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Chemical composition effect on latent print development using black fingerprint powders

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ABSTRACT

Fingerprint development has been used to visualize latent prints since the 19th century, and several companies produce a variety of commercially available black fingerprint powders. While the method to develop fingerprints has been refined over the years, the composition of fingerprint powders that are used in print development has not been studied extensively. Six different black fingerprint powders were studied using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), dynamic light scattering (DLS) and zeta potential, attenuated total reflectance infrared spectroscopy (ATR-IR), Raman spectroscopy, powder X-ray diffraction (PXRD), and solution-phase nuclear magnetic resonance spectroscopy (NMR) in addition to a quality study involving certified latent print examiners. When comparing all chemical, physical, and morphological results for the fingerprint powder, this study determined that powders ranked best by latent print examiners are fingerprint powders that mainly contain carbon and oxygen with particle sizes around 50 nm and spherical morphology. Powders with large particle sizes, irregular shape, and elemental compositions consisting of many elements ranked poorly in the quality study performed.

Introduction

From collecting suspects' prints to finding prints at crime scenes, fingerprints are a common identification tool for forensic scientists. The most common type of fingerprints found at crimes scenes are latent prints: fingerprints that are invisible to the human eye [1–3]. Visualization techniques such as powders, suspensions, and chemical enhancement are imperative when collecting this type of fingerprint for analysis [3]. Fingerprint powders in particular are often used for latent print development. Using powder to collect latent prints allows the examiner to make the print more visible by developing contrast for photographic purposes [4]. It also allows for further improvement in preserving and lifting the powdered print [4]. Commercial powders contain two common components in order to help with latent print adhesion: pigment and binder [1]. These essential features allow the powder to adhere to the latent print during collection without over powdering the substrate making it hard to discern the print [1]. This is a common problem often referred to as "painting" the substrate which can occur when the proper detection of a latent print is hindered due an increased amount of powder adhering to the substrate [1]. The pigment is used for effective visualization, while the binder provides maximum and preferential adhesion to the latent print residue [1]. Carbon black (colloidal carbon), lamp black,

Abbreviations: XPS, X-Ray Photoelectron Spectroscopy; ATR-IR, Attenuated Total Reflectance Infrared Spectroscopy; FTIR, Fourier Transform Infrared Spectroscopy; NMR, Nuclear Magnetic Resonance; SEM EDS, Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy; DLS, Dynamic Light Scattering; PXRD, Powder X-Ray Diffraction; XRD, X-Ray Diffraction; NaCl, Sodium Chloride; LED, Lower Electron Detector; SDS, Safety Data Sheet; Lightning, I.D. Technologies Lightning Black Fingerprint Powder manufactured by Safariland Group; Lynn Peavey, Lynn Peavey Black Powder supplies by the Lynn Peavey Company; Lightning Supranano, Lightning Powder Supranano Black manufactured by Safariland Group; Evident, Evident Black Fingerprint Powder manufactured by Evident; Sirchie, 101L HiFi Volcano Latent Print Powder in Silk Black manufactured by Sirchie; Arrowhead, Black Latent Print Powder supplied by Arrowhead Forensics.

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talc, kaolin, aluminum, metal flake, and dolomite have proved to be efficient particles for fingerprint powders [1]. Binders often used in combination with these particles include iron powder, lycopodium, corn starch, rosin, and gum arabic [1]. Although the manufacturers know the chemical composition, commercial powders are often sold with no chemical identification and classified by their visual characteristics only [1]. While these powders can come in a range of colors, most of the powders on the market are either black or white [2].

Black fingerprint powders, also known as carbon black or carbon based, are commonly known for their versatility on a wide range of surfaces [1,2]. Some black fingerprint powders contain cobalt oxide, cupric oxide, lamp black, and manganese dioxide which are all considered potential health hazards and caution is recommended for the user [4]. Additionally, white powders are titanium dioxide based and have been linked to the activation of cancers in humans causing them to be potentially dangerous to users over time [2]. This had led to phasing out certain types of powders and the use of respiratory protection when dealing with fingerprint powders at crime scenes [5]. Recent advancements in fingerprint powder formulation have also discovered that powders made of turmeric can be used to visualize latent fingerprints, suggesting that turmeric powder could eventually be used as an additive to current powder formulations for increased visualization [6]. Alternative powders have also been made of finely ground gambir powder, which is made from a naturally occurring plant, and has proven to be a cheap and environmentally friendly way to dust latent fingerprints [2]. A current direction for fingerprint technology is the addition of nano-engineered particles. Recent studies are working with silicon to engineer bifunctional magnetic-fluorescent nanoparticles and doping nanobeads with silica [7,8].

A list of traditional fingerprint powder formulas can be found online, from manufacturers, or general estimated formulas; however, they do not provide any indication as to which formulations produce higher quality prints [4]. Knowing the chemical, physical, and morphological composition of these powders could prove significant in powder choice and print collection. The fingerprint powder effectiveness can be gauged on how the particles stick to the ridge patterns of latent prints, suggesting that the effectiveness of the powder should be directly related to the shape and size of the nanopowders [9]. A previous study of gambir powders compared the efficiency of the powder to the particle size and it was found that a more coarse powder (0.250 mm) was more efficient on glass slides and transparent plastics, while finer particles (0.125 mm) had a higher efficiency for objects like plastic cups, compact discs and aluminum foils [2]. Furthermore, typical powders are manufactured as nonflake or flake particles [1,10]. Flake powders are usually 1 to 50 μm in diameter and they tend to "paint" the substrate more than that of the nonflake powders [1]. Commercial flake powder is manufactured by ball-milling spherical metallic particles and is considered ideal with a mean diameter of 10 μm and an average thickness of 0.5 μm [1].

Even though the use of powders with better adhesion capabilities has always been a goal, it was once considered unnecessary for investigators to have a deeper knowledge on the chemical composition of the latent print residue or even the processes that take place when using fingerprint powders [4]. As a result of commercial fingerprint manufacturers labeling powders by their color characteristics, latent fingerprint examiners are never given the chance to understand the properties of the products that they are using. Knowing the characteristics of the powders could be beneficial to examiners when collecting latent prints. By determining the chemical, physical, and morphological differences between black fingerprint powders, which are one of the most common types of powders used, latent print examiners will have background knowledge on the interactions and collection ability of the product when they are called to testify in court. In addition, this knowledge would allow companies to make crucial changes in improving formulations of the fingerprint powders in order to increase the adhesion to the prints, the quality of the prints developed, and to reduce health concerns. This study characterizes six black fingerprint powders using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), dynamic light scattering (DLS) with zeta potential measurements, attenuated total reflectance infrared spectroscopy (ATR-IR), Raman spectroscopy, powder X-ray diffraction (PXRD), and solution-phase nuclear magnetic resonance spectroscopy (NMR). A quality study of powdered latent prints involving certified latent print examiners also took place.

XPS was used to identify the chemical composition and chemical ratios of each of the powders. SEM along with EDS were used to observe morphology, particle sizes, and composition in combination with XPS. SEM was also used to analyze the quality of the powders by observing the particle adhesion to latent fingerprints. ATR-IR, Raman, and NMR spectroscopy were used to analyze the presence of organic functional groups. PXRD was used to analyze if any powder may have a diffraction pattern due to the possibility of any crystalline components. DLS was used to study the effects of various solutions on particle size by measuring the hydrodynamic diameter, which accounts for the diameter of the particle and ligands, ions, or molecules that are associated with the surface and travel along with the particle in colloids. The particle size measurements obtained using DLS differed from those obtained using SEM due to this effect [11,12]. In addition, the zeta potential was measured, which is correlated to the surface charge of the particle and the nature and composition of the surrounding medium in which the particle is dispersed [13]. Lastly, a print quality study was performed to correlate the physical, chemical, and morphological characteristics of each black powder to the quality of the print developed and lifted as determined by certified latent fingerprint examiners.

Experimental

Chemicals and materials

The following black fingerprint powders were analyzed: Lightning, Lynn Peavey, Lightning Supranano, Evident, Sirchie, and Arrowhead. Each powder manufacture, name, and label are summarized in Table 1.

All fingerprint powders were used as purchased with no further modifications. Artificial Eccrine Perspiration from Pickering Laboratories, NaCl obtained from Columbus Chemical Industries, Inc., and deionized water were utilized for DLS and Zeta Potential samples. Artificial Eccrine Perspiration - Sebum Emulsion also purchased from Pickering Laboratories was utilized for the preparation of latent prints for the quality study and for the visualization of powder adhesion to latent prints using SEM. Chloroform and deuterated chloroform used in NMR were obtained from Acros. Ethanol was purchased from Greenfield Global. Methanol and isopropanol were purchased from Fisher Scientific.

Instrumentation

XPS

XPS measurements were performed using a PHI VersaProbe 5000 Scanning X-Ray Photoelectron Spectrometer (ULVAC-PHI, Inc.) at room temperature and under vacuum lower than $1*10^{-6}$ Pa. All measurements

Table 1
Summary of all the six fingerprint powders analyzed, their manufacturer, and labelling information.

Manufacturer Label	Manufacture	Name Code
Lightning Black Fingerprint Powder	Safariland Group	Lightning
Lynn Peavey Black Powder	Lynn Peavey Company	Lynn Peavey
Lightning Powder Supranano Black	Safariland Group	Lightning Supranano
Evident Black Fingerprint Powder	Evident	Evident
101L HiFi Volcano Latent Print Powder in Silk Black	Sirchie	Sirchie
Black Latent Print Powder	Arrowhead Forensics	Arrowhead

were performed using a focused Al K-Alpha X-ray source at photon energy of 1486 eV and power of 25 W with an X-ray spot size of 100 μm. The take-off angle of the photoelectron was set at 45°. All XPS spectra were referenced to the C1s peak at a binding energy of 284.8 eV. Each fingerprint powder was analyzed in triplicate.

SEM

A JEOL JSM-7200F SEM with a Zr01W emitter electron source was used to observe morphological characteristics. The sample data was collected at an acceleration voltage of 20 kV using the Lower Electron Detector (LED). The pressure was approximately 10^{-4} Pa with a working distance of 10 mm and probe current was set to 12. Samples were analyzed using two preparations. In both preparations, the stubs were handled using gloves and the counter tops in which the samples were prepared were cleaned with isopropanol. In Preparation 1, all fingerprint powder samples were developed by placing a small amount of powder on a glass slide. A stub with a piece of spectrally pure carbon tape was then inverted and dipped into the powder on the glass slide. The stub was then lightly tapped on the side of a lab bench and blown with compressed air to remove any excess powder. Samples were then coated in carbon using a sputter coater. Each powder sample was analyzed at three sites on the stub. For Preparation 2, clean 12 mm glass circular cover slips were adhered to an SEM stub using spectrally pure carbon tape. Once attached, a latent print was made on the glass using a matrix of Artificial Eccrine Perspiration- Sebum Emulsion. The stubs were powdered with the six black powders, two stubs per sample type. Excess powder was removed by tapping the stubs on the lab bench prior to carbon coating using a sputter coater. Each latent print sample was analyzed at three sites across the print. Fingerprint samples for the SEM were prepared by the same person who prepared the fingerprint cards for the Quality Study (Section 2.2.8) The temperature at the room where the fingerprint samples were prepared was at 22.5 °C ± 0.1 °C with a relative humidity 59.9 % ± 0.6 %.

EDS. For each site and magnification of SEM Preparation 1, elemental analysis was also conducted using Oxford Instruments Ultimax 100 with an X-max detector. Samples were analyzed using a deadtime of less than 30% with a 4 min processing time. Data analysis took place using Aztec 4.2 software. An elemental spectrum was collected for 20 s, while elemental mapping data was collected for 2 min.

SEM Particle Sizing. Particle sizing was performed on the SEM images of the fingerprint powders made using Preparation 1 described above. The ImageJ software was utilized to measure particle size, calibrating the software scale using the imbedded scale in the SEM images. Particle sizing was accomplished by determining sizing within an area of ten to fifteen particles at three different site locations on each stub. The free-hand tool was used to ensure that the area of irregularly sized particles could be accurately depicted. Images at 1000× were utilized for Lightning, Lynn Peavey and Lightning Supranano. For Evident, Sirchie, and Arrowhead powders, particle sizing was achieved using images at 500× to ensure that ten to fifteen particles could be chosen, as these powders had larger particle sizes. Histograms were created in Origin comparing the area of the particles within each sample to depict the distribution of particle sizes across the various samples.

DLS and Zeta Potential Measurements

A Brookhaven ZetaPlus Zeta Potential Analyzer (90Plus PALS) was used to perform DLS and zeta potential measurements of the fingerprint powders. The DLS was used to measure powder particle size in environments in which they would potentially be used such as sweat residue. The Zeta Potential Analyzer was employed to determine the direction of particles under the influence of an electric field, allowing the estimation of the zeta potential of the fingerprint powder suspensions. The measurements were performed at 25 °C in water, a 29 mM solution of NaCl based on previous sweat composition research, and Artificial Eccrine Perspiration solution [14]. At least three trials of each sample per solution were collected. For the DLS measurements, five runs were analyzed for each trial and the collected trial values were averaged. For the zeta potential measurements, ten runs were conducted per trial and then the trials were averaged.

ATR–IR

ATR – IR was performed using a Thermo Scientific Nicolet iS50 FTIR and was used to analyze the presence of functional groups on the surface of the fingerprint powders. An air background was used for analysis purposes. In this study, two trials of 256 scans with a resolution of 2 cm^{-1} were collected for each sample.

Raman Spectroscopy

The Raman setup used in this work was a modular unit consisting of a spectrometer (Ocean Optics) and a laser connected to a fiber optic Raman probe (in Photonics). The excitation source was a 785 nm laser (260 mW) and the radiation was conducted to the fingerprint samples by a fiber optic cable. Fine focusing of the probe was achieved to maximize the Raman signal. Another fiber optic cable conducted the scattered radiation to the spectrometer for analysis. Ocean View 2.0 software was used for the acquisition and analysis of the spectra. The integration times ranged from 1 to 5 s with 1 s average scan per run. The fingerprint samples were prepared by making 0.5 cm thick tablets on a clean stainless-steel cup and the solid samples were measured directly to avoid any spectral contribution from glass containers.

Solution-Phase NMR Spectroscopy

All NMR spectra were recorded on a Bruker 400 MHz Ascend Spectrometer at 25 °C, and chemical shifts given relative to $CHCl_3$ (7.26 ppm), $CDCl_3$ (77.23 ppm). Samples were extracted with organic solvents to separate soluble components from the bulk of the powder. Samples (1 g) were placed in a cellulose thimble and extracted with refluxing ethanol in a continuous Soxhlet extractor for a period of 12 h. For samples that contained temperature-sensitive components that degraded at 78 °C, samples were extracted with $CHCl_3$. Samples were placed in a glass tube packed with cotton and sand, and $CHCl_3$ (200 mL) was allowed to flow through the sample over the course of 2 h.

PXRD

The PXRD patterns of samples were obtained using a PANalyticalX'Pert Pro MPD powder X-ray diffractometer with Cu K-Alpha X-ray source operating at 45 kV and 40 mA power in the Bragg-Brentano geometry. The spectra were collected over a 2-theta range of 5 to 80 at a step size of 0.033 with a solid-state X-ray detector.

Fingerprint Powder Quality Study

To assess the quality of the fingerprint powders in this paper, a quality study was created to determine which powders lifted the clearest latent prints. Two types of prints were utilized for this study, pristine and diminished fingerprints. Both types were deposited onto 3 × 5 in. pre-cut window glass obtained from Justice Glass cleaned twice using dish soap and methanol using Artificial Eccrine Perspiration – Sebum Emulsion as the matrix. Pristine prints were deposited using the index, middle, and ring finger with one simultaneous light touch to the glass slide after contact with the matrix. Pristine prints allowed differences between fingerprint powders to be visualized without the introduction of variability of evidentiary prints. The diminished print sets contained three prints per slide and were created using one finger touched to the matrix, lightly tapping the finger seven to eight times to a Kimwipe from Fisher Scientific to remove some matrix before laying the first print to the glass. The finger was then tapped against the Kimwipe again before laying both the second and third prints to the glass. The diminished prints were chosen to simulate evidentiary fingerprints that could be found at a crime scene. Once the prints were dry and adhered to the glass, the prints were

lightly powdered using the black fingerprint powders. Excess powder was removed by gently tapping the glass at an angle. The three prints were lifted simultaneously using one piece of clear 2-inch Evident fingerprint tape, while ensuring no bubbles were present near the prints. The lifted prints were placed onto 3 × 5-inch white Evident backing latent print cards and assigned a two-letter designation. Fingerprint cards were prepared at a room temperature of 21.6 °C ± 0.8 °C with a relative humidity range of 48.0 % ± 2.6 %. A total of five print sets were created, with each containing pristine and diminished prints for all six powders. Both pristine and diminished prints were lifted in the same fashion. Prints were powdered and lifted by two different print examiners. Each powder was powdered using a different brush. Each complete print set of diminished and pristine prints sent to the certified latent print examiners were lifted by the same person.

Each set of prints was assessed three times by five certified latent print examiners completing a survey for each set inspected, as a result each powder was analyzed a total of 15 times. Examiners were given different print sets each time the survey was completed, as so to not repeat the same inspection. The examiners were asked to rank both the pristine and diminished sets from one to six on the basis of clarity, describing the coherency and quality of the print, with one being the print card that had the best clarity and six being the print card that had the worst clarity. Ranking the prints in a way which illustrates how easy or difficult it is to clearly define each minutiae of the print and which prints have better quality. Pristine and diminished prints were given different designators to ensure that the latent print examiners completing the survey could not compare the pristine and diminished sets during their rankings. At the end of the survey, the examiners were asked exit questions for a better understanding of the personal criteria each examiner employed while ranking the prints. Questions were asked in order to gain more insight into the ways the certified latent print examiners typically looked at fingerprints. By asking examiners about how they determine clarity, it can be determined if examiners all looked for the same criteria or if there were differences in their clarity determinations. Examiners were also asked to determine whether they had any difficulty ranking prints in order to understand whether the examiners were confident in their ranking or if they saw similar quality across the powdered prints. Examiners were also asked to determine if the diminished set would be considered unusable or had unusable features for a forensic comparison.

Statistical Analysis. For statistical analysis in this study, Origin for Windows was utilized and a value of $P \leq 0.05$ was found to be statistically significant. The Kruskal–Wallis ANOVA test, with a Dunn's test as the post-hoc, was used to determine significant differences between the independent mean values obtained. This is a common non-parametric test for comparing two sets of samples with non-normal distributions and it can be used as a substitute for the two-sample *t* test [15–17]. Futhermore, a Friedman ANOVA test was used to analyze the effect of two factors and then, significant results were subjected to the Wilcoxon matched-pair test. Friedman ANOVA is a nonparametric two-way analysis of variance [18–20].

Results and Discussion

XPS

The compositional survey scans were acquired and are shown in Fig. 1, using an analyzer pass energy of 117.4 eV and energy step of 0.5 eV. Those scans allowed for the identification of the elements observed from each powder, based on labeling the observed peaks according to the original core electron level. The atomic composition in each of the black fingerprint powders studied is summarized in Table 2. For the black fingerprint powders studied, the survey spectra for all the samples showed the presence of the elements carbon (C 1s) and oxygen (O 1s).

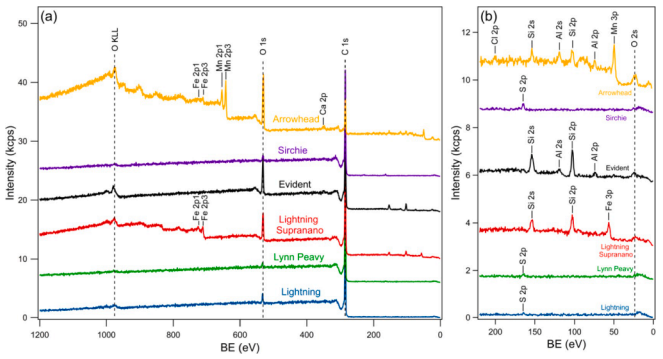

Fig. 1. (A) XPS scans from all samples. (B) Enlarged region from 0 to 200 eV for the same powders. The origins of the observed peaks are assigned and labeled according to the corresponding elements and XPS core level [21].

However, differences in the atomic composition of some of the samples can be noted. Arrowhead fingerprint powder was the most elementally different among all six samples due to the large presence of manganese (Mn 2p and 3p), and small amounts of calcium (Ca 2p) and chlorine (Cl 2p), all of which were unique to this powder. Evident and Lightning Supranano, along with Arrowhead, all had silicon in their composition (Si 2s and 2p). Evident and Arrowhead also contained aluminum (Al 2p), while Lightning Supranano powder showed the presence of iron (Fe 2p and 3p) instead. Furthermore, Lightning, Lynn Peavey, and Sirchie all had the presence of sulfur (S 2p).

SEM/EDS

SEM images were taken using secondary electron signals from the fingerprint powders made using SEM Preparation 1. Images of the powders can be seen in Fig. 2 as well as the EDS scans performed at each site. A comprehensive list of the elements detected in each powder using EDS is located in Table 2. While both XPS and EDS are used for elemental surface composition, XPS has a probing depth in an order of a few nm region, which makes it much more surface sensitive compared to SEM-EDS with has a probing depth in μm region. This suggests the elements not detected in the XPS results were distributed near the core region of the powder particle beyond the method's probing depth but could be detected by EDS with a longer probing depth.

Lightning, Lynn Peavey, and Sirchie were found to have similar compositions containing carbon, oxygen, and sulfur, which is fully consistent with the XPS observation. The XPS results (Table 2) for these three powders show atomic composition of carbon between 94 and 97%. A large amount of carbon (red) can be observed in the EDS mapping images which corresponds with a high carbon percentage in these powders (Fig. 2). Lightning Supranano powder was found to contain carbon, oxygen, silicon, and iron which is also consistent with the elements identified using XPS analysis. The iron in the EDS mapping of Lightning Supranano appears to be most prevalent around divots present across the surface of the powders.

The EDS mapping for Evident as observed in Fig. 2D showed a major "orange" color coding across the surface of the image overlay. It was found that Evident has potassium and silicon elements that in combination with the carbon may cause the "orange" color code mapping seen in Fig. 2D. Additionally, since carbon coating was used on the samples, compositional quantification could not be performed as carbon had to be excluded from the weight percentage calculated by the software.

Both Evident and Arrowhead have iron in the composition of the powders although there does not appear to be a location in these powders where the iron is concentrated like in Lightning Supranano. On the EDS mapping images for Evident and Arrowhead, some of the trace elements that were identified on the EDS spectrum were not included on the generated mapping images but are present in the comprehensive list

Table 2
All elements and the corresponding atomic composition obtained from each sample using XPS [21].

Fingerprint Powder	Atomic concentration (peak selected for calculation)								
	Carbon	Oxygen	Sulfur	Silicon	Iron	Manganese	Aluminum	Calcium	Chlorine
Lightning	94.2%	5.6%	0.2%	–	–	–	–	–	–
Lynn Peavey	96.9%	2.7%	0.4%	–	–	–	–	–	–
Lightning Supranano	81.8%	13.7%	–	3.0%	1.5%	–	–	–	–
Evident	78.2%	15.8%	–	4.8%	–	–	1.2%	–	–
Sirchie	95.7%	3.6%	0.6%	–	–	–	–	–	–
Arrowhead	35.4%	45.1%	–	3.3%	1.7%	9.1%	2.5%	1.8%	0.8%

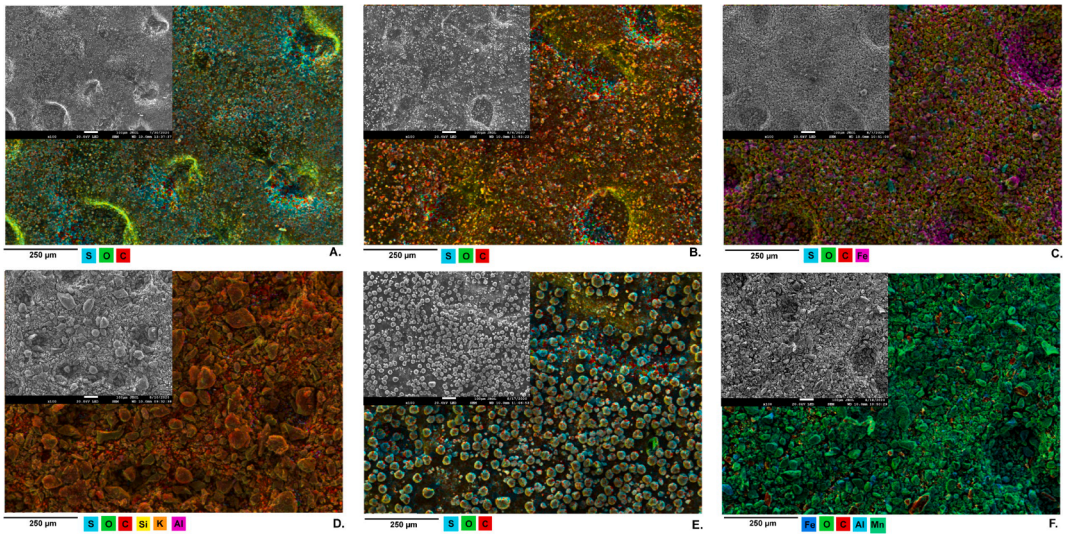

Fig. 2. SEM images at 100× with corresponding EDS of a site representation of each powder's composition for (A) Lightning, (B) Lynn Peavey, (C) Lightning Supranano, (D) Evident, (E) Sirchie, and (F) Arrowhead fingerprint powders. An individualized legend is located beneath each image indicating the element colors.

of elements detected in Table 3. Both powders have aluminum, magnesium, potassium, and silicon. However, EDS determined that Evident powder contained traces of sodium, an element which is only present in this powder. Arrowhead also has elements in its composition which are unique to this powder including calcium, manganese, and chlorine. The characteristic X-rays on the EDS mapping image that appear "green" on the Arrowhead sample correlate to oxygen and manganese in the powder, which appears to cover a large portion of the outside of the particles. It can be seen between EDS and XPS results for Evident and Arrowhead powders: in Evident powder, the XPS did not resolve peaks from potassium, sulfur, iron, sodium, and magnesium, as suggested by EDS; while in Arrowhead, the XPS also did not resolve peaks from potassium and magnesium. This is further supported by the particle sizing analysis discussed in Section 3.2.1, which suggested that the Evident and Arrowhead powders have much more µm-size particles compared to the other powders.

The Preparation 2 was utilized during the SEM imaging portion of this study. Fingerprints were powdered and carbon coated to see the distribution of particles across a latent print as seen in Fig. 3. The powder in these prints should adhere to the matrix left from ridges of the friction ridge skin with blank spaces in between the ridges where the furrows are located [4]. Lightning, Lynn Peavey, Evident, and Arrowhead appear to have a fairly uniform distribution of particles throughout the ridges of the latent prints. Both Lightning Supranano and Sirchie seemed to have issues completely covering the print. Lightning Supranano has several gaps within the ridges which are not seen in any of the other prints and could indicate a problem in the adherence of this powder to the latent print. Sirchie appears to have a uniform distribution of the particles in the center of the ridges, with a thinning of particles at the edges of the ridges. The latent prints powdered with Lynn Peavey have a very clear distinction between the ridges and the furrows with very little powder in the furrows of the print. Lightning and Lightning Supranano also have a good definition between ridges and furrows with little powder in the furrows of the latent prints. Sirchie had a larger amount of powder in the furrows which could lead to harder visualization of detail in latent prints. The prints with the worst definition between the ridge and furrow are Evident and Arrowhead powders, which are also the powders that contain the most different formulations according to EDS and XPS results observed in Tables 2 and 3.

Table 3
Elemental composition using SEM-EDS analysis on the fingerprint powders.

Fingerprint Powder	Elements Present
Lightning	carbon, oxygen, sulfur
Lynn Peavey	carbon, oxygen, sulfur
Lightning Supranano	carbon, oxygen, silicon, iron
Evident	carbon, oxygen, silicon, aluminium, potassium, sulfur, iron, sodium, magnesium
Sirchie	carbon, oxygen, sulfur
Arrowhead	carbon, oxygen, silicon, manganese, aluminium, calcium, iron, potassium, magnesium, chlorine

When safety data sheets (SDS) for each powder were investigated, three common binders were listed, lycopodium, iron powder, and starch [22–26]. Lightning was the only powder said to contain iron powder as a binder claiming 50–100%, but EDS and XPS analysis did not detect iron element within the powder [23]. Iron was found, however, in Lightning Supranano, of the same manufacturer, Evident, and Arrowhead, all of which did not directly claim to contain iron in their chemical composition [22,25,26]. Arrowhead, however, is manufactured by a company that also makes magnetic powders, which according to the SDS contain both lycopodium and iron powder; this could indicate slight cross contamination resulting in the trace amounts of iron found by both the

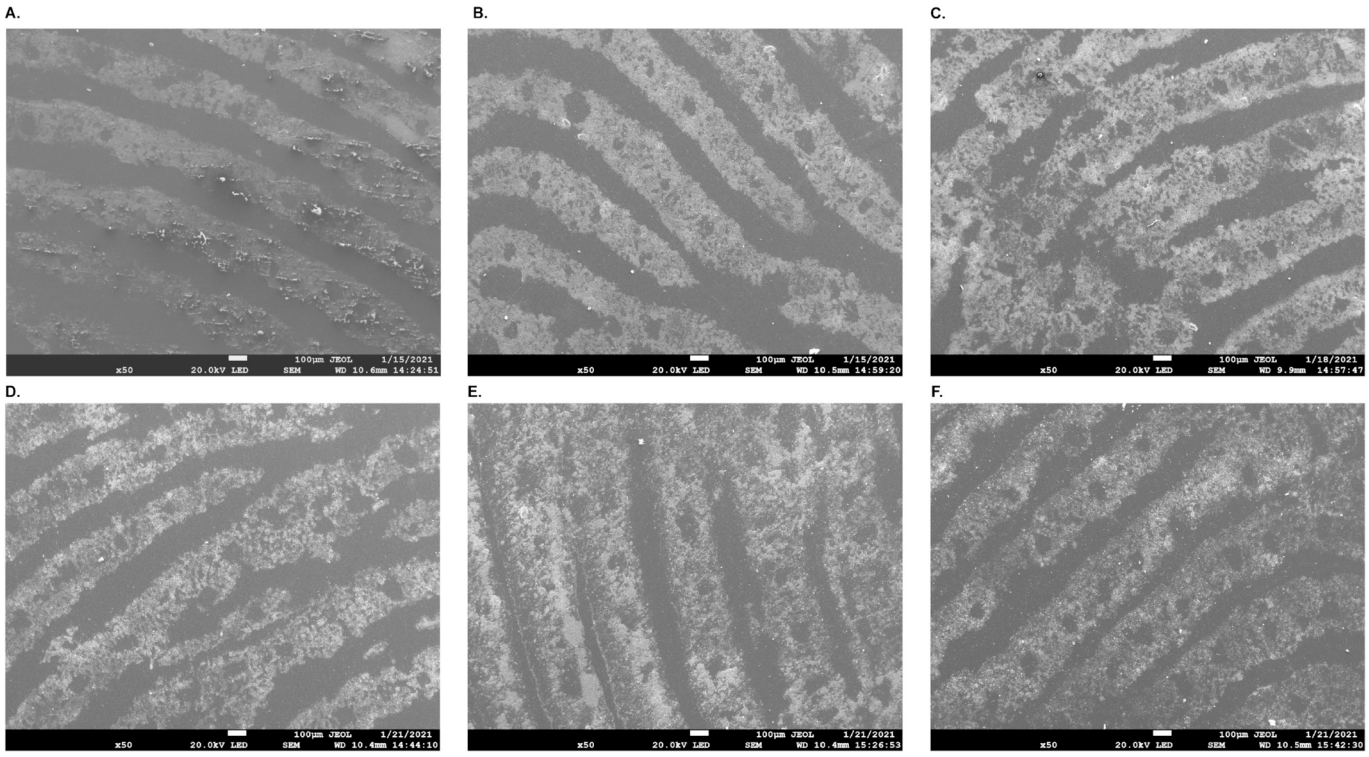

Fig. 3. SEM images of powdered latent prints using (A) Lightning, (B) Lynn Peavey, (C) Lightning Supranano, (D) Evident, (E) Sirchie, and (F) Arrowhead powders.

XPS and EDS analysis [27]. Nevertheless, there is no explanation as to the cause of the other trace elemental components found in Arrowhead. A magnet was used to test the magnetism of the particles. Lightning Supranano and Arrowhead were slightly magnetized, again suggesting the presence of iron. Lightning Supranano manufacturer listed in the SDS that they used starch as a binder which has a chemical formula of $(C_6H_{10}O_5)_n$, but also does not claim to contain iron in its SDS [22]. Lynn Peavey was the only powder that did not claim to contain a binder and

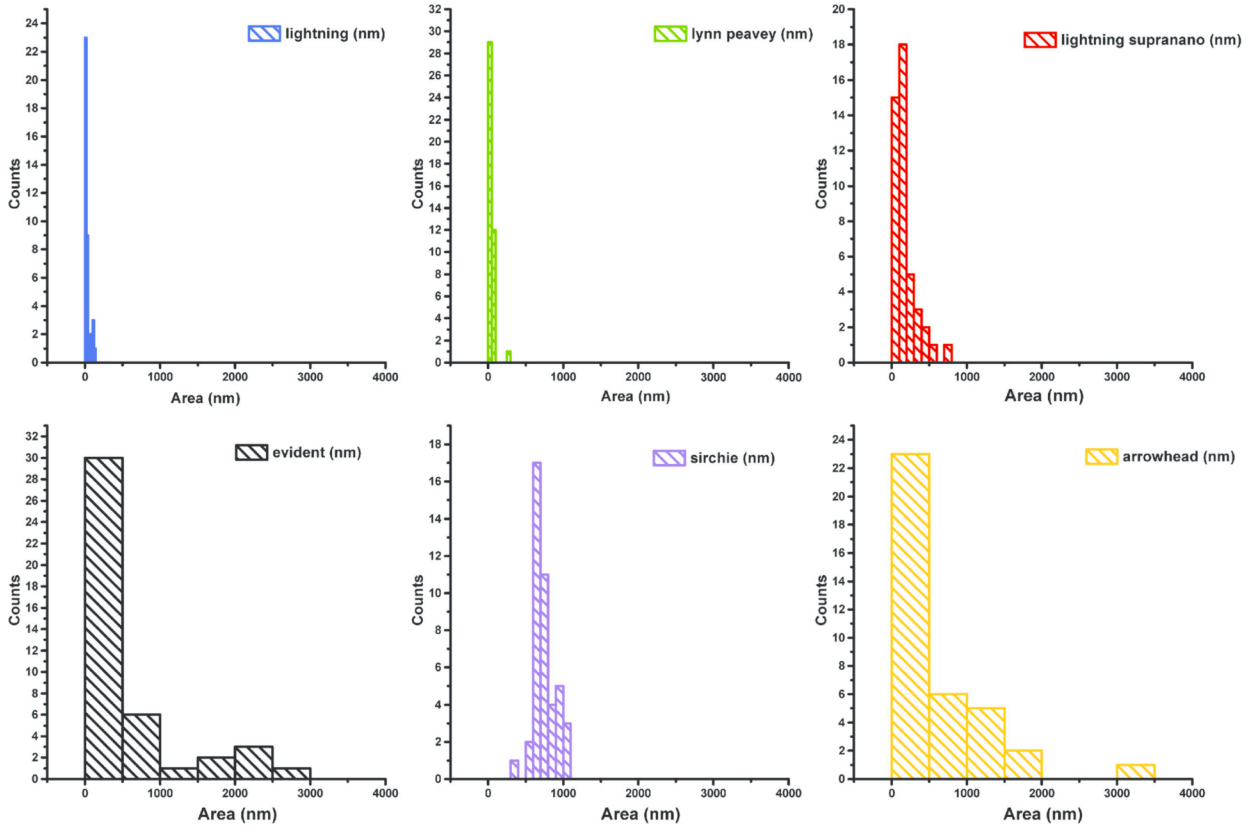

Fig. 4. Histograms depicting the distribution of particles by area from SEM images of the six fingerprint powders.

only had carbon black at 98% on its SDS [28]. On the company's website this powders formulation claimed to contain vanilla, cinnamon, nutmeg and allspice, all of which are carbon based components which do not explain the sulfur presence observed by XPS and EDS analysis [29].

Physical particle characteristics

Particle sizing was completed on the six powders using SEM images (Fig. 2) taken at 500× or 1000× magnification. Histograms showing the distribution of the area of the particles can be seen in Fig. 4. Lightning and Lynn Peavey were very similar in particle size, distribution, and morphology. Both powders consisted of particles less than 50 nm that were spherical in morphology, with average particle sizes of 30.7 nm and 40.9 nm respectively. Lightning had a particle size range of 2 to 130 nm, while Lynn Peavey had a range of 3–260 nm. Sirchie fingerprint powder was also spherical in morphology with a consistent distribution of the particles, however, its particles were between 350 and 1100 nm with an average particle size of 741.9 nm and a standard deviation of 147.0 nm. The distribution of particles, as noted in the histogram, had an average area of 600–800 nm. Lightning Supranano contained particles with areas between 50 and 760 nm with most of the particles having an area between 50 and 250 nm. This powder had a large number of particles which are spherical in morphology, with some oblong and irregularly shaped particles.

Evident and Arrowhead powders were the most different in terms of morphology in comparison to the other powders. The particles in Evident had sizes between 60 and 3000 nm with many particles around the 50–500 nm range, however, due to the large range of particle the average size was 590 nm with a deviation of 701 nm. This powder had many large spherical particles, small irregularly shaped particles, as well as a few very large geometrically shaped particles. The particles between the 2000–3000 nm range had sharp edges, many with a rectangular shape. Furthermore, Arrowhead contained large particles with sharp edges that appeared to have a rectangular, crystalline morphology. The histogram for Arrowhead particles displays the majority of the particles between 250 and 2000 nm but a few very small particles around 74 nm and a large particle at 3487 nm were also observed. However, this powder had very few spherical shaped particles, with most of the particles having no characteristic geometry. This irregularly shaped particles in Arrowhead powder accounted for the distribution of particles in the range between 70 and 3487 nm as noted in the histogram.

DLS

High variability exists within the deposition of fingerprints, both between donors and from within the same donor. This variability can be due to different donor characteristics such as age, ethnicity, medication, psychological state, health, metabolism, and diet [30]. But the variability can also be due to the type of perspiration on the hands at the time of deposition. Eccrine perspiration is secreted from the hands and is a water-based solution with both inorganic and organic components [14,31,32]. These components include NaCl and urea as well as other metabolites, minerals, electrolytes, and amino acids [14,31,32]. Sebaceous perspiration is secreted from the face but is frequently transferred to the hands and can be deposited when laying a print. This perspiration has components that are fat-soluble such as fatty acids and glycerides [14,32]. In order to create solutions that were relevant to the skins chemistry, water, 29 mM NaCl solution, and artificial eccrine perspiration were utilized for the DLS and zeta potential measurements as seen in Table 4 [14,32]. Analysis was also intended to take place in an artificial eccrine perspiration-sebum emulsion along with the artificial eccrine perspiration used, however the solution was too dense and too large for filtration. The refractive index could not be calculated using a refractometer indicating that it was too large for accurate DLS analysis, excluding the filtration of the perspiration and accurate hydrodynamic particle sizing.

Particle Sizing

DLS particle sizing for the powders were very similar ranging between 214.6 and 258.4 nm in water as seen in Table 4. These measurements were found to be consistent as noted by the low standard deviation values for the particle sizing. Whereas the NaCl solution and the artificial eccrine perspiration had a greater particle size distribution between the different powder types and had more inconsistent standard deviations. One factor to consider in DLS is the ionic strength of the media which can affect the thickness of the electric double layers of ions around the particle that contributes to the hydrodynamic diameter size [33,34]. Low conductivity media will extend the layer in turn reducing the diffusion speed and therefore increasing the apparent hydrodynamic diameter [34]. Lightning, Lightning Supranano, and Arrowhead all had a similar particle size correlation in which the largest hydrodynamic diameter was observed in the NaCl solution. While Lynn Peavey, Evident, and Sirchie all had their largest apparent particle size in artificial eccrine perspiration. The smallest hydrodynamic diameter measured for all particles was in water. Lynn Peavey and Lightning Supranano had the highest standard deviations in both NaCl and in the artificial eccrine perspiration solutions. However, there were no direct connections from the analyzed elemental compositions of the powders and their interactions in the different solutions [35].

In the SEM analysis (Table 3), Lightning and Lynn Peavey were both found to have average particle sizes of below 50 nm, but the hydrodynamic diameter of these powders was larger in all of the solutions used for the DLS analysis. Previous research has shown this type of analysis before, comparing DLS and SEM analysis studying particle sizes in solution and as "dry" particles [36–38]. Based on the increase of particle sizing of the powders in water when compared to the dry powder, there may be some agglomeration of these particles creating the larger particle size noted in Table 4. In fact, previous research has discussed the tendency of carbon black particles to agglomeration in aqueous solutions [39]. Furthermore, Lightning Supranano had a particle size range of 50 to 760 nm in the SEM analysis and both of the apparent particle sizes from the NaCl and sweat solutions fall within that range at 705.9 and 683.8 nm respectively. The apparent particle size in water, however, does not have the same effect and is much smaller than the expected particle size range at 245.0 nm. Sirchie's largest apparent particle size was in the sweat solution at 521.7 nm. This particle size value fits perfectly within the range given by the SEM particle sizing which estimated the particle size between 400 nm and 1100 nm, however, the apparent particle size of Sirchie in NaCl is correlated directly to the 399.3 nm minimum dry particle size. This indicates that the powders solubility was most likely increased in water and NaCl solutions causing the slight breakdown of the particles and that sweat composition most likely would not affect the size of the particle adhering to the print. Evident had the largest range of particle sizes in the SEM analysis but the DLS particle sizing it resembled the lower ranges given by the SEM, with the apparent particle size in artificial eccrine perspiration being representative of the average SEM value. This could be due to the breakdown of larger aggregates when sonicated in solutions. The analyzed SEM data for Arrowhead was considered the most irregular in shape causing an odd distribution in particle sizes, however, the measured hydrodynamic diameter in all the solutions had relatively small standard deviations and was overall less than 500 nm. Of the powders only Lightning and Lynn Peavey consistently had a larger apparent particle size in a human-like environment of artificial eccrine perspiration and NaCl solution than they did in their dry state. Arrowhead on the other hand had some dry particle sizes in the SEM that were within the range of the DLS data but due to the high distribution of particle sizes a conclusion cannot be made about agglomeration. In this situation, it can be inferred that the particle in solution may have been broken down when dispersed into the solution using sonication. Like Arrowhead, Evident had a wide distribution of dry particle sizes as seen in the SEM, however Evident had an average closer to that of particle sizes given by the hydrodynamic diameter from the DLS data. Thus, while a final determination can still not be completely drawn

Table 4
Particle size and zeta potential values of the hydrodynamic diameters of the fingerprint powders obtained using DLS.

Fingerprint Powder	Water		29 mM Sodium Chloride Solution		Artificial **Perspiration**Eccrine	
	Particle Size (nm) ± std deviation	Zeta Potential (mV) ± std deviation	Particle Size (nm) ± std deviation	Zeta Potential (mV) ± std deviation	Particle Size (nm) ± std deviation	Zeta Potential (mV) ± std deviation
Lightning	257.9 ± 8.3	−33.3 ± 4.5	637.1 ± 48.1	−25.6 ± 12.2	560.1 ± 62.6	−11.7 ± 2.9
Lynn Peavey	214.6 ± 10.2	−32.2 ± 4.8	609.8 ± 173.5	−32.6 ± 14.9	1139.8 ± 122.0	−13.1 ± 2.3
Lightning Supranano	245.0 ± 13.8	−25.0 ± 1.6	705.9 ± 135.5	−24.4 ± 2.5	683.8 ± 74.8	−8.6 ± 1.7
Evident	225.4 ± 9.6	−29.8 ± 2.2	264.9 ± 8.5	−41.1 ± 2.2	605.1 ± 61.0	−11.5 ± 7.0
Sirchie	258.4 ± 11.2	−32.1 ± 2.3	399.3 ± 85.6	−37.3 ± 6.5	521.7 ± 67.3	−15.4 ± 1.4
Arrowhead	234.9 ± 17.8	−26.6 ± 2.1	402.6 ± 15.8	−29.59 ± 5.9	381.9 ± 20.2	−9.4 ± 3.0

it is presumed that the larger particles were broken down during sonication in an effort to disperse the powder in solution. This larger apparent particle size in Lightning and Lynn Peavey could be due to an aggregation of particles in solution that cannot be concluded for the other powders, due to their dry states having smaller particles than in solution, causing a better adhesion to ridges in latent prints.

Since eccrine perspiration is an aqueous solution, the apparent increase in particle size between the water and perspiration samples indicates that the inorganic and organic components within the solution had an effect on the particle size of the powders promoting large aggregate formation. This analysis can be compared directly to the images in Fig. 3, which depict the powders studied on a collected latent print. These prints were collected using the artificial eccrine perspiration - sebum emulsion and can be most closely related to the powders in artificial eccrine perspiration. Of the powders in solution, Lynn Peavey aggregated the most compared to its dry state particle size. This print's friction ridges and furrows, in Fig. 3, are the best defined in comparison to the other powders' images. In contrast, when compared to its dry particle size, Sirchie had no aggregation in any of the solutions and potentially had particle size breakdown due to dispersion, which seemed to have a less uniform distribution of particles over the print.

Zeta Ppotential

The epidermal layer of the skin has a positive electrical charge due to its secretions and other outer layer components [40]. Thus, zeta potential values of the powders were collected in order to examine the effect that skin residues like sweat have on the adhesion of fingerprint powders to latent prints. In zeta potential, the larger the absolute value the more electrically stable the sample is considered [41,42]. An absolute value of 30 mV or greater is considered more stable and generally more monodispersed, while an absolute value of 5 mV or smaller is correlated with destabilization and more agglomeration [41,42]. Changing zeta potential conditions like pH, conductivity (ionic strength), temperature, and solvent viscosity can affect the zeta potential and overall stability [33]. All solutions were analyzed for pH values between 20.5 and 21.5 °C. The deionized water had a pH of 8.6 and a voltage reading of −70.8 mV. The NaCl solution had a pH of 7.4 with a voltage of −4.5 mV, while the sweat solution had a pH of 4.3 and voltage of 165.2 mV. The most basic of solutions has been previously correlated with more negative zeta potential values [42,43]. This effect can generally be seen in the solutions used for the zeta potential measurements in Table 4, as the slightly basic deionized water and near neutral NaCl solution yielded more negative zeta potentials values with the fingerprint powders than that of the sweat solution which is more acidic. The acidity and more positive zeta potential of the artificial eccrine perspiration caused a smaller net negative zeta potential in all the powders. This decreased their stability and caused the artificial eccrine perspiration to have the overall least stability for all powders. This can be attributed to the zeta potential decreasing, due to the acidic and ionic environment between the hydrophobic carbon black powder and the sweat solution, which promoted its aggregation as supported by the increased particle size distribution [44].

Lightning and Lightning Supranano, which were manufactured by the same company, are the only powders to have the highest stability in water, whereas the other powders all had the greatest stability in NaCl solution. Previous research has shown a decrease in zeta potential stability when analyzed in increasing amounts of NaCl solutions, but NaCl solution in this study did not have a consistent stability decreasing effect on these products [33]. This could be due to the high concentration of carbon black within the samples as stated by the XPS analysis. Lightning Supranano and Arrowhead were the only powders with a zeta potential below an absolute value of 30 mV in both the NaCl solution and water, suggesting that neither powder was stable in solution. Lightning, Lynn Peavey, and Sirchie powders were found to have zeta potentials above the absolute value of 30 mV indicating a moderate stability in water. Using XPS and EDS analysis, these powders were determined to have the same elemental composition: carbon, oxygen, and sulfur. This arrangement of having the three most stable zeta potentials for the solution can also be seen in artificial eccrine perspiration. Evident, while not considered compositionally similar to the other powders, can also be considered stable in water with a zeta potential of 30 mV. The other two powders tested had zeta potentials between the absolute values of 25 to 30 mV indicating that there is some instability in the particles within these powders when interacting with water.

Overall, the zeta potentials for the powders in NaCl solution are similar to that of the zeta potentials measured for the samples analyzed in water, with the exception of Evident, which had a much more stable potential in NaCl solution, despite also being considered stable in water. Typically, when the fingerprint powders were dispersed in water, they exhibited only one or two different size distributions, however, when dispersed in the 29 mM NaCl solution, more size distributions were observed. This could be due to interactions between sodium and chloride causing the formation of micelles, in which such interactions could have occurred between the fingerprint powders and the sodium and chloride ions as they would normally interact with the secretions from sweat [45]. Micellar formation would explain what is causing these groupings in particle sizes in the NaCl solution. Zeta potentials for all the powders in artificial eccrine perspiration were low. The values ranged between −8.63 to −15.40 mV. This indicates an instability or destabilization of the powders in this liquid that would lead to aggregation of particles as there is not enough electrostatic repulsion between the molecules in the liquid to keep the particles from agglomerating [20,21]. However, while the aggregation of particles was likely observed for all powders in DLS analysis for all preparations, only Lynn Peavey and Lightning powders showed the highest amount of particle aggregation when compared to the particle size of the dry powders by the SEM analysis with recorded values increasing nearly fourfold. These prints when analyzed in the SEM were considered to have a uniform distribution throughout the ridges and with little powder in the furrows.

IR and Raman

IR

IR spectra were collected for all six fingerprint powders; of these, four contained groups that were IR active. Lightning and Lynn Peavey

powders had no active functional groups in the IR region. Sirchie powder had IR peaks at 2919 cm^{-1} and 2850 cm^{-1}. These peaks can be attributed to C–H asymmetric and symmetric vibrations. Another peak was observed at 1706 cm^{-1} that can be attributed to a C = O vibration. Arrowhead powder had the most vibrational peaks in the infrared spectrum. Peaks for Arrowhead powder can be observed at 2936 cm^{-1}, 2859 cm^{-1}, 1743 cm^{-1}, along with a broad peak around 1412 cm^{-1}, and additional peaks at 1035 cm^{-1}, and 1006 cm^{-1}. Arrowhead powder seemed to have C–H asymmetric and symmetric vibrations at 2919 and 2851 cm^{-1}. Lightning Supranano powder had IR peaks at 1149 cm^{-1}, 1079 cm^{-1}, and 1018 cm^{-1}. Both of these powders' chemical composition included silicon and oxygen as shown by XPS analysis (Fig. 1). When silicon is chemically bonded to oxygen, strong and broad peaks are present between 1000 and 1100 cm^{-1}. Based on the positioning of the IR active bands and known chemical compositions of the fingerprint powders, the bands present can likely be attributed to this silicon/oxygen interaction. Evident powder had an IR peak at 1022 cm^{-1} (Fig. 5). This powder's chemical composition included sulfur as seen in XPS analysis. This peak can be attributed to either S = O or C-S vibration. Both Evident and Lightning Supranano showed the presence of small peaks around the 2900 to 3000 cm^{-1} (not shown) possibly indicating C–H vibrations.

Raman

In the Raman experiments, all the spectra (Fig. 6) were obtained during the first 1–10 s upon irradiation, to avoid the acquisition of signals of the products associated with the decomposition or photobleaching of the fingerprint powders. During this experiment, it was found that Lightning, Lynn Peavey, Lightning Supranano, and Evident decomposed between 6 and 10 s upon irradiation, while the samples of Sirchie powder decomposed faster in a 1–5 s range after excitation started. None of the experiments completed with the Arrowhead powder showed any evidence of decomposition and the Raman peaks were stable for more than 10 s during the acquisition of the spectra. Another observation in the Raman experiment was the change of color of some of the fingerprint powders, which could be associated with the photooxidation of some of the metals or the transformation of some of the oxides in the samples. Lightning Supranano formed a burned red powder and Evident formed a white spot in the area where the 785 nm laser was focused. In general, all fingerprint powders shown similar Raman spectra upon radiation and strong frequency peaks are found at 410 cm^{-1}, 600 cm^{-1}, 1150 cm^{-1}, 1500 cm^{-1}, and 1780 cm^{-1}. Considering

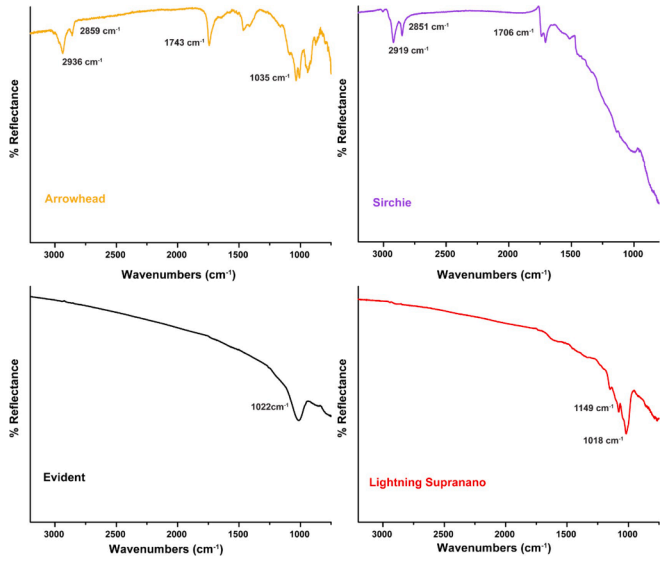

Fig. 5. IR spectra of Arrowhead powder, Sirchie powder, Evident powder, and Lightning Supranano powder.

that Lightning, Lynn Peavey, and Sirchie powders atomic composition (Table 2) are similar to the typical elemental Carbon Black composition (96–99.5% C, 0.2–1.3% H, 0.2–0.5% O, 0–0.7% N, and 0.1–1.0% S), it could be expected that these frequencies correspond to possible binding forms that oxygen and sulfur can do on the surface of Carbon Black [46]. The frequency peak found at 410 cm^{-1} could be associated to the S-S vibration, while the one at 600 cm^{-1} to the C-S (aliphatic) vibration, and the peak at 1150 cm^{-1} to a possible combination of C = S and C-S (aromatic) vibrations. The peak found at 1500 cm^{-1} correlates with C = C vibration and the peak at 1780 cm^{-1} could be associated to the C = O vibration. Other medium peaks found in some of the fingerprint powders could correspond to additional functional groups of oxygen and sulfur on the surface of Carbon Black that are formed because of the differences in the production method used for obtaining Carbon Black. When the spectra was analyzed for Lightning Supranano, Evident, and Arrowhead, characteristic frequency peaks could not be identified that would correlate with the presence of silicon dioxide, and the C-Si or O-Si vibration. It is possible that these Raman signals are masked by the signals of Carbon Black complex.

NMR spectroscopy

The NMR of the fingerprint powders had several classes of organic binders, which were extracted with solvent. Sirchie (Fig. 7) and lightning powders had oils that resembled unsaturated triglycerides. Both of the oils from these samples had ^{13}C NMR (not shown) with a peak at 179 ppm, indicating the presence of a carbonyl and peaks around 130–128 ppm, indicating olefins. The IR of these samples contained a carbonyl stretch at 1706 cm^{-1}, which is likely due to the presence of the carbonyl in the fatty ester. Lightning Supranano (Fig. 7) and Evident powders contained oils that spectrally resembled mineral oils. The low oil content and lack of other functional groups is in line with the IR spectra (Fig. 5). Powders, Lynn Peavey and Arrowhead (Fig. 7), have oils that showed spectra with a mixture of many different organic compounds.

PXRD

PXRD was collected for all six fingerprint powders. PXRD was used for the possible identification of crystal phase and crystallinity of the materials. Lightning, Lynn Peavey, Evident, and Sirchie powders did not show any diffraction pattern as they seemed to be amorphous powders. Those four powders' diffraction patterns showed a broad peak between 15 ° and 40 ° (*2θ*). The X-ray powder diffraction pattern for Arrowhead powder seemed to have some crystallinity since it exhibits diffraction peaks at 26.7°, 28.8°, 33.2°, 37.6°, and 38.3° (*2θ*) (Fig. 8). Arrowhead has the highest variety of elements detected by XPS and it has many vibration peaks detected in the IR spectrum. Furthermore, the Arrowhead manufacturing company, Arrowhead Forensics, stated in their website that "the powder is a mixture of carbon black" [47]. The website also stated they manufacture magnetic powders, which include iron, but iron is not listed as a part of the chemical composition in the SDS of the powder of interest [25,27,47]. Another fingerprint powder that exhibits some diffraction peaks was Lightning Supranano. Diffraction peaks were observed at 18.7°, 30.3 °, 35.7 °, and 43.2 ° (*2θ*). Iron and silicon elements were found in the Lightning Supranano powder and the inclusion of a metal ion may increase the possibility of crystalline sizes in the powder [48]. Here, the particle sizes of Lightning Supranano and Arrowhead powders were larger compared to the other four fingerprint powders suggesting the particle size was not the major influence on the diffraction peaks observed for those two powders. All the fingerprint powders have listed in their SDS that the bulk chemical composition was carbon black but Arrowhead and Lightning Supranano powders have metal elements that were observed in the XPS and EDS analysis [22–26,28]. Carbon black has been previously studied and stated that it is composed of an amorphous core with the possibility of some well-arranged atom layers [49].

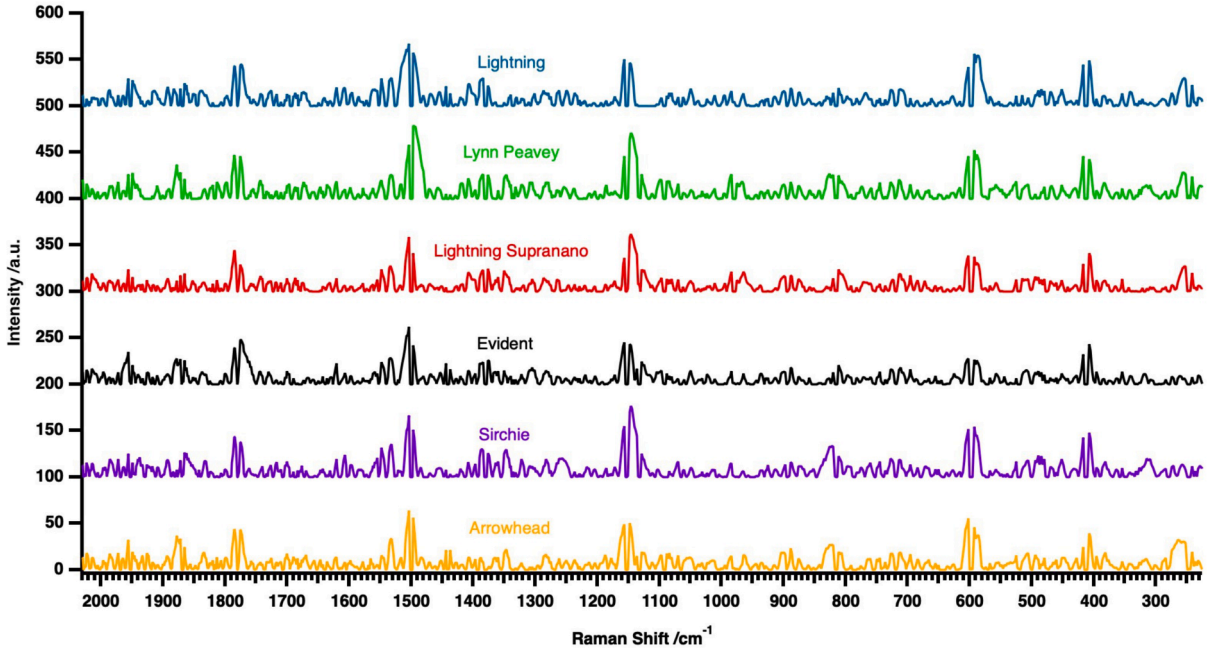

Fig. 6. Raman spectra for all six fingerprint powders.

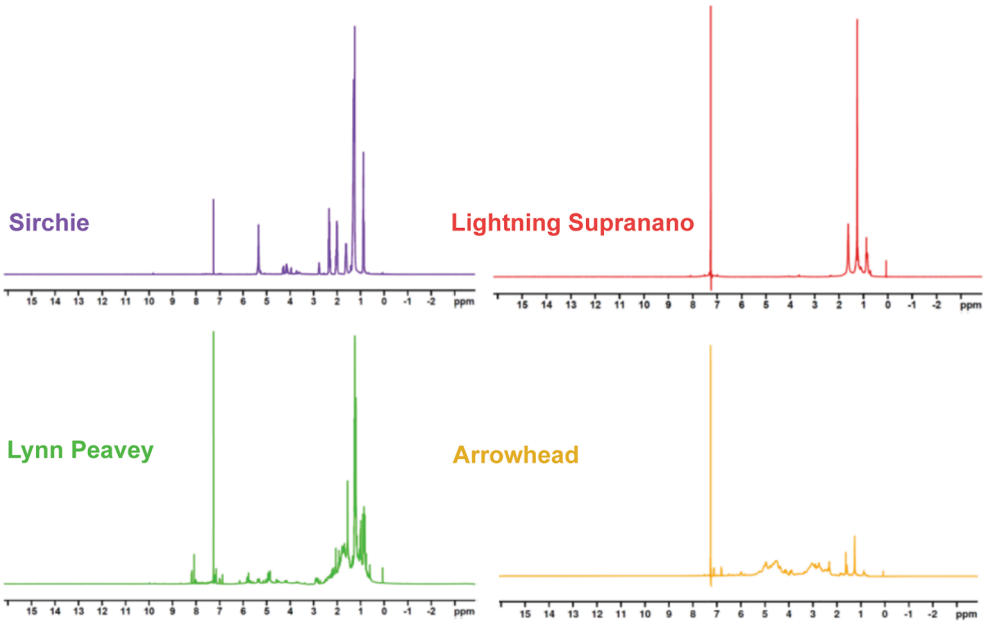

Fig. 7. ^{1}H NMR of Sirchie powder, Lightning Supranano powder, Lynn Peavey powder, and Arrowhead powder. All spectra include a peak for $CHCl_3$ at 7.26 ppm and a peak for TMS at 0 ppm.

Fingerprint Powder Quality Study

Five certified latent print examiners were asked to rank each print set by quality with one being the best and six being the worst; results are shown in Table 5. These prints were ranked according to their preparation of pristine or diminished. Pristine prints were collected by pressing a fingertip in artificial eccrine perspiration-sebum emulsion then pressed to the glass surface and the diminished which were pressed successively on the glass surface before creating a print. Glass was used in order to provide a nonporous reusable substrate that could be cleaned to provide the same substrate for each trial. It also allows for consistency that a porous substrate could not provide. According to the rankings provided by certified latent print examiners, Lynn Peavey ranked the highest with an ordered rank of 1 for the pristine prints despite being ranked number 1 by examiners only two times since its rankings never fell below a 3. In the diminished comparison, Lynn Peavey averaged ranking of 2.1, which gave it an ordered ranking of 2. This powder was rank number 1 by examiners 6 times, but it also had rankings as low as 4 for the diminished analysis bringing its ranking down. Lightning ranked at number 2 for pristine prints in 3 out of the 15 surveys and ranked first 8 times within the diminished rankings earning it the ordered rank of 1.

At the end of this study, the latent print examiners were given an exit survey to elucidate the basis for their rankings. Many of the latent print examiners ranked clarity in Level 2 detail as a defining quality of good prints. One examiner stated that they preferred darker prints while several others stated that their rankings were based on the amount of

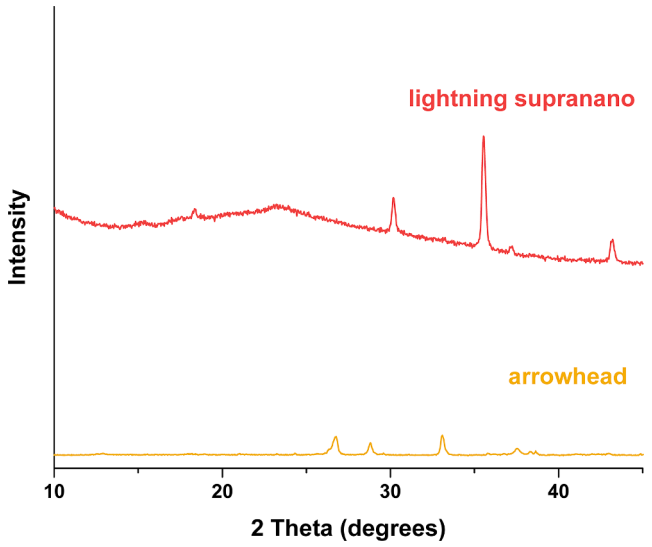

Fig. 8. PXRD pattern for Arrowhead powder and Lightning Supranano powders.

Table 5
Quality study average rankings, standard deviations, and numbered rank of the fingerprint powders.

Fingerprint Powder	Pristine Average Ranking ± std deviation	Ordered Rank	Diminished Average ranking ± std deviation	Ordered Rank
Lightning	2.4 ± 1.5	2	1.9 ± 1.2	1
Lynn Peavey	2.1 ± 0.6	1	2.1 ± 1.2	2
Lightning Supranano	4.3 ± 1.0	4	4.5 ± 1.4	5
Evident	4.7 ± 0.9	6	3.6 ± 1.3	3
Sirchie	3.2 ± 2.1	3	4.9 ± 1.1	6
Arrowhead	4.3 ± 1.7	4	3.9 ± 1.6	4

level 1 features, which are indicated in the loops, arches, and whorls present, as well as level 2 details, which focuses on ridge positions, paths and the length of the ridge paths [1]. Another examiner looked for contrast and distinction between the ridges and furrows of the prints. With the diminished prints, one of the examiners stated that on a few of the print cards out of the set each had a print that was unusable, however, this was only stated on one of the surveys collected. On a few surveys, the examiners mentioned that they had difficulty ranking the diminished prints due to the similarities in the quality and clarity of the lifted prints between the powders. Difficulty ranking the prints was never stated for the pristine prints as the quality differences of the lifted prints was considered clear between the powders making it easier to differentiate between good and bad lifted prints.

The Kruskal-Wallis non-parametric analysis was performed to assess the possible relationship between fingerprint powders rankings for each print quality type within the study. This showed that Lightning which was ranked as the second highest in quality of pristine prints was statistically different ($p < 0.05$) compared to Evident, Lightning Supranano, and Arrowhead powders; it was not statistically different from Lynn Peavey and Sirchie powders. Furthermore, the Lynn Peavey powder, which ranked the first in quality for pristine fingerprint quality, was statistically different from Evident, Lighting Supranano, and Arrowhead powders. For diminished prints, Lightning powder which is ranked first and was statistically different from Lightning Supranano, Sirchie, and Arrowhead powders. The second ranked Lynn Peavey powder was statistically different from the Sirchie and Lightning Supranano powders. Later, a Friedman ANOVA non-parametric analysis was performed to analyze the powders. The Friedman ANOVA will analyze one variable with two or more categories within-subjects, and it is equivalent to a repeated measures ANOVA [50]. For pristine prints, Evident powder was statistically different from Lightning and Lynn Peavey powders. Lynn Peavey powder was also statistically different with Arrowhead and Lightning Supranano. For diminished prints, Lightning powder was statistically different from Lightning Supranano, Sirchie, Arrowhead powders. Lynn Peavey powder was statistically different from Lightning Supranano and Sirchie. These different statistical tests have concluded that the powder which can be described as the "best" for pristine prints is Lynn Peavey and the best powder for diminished prints is Lightning, clearly differentiating them from the "worst" powders which are Arrowhead, Sirchie and Lightning Supranano.

Lightning and Lynn Peavey powders have almost identical elemental compositions, morphology, and particle size. These powders were also the most similar in the DLS analysis forming agglomerations in solution larger than their average dry particle size. The determined composition for these powders included carbon, oxygen, and sulfur. These powders are similar in all aspects of the study including the quality study previously discussed. This gives an indication into the chemical, physical, and morphological characteristics best for a latent fingerprint powder. Powders with small, uniform spherical particles with compositions primarily consisting of carbon are best suited for use as latent print fingerprinting powders. Sirchie powder was similar in composition and morphology, but the increase in particle size of the powder correlated to a decreased ranking. The Lightning Supranano powder was determined to have a slightly different elemental composition from XPS analysis including iron and silicon. The particle size of this powder was larger than that of Lynn Peavey and Lightning which could explain why the powder ranked lower on the quality study. A larger particle size could also likely reduce the agglomeration to the particle reducing its ability to securely bind the substrate. This could also further explain the quality of the lifted diminished prints, in that as the larger particles insecurely or partially adhere, disconnecting during development when the powder should be agglomerating in the presence of skin residues. These larger particles also appeared smaller in the artificial eccrine perspiration and could be interacting with the skin residues in such a way that causes the larger particle to be more suitable to breakdown in the pristine prints instead of agglomerating to aid in adherence.

Evident also had a vastly different chemical composition with many additional elements and an increase in particle size. The SEM images for this powder showed large irregularly shaped particles not ideal for the lifting of latent prints. Large irregularly shaped particles were also present in Arrowhead powder as well as a chemical composition that contained more oxygen than carbon according to the XPS results that could be due to the presence of metal oxides. Arrowhead ranked poorly on the quality study which indicated that powders with a low carbon content and large, irregular particle size have lower quality when lifting forensically relevant latent prints.

Conclusion

It was determined that black fingerprint powders exhibit different chemical, physical, and morphological properties that may have an effect on the quality of latent fingerprint development. This study also employed the use of the opinion and feedback of certified latent print examiners to create a comprehensive characterization of the quality of the collection of the powders. Many of the black fingerprint powders studied contained high levels of carbon and varying levels of oxygen. Other elements were also present that may have contributed to the resulting quality of fingerprint development. The morphology of each of the black fingerprint powders studied was determined using SEM, and it was observed that Lightning and Lynn Peavey had similar morphologies. These powders also have the same chemical composition and were ranked as the two best powders in the quality study. These powders were also the only powders to show particle agglomeration in artificial eccrine perspiration, aiding in the adhesion to the latent prints. While a forthright conclusion cannot be

drawn on the exact behavior of those powders in solution, it can be presumed that larger particles, seen in SEM imaging, may have been broken down during sonication. This seems to indicate that powders with high carbon content, spherical morphology, and uniform particle sizes in the 50 nm range lead to a superior quality of latent prints. Sirchie powder has the same chemical composition and morphology as Lightning and Lynn Peavey, but the much larger particle size of this powder and the lack of clear agglomeration in solution likely led this powder to rank lower in the quality study. Arrowhead fingerprint powder contained much less carbon than the other five powders examined, and had large, irregularly shaped particles. This powder ranked poorly in the quality study completed also indicating that powders with a high level of carbon and smaller particle size are ideal for the powdering of latent prints. For fingerprint examiners and manufacturers, this means powders with simpler composition containing elements like carbon and oxygen, lift the prints with higher quality. This is also true for powders with smaller more uniform particles, which better adhere and agglomerate to the skin residue in the print.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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