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Research article

Development of Latent Fingerprints on Wet, Non-Porous Surfaces by Small Particle Reagent with Zinc Oxide Nanoparticles

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Abstract

Small particle reagent (SPR) technique is a method used for detecting latent fingerprints on wet, non-porous surfaces by suspending nanoparticles in a reagent that binds with fatty acid residues on fingerprints. The small particle reagent technique is particularly effective for detecting latent fingerprints on evidence that has been submerged underwater for prolonged periods. However, due to its reliance on imported reagents, SPR is often expensive and involves a lengthy waiting period. Consequently, many researchers have attempted to develop SPR formulations using easily obtainable, cost-effective, and safe chemicals. In this study, we prepared two new SPR formulations containing zinc oxide nanoparticles mixed with diethylene glycol monoethyl ether. Both formulations used a surfactant composed of two types (sodium tetradecyl sulfate and Tergitol NP-9) for the development of latent fingerprints on wet surfaces. Latent fingerprints were deposited on four different non-porous surfaces, including stainless-steel spoons, glass slides, aluminum foil, and plastic slides. These surfaces were immersed in tap water for 1, 3, 7, 14 and 30 days. The resulting latent fingerprints were analyzed using the Mini Automated Fingerprint Identification System and were shown to produce clear, sharp, and detailed fingerprints on the non-porous surfaces. The best results were found on the surfaces of stainless-steel spoons with both formulations, where minutiae were detectable at more than 40 points even after the surfaces had been immersed in water for up to 30 days. This study provides forensic scientists and crime scene investigators with a faster and safer method for developing latent fingerprints using non-hazardous materials, which could serve as an alternative to conventional formulations.

Keywords: latent fingerprints; small particle reagent; zinc oxide nanoparticles; non-porous surfaces

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1. Introduction

Fingerprints are among the most valuable forms of evidence in forensic investigations. Because fingerprints are unique to each individual and remain permanent, they do not change with age. Their development serves as a highly accurate method for law enforcement agencies to identify suspects (Lee et al., 2001). The Office of Police Forensic Science has determined that at least 10 points of minutiae must match to confirm that the fingerprints belong to a given suspect (Klamkliang et al., 2022).

In some cases, offenders attempt to destroy their fingerprints by immersing items such as bottles, firearms, plastic, or foil in water. Notably, latent fingerprints may be found on items that have been accidentally or deliberately wetted. One of the most effective techniques for developing latent fingerprints on wet, non-porous surfaces without waiting for the surfaces to dry, is achieved by small particle reagent (SPR). This technique is based on suspending nanoparticles in a reagent that binds to fatty acid residues on fingerprints. The reaction occurs between the fatty acid residues in the fingerprints and the hydrophobic tails of the surfactant in SPR. These tails are linked to a hydrophilic head, which reacts with metal salts to produce a colored precipitate (Rohatgi & Kapoor, 2016).

In the past, powder dusting, cyanoacrylate fuming, and iodine fuming were the most commonly used techniques for latent fingerprint development on non-porous surfaces (Sodhi & Kaur, 2001; Jasuja & Singh, 2009; Bumbrah, 2017). At times, these traditional techniques have also been used instead of SPR for fingerprint development on wet non-porous surfaces (Bumbrah, 2016). Currently, investigative institutes still import SPR from abroad, which is both expensive and time-consuming.

However, many researchers have attempted to develop SPR formulations that can be easily prepared from non-hazardous chemicals. One example is the use of a black suspension (SPR Black), consisting of a mixture of carbon black or molybdenum disulfide suspended in a detergent solution (Kabklang et al., 2009; Joshi & Kesharwani, 2015; Madkour et al., 2017) for the development of latent fingerprints on wet, light-colored, non-porous surfaces. Another group used white suspensions (SPR White), such as zinc carbonate (Kabklang et al., 2009; Joshi & Kesharwani, 2015; Rohatgi et al., 2015; Rohatgi & Kapoor, 2016; Verma et al., 2021), titanium dioxide (Williams & Elliott, 2005), ferric oxide, and zinc oxide (ZnO) (Kabklang et al., 2009; Nualkul & Eksinitkun, 2017), which were suitable for dark, non-porous, wet surfaces. However, as a suspension of molybdenum disulfide is grey in color, fingerprints that have been developed on dark colored surfaces may not be sufficiently clear due to a lack of contrast between the surface and the print itself. To enhance the sharpness of latent fingerprints, some studies have involved adding both natural dyes (Dorbut & Benchawattananon, 2016) and commercial dyes (Rohatgi et al., 2015; Rohatgi & Kapoor, 2016; Verma et al., 2021) to the SPR formulation.

In recent years, nano powder-based compositions have been used in place of conventional fingerprint powders to develop latent fingerprints due to their strong adherence, high resolution and low background staining. The adhering properties of a powder formulation depend on the shape and size of the particles. Small, fine particles adhere more effectively than large ones (Bumbrah et al., 2022). Most research studies preferred to use zinc carbonate for developing SPR formulations (Kabklang et al., 2009; Joshi & Kesharwani, 2015; Rohatgi et al., 2015; Rohatgi & Kapoor, 2016; Verma et al., 2021). However, some studies have utilized titanium dioxide, which has yielded superior results. Jasmine & Kapoor (2016) compared three types of suspension materials and found the efficiency of SPR formulations to be in the order of TiO_2 > $ZnCO_3$ > ZnO. In their study, the particle size of ZnO was 464.7 nm, which was larger than the particle size used in this research. In general, it has been observed that very few studies have been conducted on the development of latent fingerprints using zinc oxide nanoparticles. Consequently, ZnO was selected to demonstrate its potential as an alternative for the development of SPR formulations.

This study aimed to develop a new SPR formulation for detecting latent fingerprints on wet, non-porous surfaces. Our formulation employed a white suspension of zinc oxide nanoparticles mixed with diethylene glycol monoethyl ether as a solvent that allows for even distribution of the components throughout the reagent. This formulation uses a surfactant composed of two types (sodium tetradecyl sulfate and Tergitol NP-9). Tergitol NP-9 is selected for its low solubility in fats, its ability to develop superior latent fingerprint quality compared to other surfactants (Nualkul & Eksinitkun, 2017), and is considered non-hazardous to users. The present study was done to determine whether this novel SPR formulation could allow investigators to recover latent fingerprints on stainless-steel spoons, glass slides, aluminum foil, and plastic slide surfaces that had been submerged in stagnant water for various time intervals. Herein, we determined the quality of the detected latent fingerprints by counting the number of minutiae, which would justify the potential application of this process in the future.

2. Materials and Methods

2.1 Materials

Zinc oxide (particle size ~38 nm, CAS no: 1314-13-2, purity 91%) Tergitol NP-9 (CAS no: 127087-87-0, purity 97%, HLB 12.9) and deionized water (pH 6.9) were purchased from Chemipan Corporation Co., Ltd. The chemicals used in the experiment, sodium tetradecyl sulfate (CAS no: 1191-50-0, purity 95%) as the anionic surfactant and diethylene glycol monoethyl ether (CAS no: 111-90-0, purity 99%), were procured from Sigma-Aldrich Co., Ltd.

2.2 Characterization of ZnO nanoparticles

Zinc oxide nanoparticles were coated with platinum using an auto fine coater (JEOL JFC-1600). The thickness of the coating was 6 nm and was applied under vacuum at 10 mA. The particles were characterized using a field emission scanning electron microscope (FESEM, JEOL JSM-7600F) to analyze their morphology and particle size. Additionally, the structural properties of the ZnO nanoparticles were confirmed through X-ray diffraction (XRD, Bruker D8 ADVANCE ECO) using a Cu-Kα1 radiation source (λ = 1.5406 Å).

2.3 Sample preparation process

This study involved pressing the fingerprints from a single donor onto four different non-porous surfaces that included stainless-steel spoons, glass slides, aluminum foil, and plastic slides. This process was repeated three times. The surfaces were then submerged in tap water (pH 7.4, TDS 190 mg/L) for 1, 3, 7, 14, and 30 days and were subsequently developed using the SPR composition. The experiment was conducted during the summer season in Bangkok, Thailand when temperatures were typically within a range of 34-36°C and relative humidity was recorded between 65-90%.

2.4 Methods

Two formulations, labelled A and B, were prepared as shown in Figure 1. For formulation A, 5.0 g of zinc oxide was mixed in 96.5 mL of deionized water, to which 0.25 g of diethylene glycol monoethyl ether and 0.25 g of sodium tetradecyl sulfate were added. Formulation B was prepared by adding 0.25g of Tergitol NP-9, a commercial liquid detergent, to a suspension of 5.0 g of zinc oxide in 96.5 mL of deionized water, along with 0.25 g of diethylene glycol monoethyl ether. The surfaces containing latent fingerprints were then immersed in tap water for durations of 1, 3, 7, 14, and 30 days. This immersion step was repeated three times. To simulate the conditions of evidence being recovered from a stagnant pool of water, the surfaces were pulled from the water and sprayed with each SPR formulation separately to allow the wetted latent fingerprints to react with the formulations. The surfaces were then left for a period of three minutes (Verma et al., 2021). After the designated time, they were washed under a gentle stream of water for a few seconds and left to dry at room temperature. The surfaces were then photographed using a Canon 1300D DSLR camera. The resulting latent fingerprints were analyzed using the Mini Automated Fingerprint Identification System (Mini AFIS) to count the number of minutiae as shown in Figure 2 and to evaluate their quality (Eksinitkun et al., 2019).

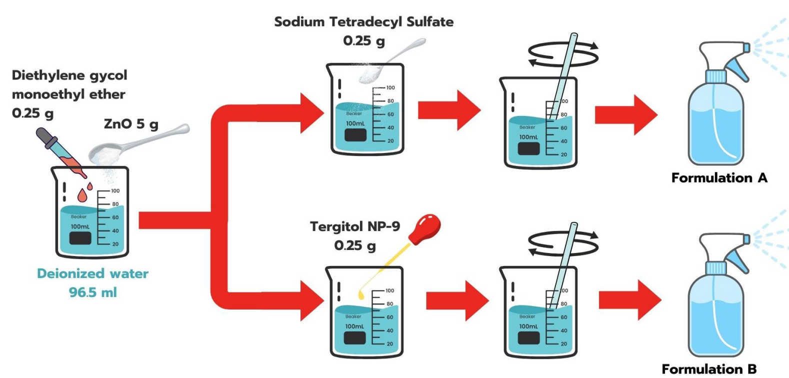
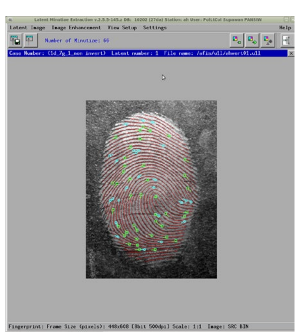


Figure 1. Preparation of the SPR formulations

(a) 

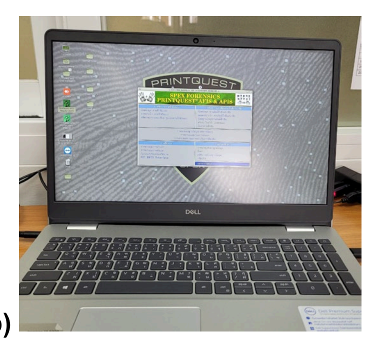
(b) 

Figure 2. (a)The number of minutiae detected; (b) Mini Automated Fingerprint Identification System (Mini AFIS)

2.5 Evaluation of results

The quality of the latent fingerprints was analyzed based on the number of minutiae detected in each sample. The score ranges were divided into five grades (Eksinitkun et al., 2019; Nualkul & Eksinitkun, 2017). The equation involves subtracting the minimum number of detected minutiae (in this study, 8) from the maximum number of detected minutiae (in this study, 73), and then dividing the result by 5 to represent the fingerprint quality levels. This process yielded a value that corresponded to the range of width for each quality level. In this study, the range for each quality level was determined to be 13 and the results were used to describe the quality grade of the latent fingerprint verification as shown in Table 1.

$$\frac{\text{(Number of Minutiae (Max)) - (Number of Minutiae (Min))}}{\text{(Grade of fingermark quality (5))}} = \frac{73-8}{5} = 13.00$$

Table 1. Fingerprint quality scales

Number of Minutiae	Grade	Description
More than 60.00	5	Excellent quality, very clear prints (Latent print was distinctly clear and clean)
47.01 – 60.00	4	Good quality, ridge-details visible (Latent print was clear and clean)
34.01 – 47.00	3	Medium quality, ridge-details and some characteristics visible (Latent print was moderately clear with limited contrast)
21.01 – 34.00	2	Poor quality, some ridge details visible (Latent print was slightly clear with little contrast. The background was dirty.)
8.00 – 21.00	1	Poorest quality, very few visible ridges (Latent print was unclear and without contrast. The background was dirty.)

3. Results and Discussion

3.1 Scanning electron microscope

The scanning electron microscope (SEM) images of zinc oxide nanoparticles provided essential information about their morphology and size distribution as shown in Figure 3. These images revealed that the powder consisted of spherical particles. Particle size measurements were randomly taken for 30 particles, with an average size of approximately 38 nm. The SEM images showed a relatively uniform particle distribution. This characteristic makes zinc oxide nanoparticles suitable for the development of latent fingerprints.

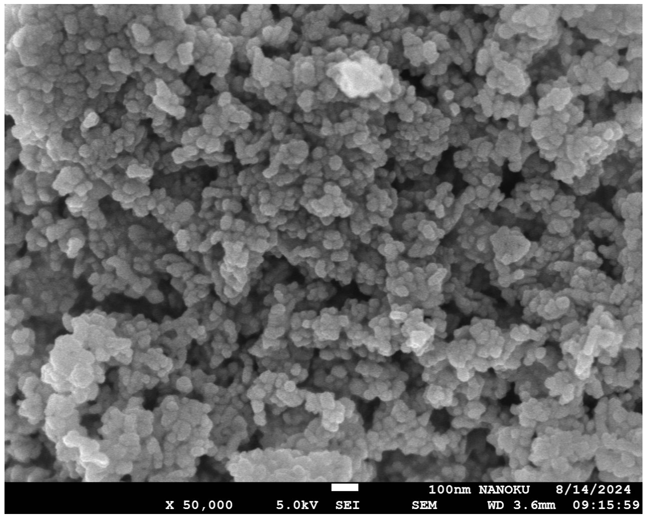


Figure 3. SEM image of zinc oxide nanoparticles

3.2 X-ray diffraction

The X-ray diffraction (XRD) pattern of zinc oxide nanoparticles provided valuable information about the crystalline structure of the material. The corresponding crystal planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) were clearly observed in the XRD data between 20 and 80 degrees (2-theta). Peak indexing was performed using the standard JCPDS data file no. 00-036-1451, and the corresponding planes are shown in Figure 4 (Verma et al., 2022).

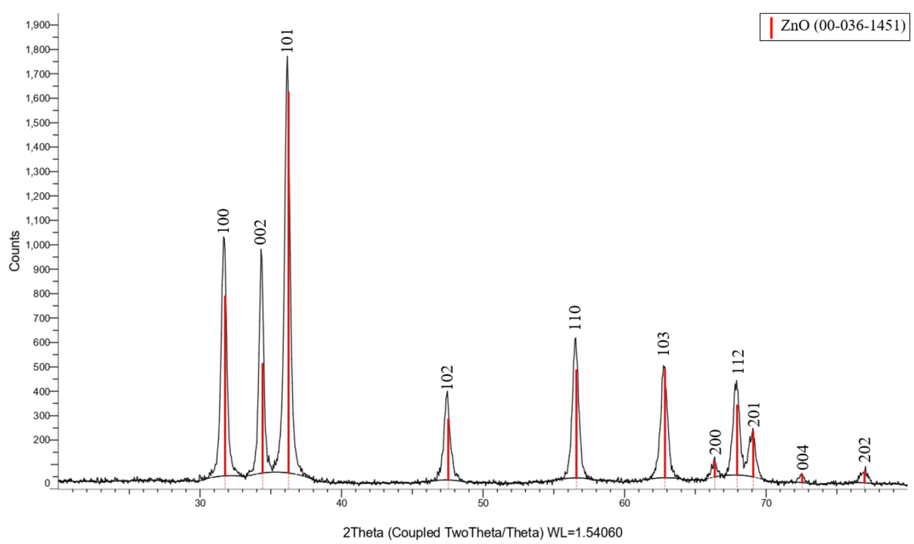


Figure 4. XRD Pattern of zinc oxide nanoparticles

3.3 Detection of latent fingerprints

The small particle reagent (SPR) technique has been proven effective for detecting fingerprints on wet, non-porous surfaces. In the present experimental study, formulation A developed sufficiently clear fingerprints with good contrast. The most suitable surface associated with reasonable quality of ridge detail and identifiable characteristics was the stainless-steel spoon. These spoons had been immersed in water for up to 30 days and still exhibited more than 43 points of minutiae, resulting in a print grading of 3. This was followed by the glass slide, aluminum foil, and plastic slide, where minutiae were detected at 22 points (grade 2). In this experiment, it was observed that the clarity of the fingerprints decreased as the immersion period increased, irrespective of the surface type. This result can be used for the visualization and identification of latent fingerprints. The results are presented in Tables 2 and 3.

Table 2. Latent fingerprints developed on four non-porous surfaces with formulation A

Duration	Surfaces			
	Stainless-steel Spoon	**Glass Slide**	**Aluminum Foil**	**Plastic Slide**
1 day				
3 days				
7 days				
14 days				

Table 2. Latent fingerprints developed on four non-porous surfaces with formulation A (continued)

Duration	Surfaces			
	Stainless-steel Spoon	Glass Slide	Aluminum Foil	Plastic Slide
30 days				

Table 3. Average number of minutiae and grades of SPR formulation A on four non-porous surfaces for various period of time

Surfaces/Periods of Immersion	1 day	3 days	7 days	14 days	30 days
Stainless-steel spoons	63.00 (5)	64.33 (5)	60.33 (5)	56.00 (4)	43.33 (3)
Glass Slides	64.00 (5)	60.33 (5)	48.33 (4)	43.33 (3)	22.33 (2)
Aluminum Foil	57.33 (4)	57.00 (4)	56.67 (4)	32.67 (2)	22.00 (2)
Plastic Slides	58.00 (4)	54.67 (4)	46.00 (3)	26.33 (2)	22.00 (2)

Next, the SPR formulations were modified by replacing sodium tetradecyl sulfate (STS) with the commonly available and cost-effective surfactant Tergitol NP-9. SPR formulation B was tested on four different non-porous surfaces: stainless-steel spoons, glass slides, aluminum foil, and plastic slides, which had been immersed in tap water for durations of 1, 3, 7, 14, and 30 days. Formulation B yielded reasonably good results on all four surfaces up to 14 days, developing clear, sharp, and detailed fingerprints on the stainless-steel spoons and plastic slides after the immersion for up to 30 days, with average minutiae of around 46 points (grade 3) and 28 points (grade 2), respectively. In contrast, the aluminum foil and glass slide surfaces were less effective for developing latent prints under wet conditions, resulting in fingerprint grades below 2, based on detected minutiae of 18 and 14 points, respectively. Additionally, the experiment showed that the clarity of the prints decreased as the period of immersion increased, irrespective of the surface type. The results are presented in Tables 4 and 5.

In our study, both SPR formulations produced the best results on stainless-steel spoon surfaces that had been immersed in water for up to 30 days. This finding was consistent with the results of previous research studies (Dorbut & Benchawattananon, 2016; Nualkul & Eksinitkun, 2017). The superior performance on stainless steel can be attributed to the surface's smooth and less slippery nature, which allows fatty acids to adhere more effectively compared to other surfaces. Additionally, our study observed a decrease in fingerprint clarity as the immersion period increased across all surface types. This observation suggests that the longer an object remains submerged, the more difficult it becomes to visualize and develop latent fingerprints.

Table 4. Latent fingerprints developed on four non-porous surfaces with formulation B

Duration	Surfaces			
	Stainless-steel Spoon	**Glass Slide**	**Aluminum Foil**	**Plastic Slide**
1 day				
3 days				
7 days				
14 days				
30 days				

Table 5. Average number of minutiae and grades of SPR formulation B on four non-porous surfaces for various period of time

Surfaces/Period of Immersion	1 day	3 days	7 days	14 days	30 days
Stainless-steel spoons	57.33 (4)	56.00 (4)	52.33 (4)	50.33 (4)	45.67 (3)
Glass Slides	62.67 (5)	61.33 (5)	60.67 (5)	42.67 (3)	14.00 (1)
Aluminum Foil	72.33 (5)	62.33 (5)	53.67 (4)	38.00 (3)	18.00 (1)
Plastic Slides	66.33 (5)	53.00 (4)	45.00 (3)	37.33 (3)	28.33 (2)

In our comparison of the two surfactants, sodium tetradecyl sulfate (STS) and Tergitol NP-9, the differences in fingerprint development results were not significant. Sodium tetradecyl sulfate (STS), an anionic surfactant and effective wetting agent, tends to leave excess chemical residues on surfaces. These residues adversely affect fingerprint clarity and result in less distinct prints, especially on aluminum foil and plastic slide surfaces. In contrast, Tergitol NP-9, a nonionic surfactant, proved more effective on certain surfaces, particularly aluminum foil and plastic slides where minutiae of up to 72 and 66 points, respectively, were detected after 1 day of immersion. This effectiveness is attributed to Tergitol NP-9 producing fewer bubbles, dissolving well in water, and having lower solubility in fats, as supported by previous research (Nualkul & Eksinitkun, 2017). Both SPR formulations were capable of developing latent fingerprints of adequate quality, with minutiae detected at more than 10 points. However, formular B with Tergitol NP-9 emerged as the preferred option in our study because sodium tetradecyl sulfate, while commonly used across the medical field, is sold at a higher price.

4. Conclusions

This study was aimed at developing SPR formulations for latent fingerprint development on non-porous surfaces submerged in water. Both SPR formulations effectively recovered adequate prints and could be used for identification because minutiae were detected at more than 10 points. This capability enables investigators to develop fingerprints under wet and moist conditions. Crime scene investigators can effectively recover fingerprints from evidence found in canals, pools, rivers, and other bodies of water. The raw materials used for preparing our SPR formulation are both cost-effective and easily available. Consequently, this formulation can serve as an alternative to commercial SPR products, allowing domestic agencies to reduce their reliance on imported SPR formulations from foreign sources.

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6. Conflicts of Interest

The authors declare that they have no conflicts of interests.

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