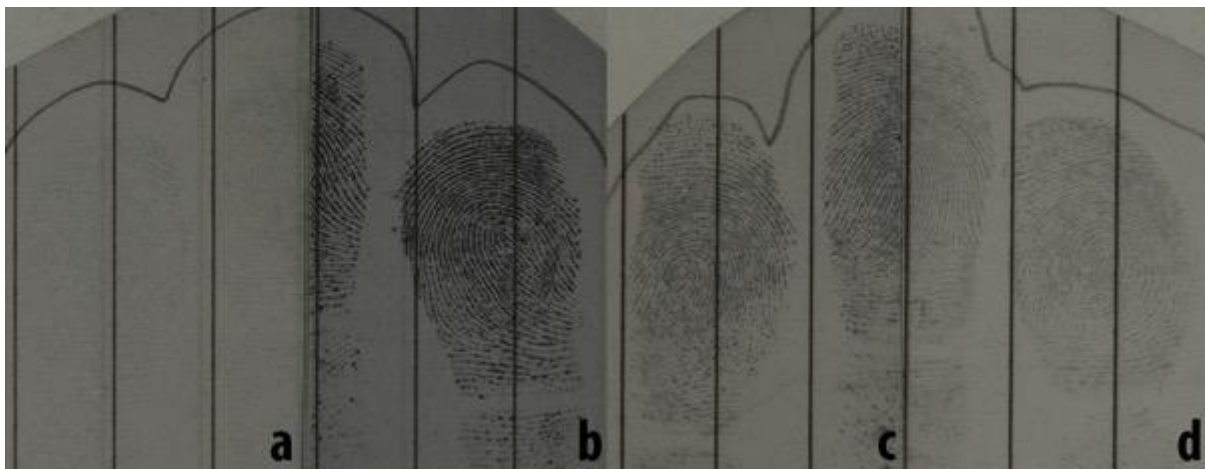


Figure 5: Latent fingerprints developed on Nu World Stone Paper using SMD II with solutions containing gold nanoparticles of diameter (a) 6 nm, (b) 17 nm, (c) 21 nm, (d) 34 nm.

The application of 6 nm gold nanoparticles resulted in low levels of fingerprint development and minimal contrast achieved, with fingerprints most frequently being graded at 1. Increasing the nanoparticle diameter to 17 nm resulted in elevated levels of fingerprint development with high contrast attained against the surface, causing a fingerprint grade of 3 to be produced by the majority of samples. Similar results were obtained through the use of 21 nm gold nanoparticles, achieving comparable levels of development with only slightly reduced contrast of the fingerprint, maintaining the mode of 3. When the nanoparticle diameter was increased further to 34 nm, there was a significant reduction in the level of contrast achieved, as well as a slight deterioration in the degree of development. These

samples most frequently produced a fingerprint grade of 2. The level of development and contrast obtained through the use of SMD II is heavily dependent on both the deposition of the gold nanoparticles onto the fingerprint residue, as well as the reduction of gold salt induced by the already deposited nanoparticles. Smaller nanoparticles, such as those at 6 nm, may be too small to seed satisfactory reduction of the gold salt in the reinforcement bath, resulting in what appears to be hindered levels of detection of the fingerprint residue. On the opposite end of the spectrum, larger nanoparticles tend to be less surface-active than smaller particles due to the decreased surface area-volume ratio (34). Due to the reduction in surface activity of these larger nanoparticles, such as those at 34 nm, the strength of their interactions with the fingerprint residue may be minimised, resulting in smaller amounts of gold nanoparticles being deposited onto the ridge detail. This conclusion is consistent with the previous observations made by Schnetz and Margot that nanoparticles of diameters larger than 20 nm result in inhibited deposition of gold onto the fingerprint when applied within the MMD procedure (35). It is evident from these results that gold nanoparticles of approximate diameter 15-21 nm are optimal for producing high levels of latent fingerprint development and contrast, and these nanoparticle sizes are obtained through the synthesis of colloidal gold solutions that appear red. By definition of the UK Home Office fingerprint grading system, the two stock solutions containing nanoparticles within this range and therefore exhibiting the desired red colour were the only samples to achieve grades indicating fingerprints that could be used operationally as a means of identification.

3.3 Effect of the solution temperature

Altering the temperature of the SMD II gold nanoparticle stock solution #4 (17 nm) before the addition of citric acid and the application to latent fingerprints resulted in varying levels of development and contrast, as evident in Figure 6.

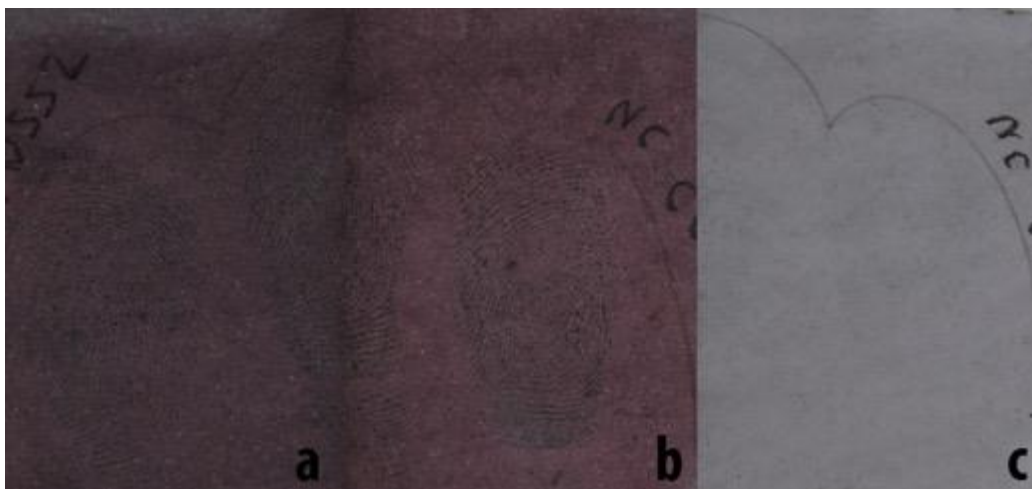


Figure 6: Latent fingerprints developed on Fuji Xerox white copy paper using SMD II with the gold nanoparticle solution bath at (a) 4 °C, (b) 20 °C, (c) 30 °C.

Gold nanoparticle stock solutions that were applied at 4 °C, immediately after removal from the refrigerator, resulted in a heavy degree of background staining. This made it difficult to observe the developed fingermarks on the surface, with the majority of these samples resulting in a grade of 0. By allowing the solution to warm up to room temperature before application, as recommended in the proposed SMD II method, the level of background staining is decreased enough to allow visualisation of the fingermark on the substrate, with most samples giving an increased grade of 1. Stock solutions heated to 30 °C resulted in a significant reduction in background staining, but also experienced a large decrease in the contrast of the fingermark ridge detail, again making it difficult to visualise on the substrate. The majority of heated samples obtained a grade of 1, although the median was only 0.5 in comparison to a median of 1 for room temperature solution samples. From this data it is evident that room temperature solutions improved the ratio between the level of background staining and the contrast achieved to allow for the best possible visualisation of latent fingermarks. While these results contrast the observations made by Schnetz and Margot in regards to the effect that temperature has on the MMD development process, their conclusions once again support that room temperature solutions allow for optimisation of the procedure (35). When analysing the gold nanoparticles using DLS, trials were done at different temperatures to see if this had any notable effect on the size of the nanoparticles in solution. Heating the gold nanoparticles over 25 °C before analysis caused an apparent doubling in the nanoparticle diameter, indicating that aggregation takes place at these higher temperatures. Aggregation of the gold nanoparticles affects their ability to deposit onto the fingermark residue, resulting in inhibited development of latent fingermarks using SMD II.

3.4 Effect of the bath agitation

The degree of agitation imposed on both the gold nanoparticle solution bath (based on stock #4) and the reduction solution bath significantly affects the level of latent fingermark development and contrast achieved, as seen in Figure 7.

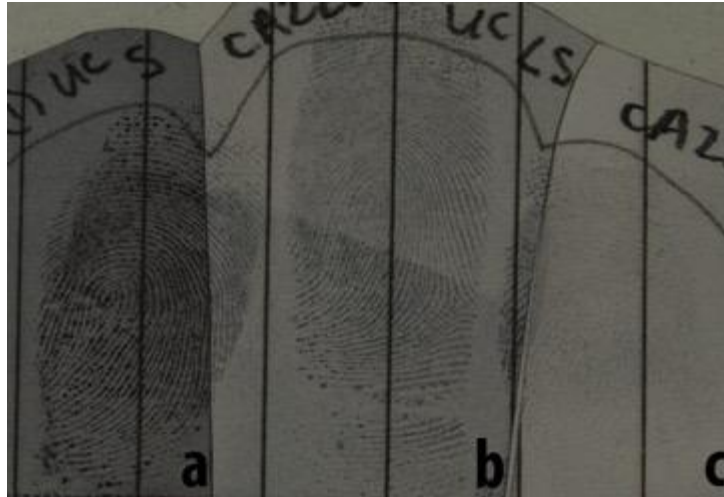


Figure7: Latent fingerprints developed on Nu World Stone Paper using SMD II with both active solution baths under (a) constant agitation, (b) minimal agitation, (c) no agitation.

No agitation of the solution baths resulted in very low levels of development and contrast, with the majority of fingerprint samples achieving a grade of 0. Minimal agitation of both solution baths throughout the fingerprint submersion time resulted in higher levels of development, but produced very patchy distribution of contrast. This could be due to the overlapping of samples in the solutions, but it could also be hypothesised that it is caused by the lack of a constant gold supply to certain areas of the sample; gold that is deposited onto the fingerprint is not replenished in areas without mixing, prohibiting a constant supply of gold for deposition onto the sample. The majority of these samples produced a grade of 2. When both the gold nanoparticle solution bath and the reduction solution bath were under constant agitation for the entire submersion time, higher levels of development were achieved with even distribution of contrast throughout the fingerprint samples, resulting in most samples being graded at a 3. To investigate the dependency of higher levels of fingerprint development on the agitation of the individual solution baths, a trial was done in which only the gold nanoparticle solution bath was under constant agitation for the submersion time and the reduction bath was left untouched. This was compared to samples that underwent the process with both solution baths under constant agitation, as illustrated in Figure 8.



Figure 8: Latent fingerprints developed on Nu World Stone Paper using SMD II with (a) only the gold nanoparticle solution bath under constant shaking and (b) both active solution baths under constant shaking.

Higher levels of fingerprint ridge detail development appear to be primarily dependent on the constant agitation of the gold nanoparticle solution bath, as the majority of samples from both trials achieved the same grade of 2. The contrast obtained by the fingerprints processed under constant agitation of both solution baths, however, is much greater. This is evident when comparing the resulting median of 2.5 to a median of 2 for samples processed with only the nanoparticle bath under constant agitation. The level of fingerprint development achieved is therefore affected by the deposition of gold nanoparticles onto the fingerprint residue, while the degree of contrast is influenced by the reduction of gold onto the deposited nanoparticles. This result is consistent with the findings of Durussel *et al.* on SMD I (15).

3.5 Operational substrates experimentation

The SMD II procedure was applied to latent fingerprints on a range of different substrates to test its efficacy. A summary of the achieved fingerprint grades on these various surfaces is listed in Table 5, along with a categorisation of the type of fingerprint development obtained on each surface.









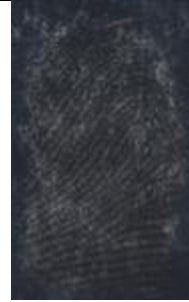

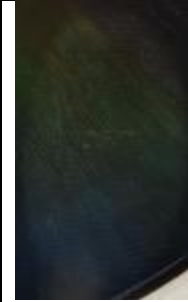




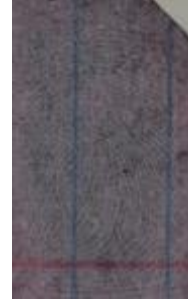


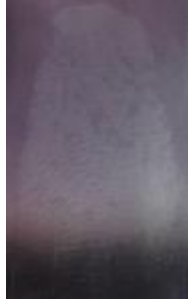


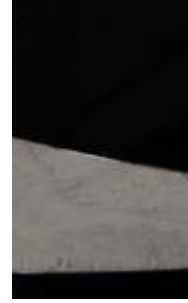
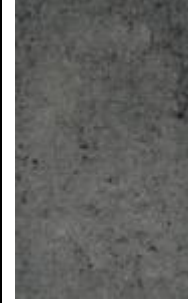
Table 5: Grading and fingerprint development data obtained on a range of different substrates tested using SMD II.

Substrate	Most common fingerprint grade	Contrast obtained
OfficeMax® recycled white copy paper	3	Dark ridges
Nu World® Stone Paper	4	Dark ridges
White Post It® note	1	Dark ridges
HP® matte photo paper	2	Dark ridges
Optix® green copy paper	4	Dark ridges
Marbig® polypropylene document sleeve	3	Dark ridges, with light gold plating of background
Fuji Xerox® white copy paper	1	Dark ridges, with heavy purple background staining
Confoil® aluminium foil	2	White ridges
Glossy white paper from International Association for Identification's "IDentification News" newsletter	2	White ridges
Polymethyl methacrylate white car paint	4	White ridges, with heavy gold plating of background
Polycarbonate Lite-On® Compact Disk	4	White ridges, with light gold plating of background
Optix® black cardboard	1	Gold ridges
Patterned wrapping paper	3	Gold ridges
Curtin University cardboard document wallet	1	Dark ridges, with damage to substrate
Gormack Graph Papers® ruled graph paper	1	Dark ridges, with damage to substrate
Olympic® thin white exercise book paper	2	Dark ridges, with damage to substrate
Spank Publishing® thick white notebook paper	1	Dark ridges, with damage to substrate
Polyethylene Kartell® laboratory bottle	1	Reversed development
Polyethylene terephthalate Cool Ridge® water bottle	2	Reversed development
Polypropylene takeaway container	1	Reversed development
Mikro® glass microscope slide	1	Reversed development
Coke Zero® aluminium can	1	No visible ridge detail
White paper from American Academy of Forensic Sciences' "Academy News" newsletter	1	No visible ridge detail

An example of each of these individual categories of fingerprints obtained is illustrated in Table 6 below. Samples that have been categorised under 'dark ridges' allowed for the visualisation of an expected dark grey coloured fingerprint on their surface, while samples

labelled as 'white ridges' and 'gold ridges' resulted in white or gold coloured fingermarks on their respective surfaces in a similar fashion.

Table 6: Examples of fingermarks developed using SMDII on a range of different surfaces.

					
OfficeMax® recycled white copy paper	Nu World® Stone Paper	White Post It® note	HP® matte photo paper	Optix® green copy paper	Marbig® polypropylene document sleeve
					
Fuji Xerox® white copy paper	Confoil® aluminium foil	International Association for Identification's "IDentification News" newsletter	Polymethyl methacrylate white car paint	Polycarbonate Lite-On® Compact Disk	Optix® black cardboard
					
Patterned wrapping paper	Curtin University cardboard document wallet	Gormack Graph Papers® ruled graph paper	Olympic® thin white exercise book paper	Spank Publishing® thick white notebook paper	Polyethylene Kartell® laboratory bottle
					
Polyethylene terephthalate Cool Ridge® water bottle	Polypropylene takeaway container	Mikro® glass microscope slide	Coke Zero® aluminium can	American Academy of Forensic Sciences' "Academy News" newsletter	

The majority of the 'white ridge' fingermarks obtained were on surfaces that experienced a significant degree of background staining, or in some cases gold plating, such as on the polymethyl methacrylate white car paint sample. The 'gold ridge' fingermark illustrated on the wrapping paper surface is a very significant result, as attempts at latent fingermark detection on this substrate using techniques such as Nile blue and Oil Red O have been unsuccessful due to both the smooth, glossy material and the various bright colours and patterns covering the surface (36, 37). A small number of substrates experienced a degree of damage throughout the SMD II procedure due to the long immersion time in water as well as the acidic conditions of the gold nanoparticle solution bath (pH 2.40), although they still resulted in visible fingermark development, such as that obtained on the thin exercise book paper. Finally, samples categorised as 'reversed development' appeared to experience heavy pink background staining of the substrate yet no staining of the fingermark ridges, generally resulting in the so-called reverse fingermark, or in some cases a blank space where the fingermark was situated. A similar phenomenon has been noted on paper surfaces when using gold nanoparticles modified to specifically target the cellulose substrate (38, 39). In this work we did not observe reversed or "empty" developed marks on paper, which is not surprising as the gold nanoparticles were not modified as those in the earlier work by Almog and co-workers. In a similar fashion this phenomenon has been observed through when using vacuum metal deposition (VMD) for latent fingermark detection, with reverse fingermarks being obtained on low-density polyethylene surfaces (40-42). The deposition of zinc onto the fingermark residues rather than the substrate is suggested to be due to the plastic surface absorbing the organic constituents of the fingermark residues, leaving behind a solid inorganic material that is less permeable to the gold than the plastic (43). Alternatively, it has been proposed that the unusual result may be produced by interactions between the substrate and gold layer, leaving the gold unable to act as a viable nucleation site for zinc deposition (40). While the mechanism of SMD II is currently undetermined, these suggestions regarding VMD can potentially also explain the reversed development obtained on plastic surfaces through the use of SMD II. In recent studies using atomic force microscopy we observed the propagation of thin films (0.2-1.1 nm in thickness) of material across the furrows of latent fingermarks deposited on glass over the first 24 hours after deposition (44). We postulated that this may also contribute to the "reverse" development encountered in VMD, and that may also be the case here.

These diverse results are clearly dependent on the properties of the substrate and their interactions with the gold nanoparticles; however, without knowing how the method operates to target the latent fingermark residue, it is difficult to explain the production of these fingermarks with various appearances. To gain an idea of why certain substrates interact with the gold nanoparticles and others do not, it is important to acquire an understanding of the mechanism behind the development technique (4). Regardless of the type of fingermark visualisation obtained, the SMD II procedure is clearly applicable to a wide range of substrates, including porous, non-porous, and semi-porous surfaces. It has

also proven to be successful for latent fingerprint detection on substrates such as wrapping paper that are difficult surfaces known to result in poor fingerprint visualisation using a range of differing development procedures.

4. Conclusions

The purpose of this study was to investigate single metal deposition (SMD) II as a latent fingerprint detection technique from an operational point of view. Gold nanoparticles of different diameters were synthesised by altering the length of the boiling time of gold salt in water prior to adding the reducing agents; larger nanoparticles than desired can be obtained by minimising the boiling time, while much smaller nanoparticles are produced through extended boiling time. After experimentation with a range of different gold nanoparticle sizes, solution temperatures, and levels of agitation, it was found that optimal development of fingerprints using SMD II was achieved through the use of red-coloured gold nanoparticle stock solutions containing nanoparticles of approximate diameter 15-21 nm, applied to fingerprints at room temperature (20-25 °C), with both the gold nanoparticle solution bath and the reduction bath under constant agitation throughout the entire submersion time. These parameters are consistent with those published, validating that the SMD II technique does not appear to be dependent on the geographic location. While the procedure's efficacy was sensitive to all of these conditions, satisfactory levels of development can still be achieved with slight variation of these parameters, demonstrating the robustness of the method and its associated suitability for operational use. The procedure was shown to be effective on a large range of porous, non-porous, and semi-porous substrates, including previously difficult surfaces that are known to hinder latent fingerprint development when using various other detection techniques. The properties of each substrate had a significant effect on the appearance of the development obtained, allowing for the production of a range of visually different fingerprints, some of which have been similarly observed with the use of other detection methods such as vacuum metal deposition (40, 41).

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