JOURNAL OF CHEMICAL EDUCATION

Article

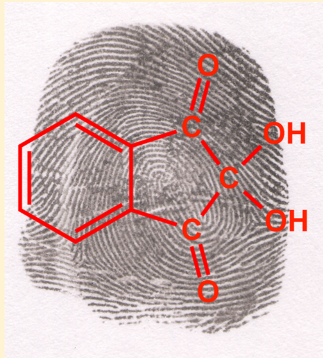
pubs.acs.org/jchemeduc

Forensic Chemistry: The Revelation of Latent Fingerprints

J. Brent Friesen*

Physical Sciences Department, Rosary College of Arts and Sciences, Dominican University, River Forest, Illinois 60305, United States

ABSTRACT: The visualization of latent fingerprints often involves the use of a chemical substance that creates a contrast between the fingerprint residues and the surface on which the print was deposited. The chemical-aided visualization techniques can be divided into two main categories: those that chemically react with the fingerprint residue and those that adhere to the fingerprint residue by intermolecular forces. A plethora of empirically effective fingerprint revelation methods have been developed but the chemistry is often incompletely understood. This article briefly describes the chemical rationale of most fingerprint visualization techniques practiced today. This material is suitable for a forensic chemistry course or for an introductory chemistry course to introduce the relevance of chemistry in law enforcement. This material may also apply to an organic or biochemistry course when discussing noncovalent intermolecular interactions.



KEYWORDS: *High School/Introductory Chemistry, Interdisciplinary/Multidisciplinary, Forensic Chemistry*

■ INTRODUCTION

The application of chemistry to solve crimes, forensic chemistry, is a popular theme in both introductory and advanced educational settings. The human interest of performing a chemical procedure is heightened by the possibility that a criminal event is being investigated. For example, chemistry plays a significant role in several television crime scene investigation shows. The fascination of solving crimes through chemistry has not escaped educators. Forensic science lessons involving fingerprints have been produced for every educational level. Making fingerprints with ink can be done with elementary school students.[1] Even the revelation of latent fingerprints by dusting is a fun (and messy) elementary age activity.[2] Superglue is commercially available and therefore accessible to anyone who wants to experiment with its properties of revealing latent prints.[3] In high school and postsecondary school, experiments with the revelation of latent prints are likely to be included in a forensic science or forensic chemistry course. Several textbooks and lab manuals are available for these courses.[4−10] Over the years this journal has published several articles that discuss the chemical composition of latent prints and methods to reveal them.[3,11−15] However, a discussion of the chemical reactions and interactions that create these procedures is often lacking when fingerprint revelation techniques are presented in an academic setting.

■ HISTORICAL

At the end of your fingers is a pad of flesh, known as a volar pad, which is designed to allow you to grip surfaces without slipping. The skin ridges that comprise this volar pad create a distinct pattern that is unique to each person: a fingerprint. By itself, the particular pattern or print does not contain any specific information about the individual such as race, gender, or age, but because it is unique, it can be used to match the print with its origin. The importance of fingerprints as identity marks has been known from ancient times when fingerprint impressions had been used as a seal. If you make the impression on a soft surface or if you transfer a colored substance from your volar pad to a surface, the prints will be immediately perceptible to the naked eye.

Latent fingerprints are created when you touch a surface and transfer a thin layer of transparent chemical residue from your volar pads in the pattern of your unique skin ridges. In fact, every time you touch or grip a surface with your hands latent fingerprints are likely to be deposited. Various methods have been developed to create a color contrast between the residue associated with the fingerprint and the surface on which the residue has been deposited. Latent prints are surprisingly abundant and durable. You unintentionally deposit hundreds of latent prints every day onto the surfaces you touch. Many of these prints could be revealed with specialized techniques.

The use of fingerprints in the investigation of crimes has been documented for over 100 years.[16] If your latent fingerprint is found at a crime scene, you were present at the crime scene at some point. If your fingerprint is found on a weapon, the weapon was handled by you at some time. In brief, latent prints can be used to connect the physical evidence associated with the crime to the criminal. Even in an age of DNA analysis, fingerprints continue to be of importance because they can be rapidly and inexpensively revealed to provide the same individual match as DNA. Fingerprints are usually taken at the time of arrest for most crimes, whereas obtaining DNA requires a court order in many jurisdictions.[17] Extensive searchable fingerprint databases are maintained by law enforcement.[18] Furthermore, fingerprints can distinguish between individuals with identical DNA.[19]

Published: October 8, 2014

DOI: 10.1021/ed400597u
J. Chem. Educ. 2015, 92, 497−504

The chemical methods used to reveal latent prints can be divided into those techniques which involve chemical reactions and those which are based on intermolecular forces to create adhesion. A good technique will create a contrast between the fingerprint residue and the surface on which the residue has been deposited. An optimal method must be simple to perform, inexpensive, sensitive, and reliable. It is best if it can be durable as well, though revealed prints can easily be preserved with photography. Some methods are nondestructive to the prints so that different methods can be used sequentially to analyze a print. The difficulties arise from the variety of surfaces on which the print can be deposited as well as the conditions to which it may be subjected. In addition, the quantity of fingerprint residue that the fingerprint contains may vary widely.

■ THE CHEMICAL COMPOSITION OF FINGERPRINT RESIDUE

Understanding the chemical composition of fingerprint residue is crucial in studying the way other chemicals react with latent fingerprints. There are two broad classifications pertaining to the origins of fingerprint residue: the chemical constituents must originate from endogenous or exogenous sources. Whatever you have touched might transfer chemical residue on to your volar pads that could end up in your latent fingerprints. Cooking oil from that donut you ate for breakfast will probably be present in your fingerprints until you wash it off. Then residues from the soap you used to wash your hands may be a chemical constituent of your latent fingerprints. In fact, residue from personal care products is often found in latent fingerprints.[15,20]

Endogenous sources may be more predictable but still are complex. What we would call sweat and/or body oil comes from 4 different types of glands: eccrine, apocrine, apoeccrine, and sebaceous. Each gland secretes a slightly different blend of chemical components. Generally, eccrine glands secrete classic sweat, an aqueous solution of electrolytes and hydrophilic compounds such as urea.[21] The other three glands secrete lipophilic fatty and waxy substances such as squalene and cholesterol.[22,23] There have been many studies on the composition of latent fingerprint materials, sweat, and "body oil." One article reports "We found an average of 241 peaks in the GC–MS of sweat."[24]

Constituents representing nearly all of the common chemical classifications can be detected in sweat and latent fingerprints: alcohols, phenols, aldehydes, ketones, esters, hydrocarbons, amines, amides, amino acids, and carboxylic acids.[25−27] Common endogenous components of body oils that can be detected by gas chromatography–mass spectrometry (GC–MS) are squalene, cholesterol, and fatty acids such as stearic acid.[15,28−31] However, some components may be difficult to detect with GC such as inorganic and organic metallic salts.[32,33] Judging by the success of ninhydrin and related compounds as revealing agents, amino acids are common constituents of fingerprint residue, but they are not readily detected with GC–MS without prior derivatization.[34−36] Various studies have been done to try to glean information from an individual's cocktail of skin secretions.[24,37−39] In fact, a particular mix of chemicals may be as individualistic for a particular person as a fingerprint. A thorough chemical analysis of fingerprint residues may even reveal if the person habitually inhales or ingests certain chemical substances.[40,41] In addition, it is quite likely, that the composition of latent fingerprints change as a person ages.[13,39]

■ CHEMICAL REACTIONS IN THE REVELATION OF LATENT FINGERPRINTS

Reactions of Free Amino Acids: Ninhydrin and Its Mimics

The revelation of latent fingerprints with ninhydrin occurs via a very plausible sequence of chemical reactions as shown in Figure 1. The chemical substance known as ninhydrin (2,2-dihydroxyindane-1,3-dione) was first described in 1910 by Ruhemann.[42] Reacting latent prints with ninhydrin has been credited to Oden and von Hefsten in a 1955 British patent.[43] Ninhydrin is often the method of choice when attempting to reveal latent prints on paper.[44] Typically, ninhydrin is mixed with a volatile solvent such as ethanol and sprayed on the paper.[12] The paper may be heated in an oven to accelerate the reaction of ninhydrin with the amino acid residues contained in the latent print.[12] The result is a bluish or purplish print. To generate a chromophore, ninhydrin must first condense with the primary amine of an amino acid to form an imine. The resulting imine can decarboxylate and hydrolyze in the presence of water to form a primary amine that can condense with a second molecule of ninhydrin to form diketohydrindylidene-diketohydrindamine or "Ruhemann's purple" as shown in Figure 1.[44] As the prints have a tendency to fade with time, it is best to take a photograph. It is reported that ninhydrin stained fingerprints can be readily subjected to other development techniques as well.[32]

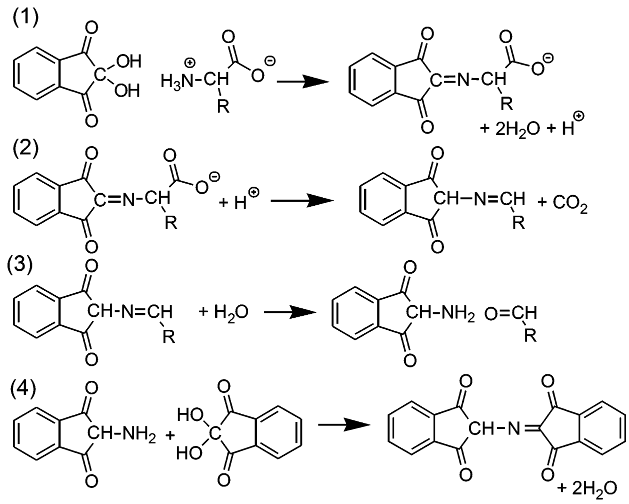


Figure 1. A possible mechanism for ninhydrin revelation of amino acid residues.[44]

The success of ninhydrin as a method of revealing latent fingerprints by chemically reacting with the primary amines present in amino acid residues has extended the technique. Several reagents have been developed to react in similar way as ninhydrin to form a colored and/or fluorescent compound in the presence of primary amines.[11,45−47]

Dansyl chloride (5-(dimethylamino)naphthalene-1-sulfonyl chloride) is a well-known reagent used to modify amino acids to facilitate UV–vis and fluorescent detection as they are eluted from a high-performance liquid chromatography (HPLC) column.[11,48] Lawsone, (2-hydroxy-1,4-naphthoquinone) a natural dye, is another fluorescent compound that can be used to react with amino acid residues in latent fingerprints.[14] Lawsone is found in extracts of the henna plant which are used as skin dyes.[49] Reagents such as dansyl chloride and lawsone

DOI: 10.1021/ed400597u
J. Chem. Educ. 2015, 92, 497−504

(Figure 2) form highly active fluorescent adducts that can be more easily detected and distinguished from the background than ninhydrin treated finger prints.

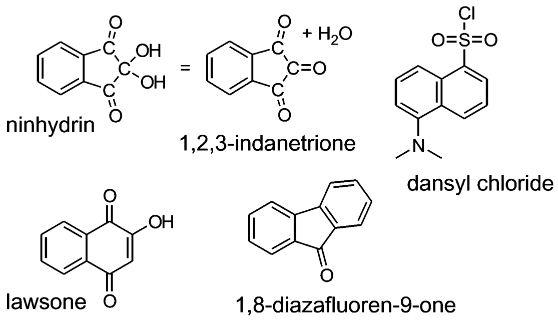


Figure 2. Structure of ninhydrin and related compounds.

A modern alternative to ninhydrin is 1,8-diazafluoren-9-one (DFO), which is reported to be more sensitive than ninhydrin while producing a fluorescent product.[50,51] After two molecules of DFO (Figure 2) react with an amino acid residue in latent fingerprints, the resulting highly conjugated Ruhemann's purple analog is red or pink colored. This substance also shows excitation at approximately 470 nm with a green-yellow fluorescent emission at 560 nm. Besides enhanced sensitivity, the advantage of having a fluorescent print is that it can be easily distinguished from a colored and/or printed background. This new reagent was introduced in a 1990 chemistry journal article rather than a forensic journal, which shows the considerable overlap between basic chemistry and forensic science applications of that chemistry.[52]

Silver Nitrate

The use of silver nitrate ($AgNO_3$) to reveal latent prints has been practiced by law enforcement since the 1930s. The technique was first used in the United States to solve the 1933 kidnapping of William A. Hamm, Jr., president of the Theodore Hamm Brewing Company.[53] Very simply, an aqueous solution of silver nitrate is sprayed onto a paper or cardboard surface. The paper is left to dry while being exposed to sunlight or UV light. The ridge detail emerges as a dark image.[12,54] The first reaction is a precipitation of silver chloride when the silver ions react with chloride ions in the fingerprint residue to form AgCl:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

Under UV light, the silver chloride disproportionates into elemental silver and chlorine gas.[55]

$$2AgCl(s) \rightarrow 2Ag(s) + Cl_2(g)$$

The reduction of silver chloride may also be effected chemically by immersion of the object in a bath of formaldehyde and sodium hydroxide.[56]

Physical Developer

The physical developer method of revealing latent fingerprints has its origins in the development of photographic film. The physical developer solution is rather complex because it contains three different metal ions: Ag^+, Fe^{2+}, and Fe^{3+}. In one scenario, the silver ions are attracted to fingerprint residue much like what was described in the silver nitrate development paragraph. The silver ions associated with the fingerprint are reduced by the iron(II) ions to silver metal and iron(III) by simple reduction/oxidation chemistry. The presence of iron(III) and citrate in the physical developer solution stabilizes the solution by suppressing the spontaneous formation of silver from the reaction with silver ions and iron(II).[57,58] In an alternate scenario, the physical developer solution facilitates the formation of silver nanoparticles, which are (initially) highly negatively charged due to the presence of negatively charged organic ions. These nanoparticles are attracted to the positively charged latent print residue. The presence of a cationic surfactant, such as *n*-dodecylamine acetate, further suppresses the deposition of silver on the fingerprinted surface.[59] Altogether, this process facilitates the selective deposition of silver metal on the fingerprint residue and not on the surface of the object that is being fingerprinted. This method reportedly works well on porous surfaces. In the presence of bleach (hypochlorite anion), the print becomes darker from the formation of silver oxide.

$$OCl^- + 2Ag \rightarrow Ag_2O + Cl^-$$

The application of physical developer to the printed object typically involves several steps with the printed object being developed in a tray.[60]

Gun Blue

A preparation called "gun blue solution" is used to reveal fingerprints on brass shell casings. Apparently, this method was first used in forensic laboratories about 1995.[57] Gun blue solution is an aqueous mixture of selenous acid and copper sulfate in which the fired casings are soaked. When the gun blue solution comes in contact with brass, copper and selenium are formed and deposited on the surface of the metal according to the following equations except in those areas where fatty fingerprint residues are present.[61,62] Both the copper ions and selenous acid are reduced in the presence of zinc.[57] Nickel plated brass and aluminum cartridges also work with this method.[57]

$$H_2SeO_3 + 4H^+ + 2Zn \rightarrow Se + 3H_2O + 2Zn^{2+}$$

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

Chemical Reaction and Physical Adherence: Cyanoacrylate Esters

The cyanoacrylate ester fuming method of revealing fingerprints was discovered by the Criminal Identification Division of the Japanese National Police Agency in 1978.[60] It was soon practiced all over the world. Fingerprint residue exposed to cyanoacrylate ester fumes for brief periods of time becomes hardened tan-colored fingerprint impressions. There are three different esters that are popularly marketed: methyl, ethyl, and *n*-butyl cyanoacrylate. Superglue itself was first described by Dr. Harry Coover in 1942 while working for Kodak Research Laboratories to develop a clear plastic for gun sights. Coover finally realized that cyanoacrylate was a useful adhesive in 1958.[63] The chain growth of cyanoacrylate polymers initiated by the lactate anion as shown in Figure 3 has been studied.[64] The increase in mass of 45 μL droplets of solution while being superglue fumed was measured over time. Increasing the pH increased the accumulation of superglue mass.

On the other hand, another study suggests that clumps of superglue are formed during fuming and are subsequently absorbed into the oily fingerprint residue.[65] This article was written as a result of an undergraduate research project in which the authors describe a series of experiments to determine the affinity of superglue fumes for various substances. Long

DOI: 10.1021/ed400597u
J. Chem. Educ. 2015, 92, 497−504

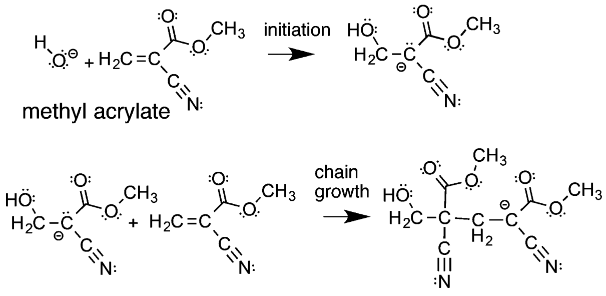


Figure 3. Proposed mechanism for methyl cyanoacrylate anionic initiation and chain growth.[65]

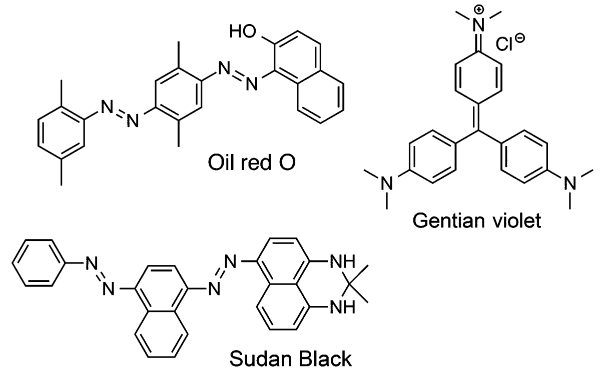


Figure 4. Chemical structures of organic dyes.

chain fatty acids absorb the cyanoacrylate fumes very well. In fact, the longer the hydrocarbon chain, the faster the deposition of the superglue. These two articles[64,65] carefully present competing theories to explain the chemistry of superglue fuming of latent fingerprints.

■ PHYSICAL ADHERENCE IN THE REVELATION OF LATENT FINGERPRINTS

Physical Adherence: Inorganics

One of the oldest and most accessible means of revealing latent fingerprints is the iodine fuming method.[66] Iodine fuming has been used extensively over the years to reveal the presence of organic compounds on TLC plates. Iodine staining is accomplished by the simple process of exposing latent fingerprints to iodine fumes in a sealed chamber.[56] Latent fingerprints on paper or cardboard tend to be the best candidates for iodine fuming revelation. Just because it is an established technique does not necessarily mean that the chemistry is well understood. The compounds revealed by iodine tend to end up uniformly brown/yellow in color. The staining with iodine usually fades rather quickly once the TLC plate or latent fingerprint is taken out of the iodine chamber. This observation points toward the possibility that the elemental iodine adheres to certain chemicals by some noncovalent intermolecular bonding phenomenon such as van der Waals interactions. Actually, the impermanence of the developed print is an advantage because the same print can then be processed with two different methods. A photograph may be the best way to preserve the print. Spray starch may also be a way to enhance the iodine stain and preserve it. Iodine has a rather unique interaction with starch that turns the iodine blue-black. According to rigorous studies color is created by trapping of I_5^- ions within the amylose helix structure.[67]

Ruthenium tetroxide (RuO_4, also known as RTX) is an inorganic oxide that adheres to fingerprint residue. A handful of scientific articles report the use of RuO_4 fuming or direct application as a method to reveal latent prints.[68−71] RuO_4 can be produced in situ by mixing aqueous $RuCl_3$ and ammonium cerium(IV) nitrate $(NH_4)_2Ce(NO_3)_6$. The resulting tetroxide is insoluble in water and is released.[69] RuO_4 may also be applied in a halogenated hydrocarbon solvent.[69] Evidently, RuO_4 is attracted to the fatty fingerprint residues forming a dark colored ruthenium dioxide in the presence of fatty fingerprint residues.[68] The chemical mechanism for this transformation is unknown.

Physical Adherence: Dyes

A lipophilic dye called oil red O, as seen in Figure 4, has attracted some attention recently as a good compound to reveal latent fingerprints on difficult surfaces. Alexandre Beaudoin in a *Journal of Forensic Identification* article proposes that oil red O is a good alternative for the silver ion based "physical developer" in revealing lipidic latent prints on wet porous surfaces such as paper and cardboard.[72] This report has been followed up with at least four more papers by the same author exploring the virtues of this dye.[58,73−75] This particular lysochrome has been used in biological staining for many years. The method involves dissolving oil red O in a methanol solution made basic with sodium hydroxide. After the stain has taken hold, the pH of the surface is adjusted to neutral with a buffer. This rather recent discovery shows that the science and art of latent fingerprint revelation is a field open to ongoing investigation.[76] It also points to an interesting link between biological stains and fingerprint analysis.

Oil red O is just one of several fat soluble (lysochrome) dyes that are used in fingerprint revelation. Sudan black (Figure 4) is another popular lysochrome dye, which is especially useful in developing prints on waxy paper and wetted surfaces.[77] Sudan black is a member of the Sudan family of azo dyes. It is typically dissolved in an alcohol and applied by immersing the object in the solution. The dye washes off the nonfingerprinted surfaces and reveals the latent print.[77]

Several fluorescent dyes are used to adhere directly to the fingerprint residue, modify dusting powders or enhance superglue fumed fingerprints.[60,77] All of these dyes fall into the category of lysochrome dyes. In general, they adhere to lipophilic surfaces with noncovalent forces. The great advantage of using fluorescent dyes is that the fingerprint ridge detail can be selectively enhanced.[60] Rhodamine dyes are commonly used for biotechnology applications such as fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy, and enzyme-linked immunosorbent assays. The disadvantage of fluorescent dyes is that specialized light sources are needed to excite the fluorophores and/or photograph the fluorescent emission light. Rhodamine 6G has an excitation wavelength of 526 nm and an emission wavelength of 555 nm. A variety of alternative light sources (ALS) are sold by forensic vendors. The sources can be as compact as a small flashlight or as big as an industrial vacuum cleaner.

Other fluorescent dyes commonly used in forensics are Basic Red 28, Basic Yellow 40, Ardrox, and 4-(4-methoxybenzylamino)-7-nitrobenzofurazan (MBD) found in Figure 5.[78] Custom mixtures of these dyes are commercially available: "RAM" (Rhodamine 6G, Ardrox, and MBD), and "RAY" (Basic Red 28, Ardrox, and Basic Yellow 40).[79]

There are several methods to reveal latent prints on the sticky side of tape.[80] Tape plays an important part in some

DOI: 10.1021/ed400597u
J. Chem. Educ. 2015, 92, 497−504

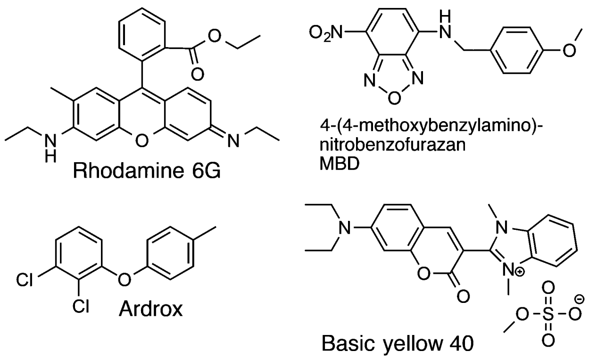


Figure 5. Chemical structures of fluorescent dyes.

crimes such as abductions. It is almost impossible to handle tape with gloves, therefore, it is difficult to tape something without leaving a fingerprint on the sticky side at some point. Very likely, the contact with adhesive leaves a somewhat different mixture of fingerprint residues than contact with a smooth surface. This has not been documented, but skin (epithelial) cells are possibly more likely to be left on tape than on other surfaces. The fact that gentian violet (also called crystal violet) stains fingerprints on the sticky side of tape may be due to the interaction of the dye and skin cell DNA. In biology, solutions of crystal violet are used to simultaneously fix and stain certain cells such as bacteria.[81] Gentian violet (Figure 4) is very easy to use—just dip the tape in an aqueous gentian violet bath for 30 s or so then wash off the excess dye under running water.[82,83]

Physical Adherence: Powders

The only criterion for a powder to reveal latent fingerprints is that it needs to adhere to the prints and not to the surface around the prints. A number of fingerprint powders are sold commercially, but even fairly commonplace substances such a talcum powder and charcoal dust will reveal latent fingerprints.[2,84] A fingerprint experiment, published on the Internet, even suggested that students pulverize pencil leads to make a fingerprint powder.[2] Amazingly, fingerprint residue composed primarily of lipids such as squalene, fatty acids, and cholesterol adheres to a large number of substances. Several fingerprint pioneers, such as Forgeot in France, Sanchez in South America, Heindl in Germany, Reiss in Roumania, and Vucetich in Argentina studied ridge patterns by using different powder compositions in the late 1800s.[85] The inventor of a fingerprint classification system, Sir Edward Richard Henry (1850−1931), used mercury and graphite-based powders.[85] Fingerprint powders can be divided into regular, metallic, and photoluminescent classifications referring to their appearances.[85] Regular powders contain a finely divided polymeric resin with a colorant. Metallic oxides, such as iron oxide, provide the base materials for metallic powders. Fluorescent and phosphorescent powders are typically comprised of organic based powders can be made from substances such organic dyes or ground up fish scales. Recently, the fluorescent natural product curcumin was proposed as a fingerprinting powder.[86]

Given the importance of developing latent prints on the sticky-side of tape, there are several methods for revealing them. Much like the "dusting" method of latent print revelation, a series of sticky-side wet powders are available. Generally, these are dry powders which are suspended in an aqueous solution with an anionic surfactant.[87] Like dusting powders, the forces that adhere the grains of powder to the fingerprint residue are noncovalent interactions. However, it is not clear what role the detergent plays. The surfactant may simply act as a wetting agent and allow the powder to spread out over the surface of the tape. On the other hand, the surfactant may also facilitate the interaction between the powder and the oily fingerprint residue. Sticky side powder materials are generally titanium dioxide based with traces of aluminum and silicon.[88] A popular surfactant solution used in commercial sticky side powders is called "Photo-Flo 200" which is an aqueous solution of propylene glycol and *p-tert*-octylphenoxy polyethoxyethyl alcohol (octoxynol 9 in Figure 6).[77] A popular article suggests

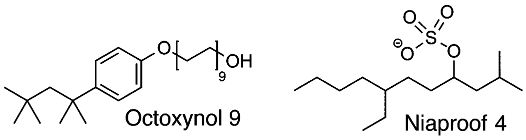


Figure 6. Chemical structures of surfactants.

that a regular fingerprint powder can be suspended in a dishwashing detergent solution to create a homemade sticky side powder.[89] Revealing prints in this way is a dramatic phenomenon. A black goo is applied to a strip of tape and washed off to reveal a clear print.

Physical Adherence: Small Particle Reagent

Small Particle Reagent is used to detect latent fingerprints left on wet surfaces.[77] The reagent is made of a suspension of fine molybdenum disulfide in a surfactant solution.[60] The fact that fingerprint residue remains largely intact even when submerged in water is further evidence that the composition of fingerprint residue is primarily water insoluble lipids. The particles adhere to oily fingerprint residue. Other materials besides molybdenum disulfide can be used as well: titanium dioxide, zinc oxide, magnetite (Fe_3O_4), graphite, or zinc carbonate.[90] It is rather like the wet version of fingerprint powders. It is unclear whether the detergent functions simply to spread out the suspension on a surface or if the detergent molecules interact with the fingerprint residue to facilitate the attraction between the particles and hydrophobic materials. The reagent is sprayed on the object and the excess material can be gently washed off. One detergent that is used is niaproof 4, an anionic surfactant with an akylsulfate group shown in Figure 6.[91] In one study, 11 different small particle reagent formulations were explored by varying the particle composition, surfactant concentration, addition of choline chloride, and pH.[92] Although molybdenum disulfide consistently gave the best images, the other factors did not seem to affect the outcome in any significant way.

Physical Adherence: Vacuum Metal Deposition

Vacuum metal deposition (VMD) is a technique that has found some popularity despite its rather great expense. The interaction of metal vapor with fingerprints was discovered by accident in 1964 by a British researcher.[57] Initially, a sample of gold metal is evaporated in a chamber containing the object to be fingerprinted.[62,93] The gold covers the whole surface and those gold particles which lie on top of the fingerprint residue are absorbed into the residue.[94] Gold nanoparticles have been shown to aggregate differently depending on if they are associated with the ridges or grooves of a fingerprint.[95] The gold deposition is followed by evaporating zinc metal under the same conditions. The zinc binds to the gold which is not absorbed by the fingerprint ridges and enhances the print to the point where it can be photographed. The background is stained

DOI: 10.1021/ed400597u
J. Chem. Educ. 2015, 92, 497−504

with the zinc and the print stands out as a negative. The efficacy of VMD on white cotton, nylon, polyester and polycotton fabrics has been studied.[96] The method worked well on these hard-to-print surfaces and has other potential applications to smooth surfaces such as polyethylene.[96]

Antibody−Antigen Interactions: Immunoassay Based Techniques

A new development in the revelation of latent prints combines visualization with targeting specific chemical substances present in the fingerprint. This has been done by attaching antibodies to gold nanoparticles that bind to specific drug metabolites such as cotinine, morphine, benzoylecgonine, Δ9-tetrahydrocannabinol, and 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine.[40,97−100] Secondary antibodies tagged with fluorescent indicators visualize only those prints containing the target substance(s).[99]

■ CONCLUSION

The role of chemistry in the forensic use of fingerprints is to provide methods to reveal the prints so that they can be compared with prints of known origin. The field of chemical fingerprint analysis has been dominated by empirical investigations. In most cases methods to reveal latent prints have been developed and adopted by law enforcement without a clear understanding of how or why they work. The chemistry has been investigated out of intellectual curiosity or as an attempt to improve the technique.

The challenge for chemistry instructors, researchers and students is to develop an understanding of the chemistry involved in latent print revelation. Therefore, it is necessary to understand the chemical composition of fingerprint residue. Without a clear understanding of the actual composition of latent fingerprints, which may be quite variable, it is difficult to provide a chemical rationale for why certain methods do work or should work. In the case of ninhydrin, it is quite clear that the presence of amino acids in fingerprint residue is responsible for the visualization.[44] However, latent fingerprint revelation methods attributed to physical adherence have rarely been studied in reference to a certain compound or class of compounds found in fingerprints. Fingerprint residue has simply been regarded as an oily substance. The studies of cyanoacrylate fuming, where attempts were made to identify the compound(s) that react with and/or bind with cyanoacrylate fumes, may serve as a model for the investigation of other techniques.[64,65]

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jbfriesen@dom.edu.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) reachoutmichigan.org. Fingerprinting: A Lesson on Classification; Http://www.reachoutmichigan.org/funexperiments/agesubject/lessons/prints.html.

(2) Oregon Museum of Science and Industry. Latent Prints; http://www.omsi.edu/sites/all/FTP/files/chemistry/NH-PDF/NH-G23-LatentPrints.pdf (accessed Aug 14, 2013).

(3) Nikitakis, A.; Lymperopoulou, K. A. Fun with Fingerprints: Cyanoacrylate Fuming. *J. Chem. Educ.* **2008**, *85*, 816A.

(4) Johll, M. E. *Investigating Chemistry*, 3rd ed.; W. H. Freeman and Company: New York, NY, 2013.

(5) Houck, M. M. *Fundamentals of Forensic Science*, 2nd ed.; Academic Press: Burlington, MA, 2010.

(6) Girard, J. E. *Criminalistics: Forensic Science, Crime, and Terrorism*, 3rd ed.; Jones & Bartlett Learning: Sudbury, MA, 2013.

(7) Meloan, C. E.; James, R. E.; Saferstein, R. *Lab Manual for Criminalistics, an Introduction to Forensic Science*, 10th ed.; Prentice Hall: Boston; London, 2011.

(8) Bell, S. *Forensic Chemistry*, 2nd ed.; Pearson: Boston, 2013.

(9) Saferstein, R. *Criminalistics: An Introduction to Forensic Science*; 10th ed.; Prentice Hall: Boston, 2011.

(10) Saferstein, R. *Basic Laboratory Exercises for Forensic Science*; Prentice Hall: Upper Saddle River, NJ, 2011.

(11) Clark, S.; Quigley, M. N.; Tezak, J. Chemical Detection of Latent Fingerprints. *J. Chem. Educ.* **1993**, *70*, 593.

(12) Sodhi, G.; Kaur, J. Chemical Methods for Developing Latent Fingerprints. *J. Chem. Educ.* **1999**, *76*, 488A.

(13) Kimbrough, D. R.; DeLorenzo, R. Solving the Mystery of the Fading Fingerprints with London Dispersion Forces. *J. Chem. Educ.* **1998**, *75*, 1300.

(14) LaFratta, C. N.; Huh, S. P.; Mallillin, A. C.; Riviello, P. J.; Walt, D. R. Visualizing Fluorescence: Using a Homemade Fluorescence "Microscope" To View Latent Fingerprints on Paper. *J. Chem. Educ.* **2010**, *87*, 1105−1107.

(15) Hartzell-Baguley, B.; Hipp, R. E.; Morgan, N. R.; Morgan, S. L. Chemical Composition of Latent Fingerprints by Gas Chromatography−Mass Spectrometry. An Experiment for an Instrumental Analysis Course. *J. Chem. Educ.* **2007**, *84*, 689.

(16) Herschel, W. J. Skin Furrows of the Hand. *Nature* **1880**, *23*, 76.

(17) Michael, K. The Legal, Social and Ethical Controversy of the Collection and Storage of Fingerprint Profiles and DNA Samples in Forensic Science. In *IEEE International Symposium on Technology and Society*; bepress IEEE: Wollongong, NSW, Australia, 2010; pp 48−60; http://works.bepress.com/kmichael/191/.

(18) Federal Bureau of Investigation (FBI). Integrated Automated Fingerprint Identification System: IAFIS; http://www.fbi.gov/about-us/cjis/fingerprints_biometrics/iafis/iafis (accessed Feb 5, 2014).

(19) Sun, Z.; Paulino, A. A.; Feng, J.; Chai, Z.; Tan, T.; Jain, A. K. A Study of Multibiometric Traits of Identical Twins. https://web.cse.msu.edu/~paulinoa/Files/Sunetal_IdentTwins_SPIE10.pdf. In *Proceedings of the SPIE*; Vijaya Kumar, B. V. K., Prabhakar, S., Ross, A. A., Eds.; Biometric Technology for Human Identification VII; SPIE: Bellingham, WA, 2010; Vol. *7667*, p 76670T 12.

(20) Gallagher, M.; Wysocki, C. J.; Leyden, J. J.; Spielman, A. I.; Sun, X.; Preti, G. Analyses of Volatile Organic Compounds from Human Skin. *Br. J. Dermatol.* **2008**, *159*, 780−791.

(21) Liappis, N.; Kelderbacher, S.-D.; Kesseler, K.; Bantzer, P. Quantitative Study of Free Amino Acids in Human Eccrine Sweat Excreted from the Forearms of Healthy Trained and Untrained Men during Exercise. *Eur. J. Appl. Physiol.* **1979**, *42*, 227−234.

(22) Labows, J. N.; Preti, G.; Hoelzle, E.; Leyden, J.; Kligman, A. Steroid Analysis of Human Apocrine Secretion. *Steroids* **1979**, *34*, 249−258.

(23) Stewart, M. E.; Downing, D. T. Proportions of Various Straight and Branched Fatty Acid Chain Types in the Sebaceous Wax Esters of Young Children. *J. Invest. Dermatol.* **1985**, *84*, 501−503.

(24) Penn, D. J.; Oberzaucher, E.; Grammer, K.; Fischer, G.; Soini, H. A.; Wiesler, D.; Novotny, M. V.; Dixon, S. J.; Xu, Y.; Brereton, R. G. Individual and Gender Fingerprints in Human Body Odour. *J. R. Soc., Interface* **2007**, *4*, 331−340.

(25) Bernier, U. R.; Kline, D. L.; Barnard, D. R.; Schreck, C. E.; Yost, R. A. Analysis of Human Skin Emanations by Gas Chromatography/Mass Spectrometry. 2. Identification of Volatile Compounds That Are Candidate Attractants for the Yellow Fever Mosquito (*Aedes eegypti*). *Anal. Chem.* **2000**, *72*, 747−756.

(26) Zhang, Z.-M.; Cai, J.-J.; Ruan, G.-H.; Li, G.-K. The Study of Fingerprint Characteristics of the Emanations from Human Arm Skin

DOI: 10.1021/ed400597u
J. Chem. Educ. 2015, 92, 497−504

Using the Original Sampling System by SPME-GC/MS. *J. Chromatogr., B* **2005**, *822*, 244−252.
(27) Ferguson, L.; Bradshaw, R.; Wolstenholme, R.; Clench, M.; Francese, S. Two-Step Matrix Application for the Enhancement and Imaging of Latent Fingermarks. *Anal. Chem.* **2011**, *83*, 5585−5591.
(28) Michalski, S.; Shaler, R.; Dorman, F. L. The Evaluation of Fatty Acid Ratios in Latent Fingermarks by Gas Chromatography/Mass Spectrometry (GC/MS) Analysis. *J. Forensic Sci.* **2013**, *58*, S215−S220.
(29) Nicolaides, N.; Ansari, M. N. A. The Dienoic Fatty Acids of Human Skin Surface Lipid. *Lipids* **1969**, *4*, 79−81.
(30) Weyermann, C.; Roux, C.; Champod, C. Initial Results on the Composition of Fingerprints and Its Evolution as a Function of Time by GC/MS Analysis. *J. Forensic Sci.* **2011**, *56*, 102−108.
(31) Archer, N. E.; Charles, Y.; Elliott, J. A.; Jickells, S. Changes in the Lipid Composition of Latent Fingerprint Residue with Time after Deposition on a Surface. *Forensic Sci. Int.* **2005**, *154*, 224−239.
(32) Chemistry of Print Residue; http://what-when-how.com/forensic-sciences/chemistry-of-print-residue/ (accessed Jan 8, 2013).
(33) Victoria Forensic Science Centre. Latent Fingerprint Composition; http://www.docstoc.com/docs/34686522/VICTORIA-FORENSIC-SCIENCE-CENTRE-FINGERPRINT-BRANCH-MODULE-NINE (accessed Oct 5, 2014).
(34) Hamilton, P. B. Amino-Acids on Hands. *Nature* **1965**, *205*, 284−285 http://www.nature.com/nature/journal/v205/n4968/abs/205284b0.html.
(35) Croxton, R. S.; Baron, M. G.; Butler, D.; Kent, T.; Sears, V. G. Development of a GC-MS Method for the Simultaneous Analysis of Latent Fingerprint Components. *J. Forensic Sci.* **2006**, *51*, 1329−1333.
(36) Knowles, A. M. Aspects of Physicochemical Methods for the Detection of Latent Fingerprints. *J. Phys. E: Sci. Instrum.* **1978**, *11*, 713−721.
(37) Down, S. Latent secrets: Fatty acids in fingermarks linked to gender and race; http://www.separationsnow.com/details/ezine/13ad590c9b8/Latent-secrets-Fatty-acids-in-fingermarks-linked-to-gender-and-race.html?tzcheck=1 (accessed Jan 8, 2013).
(38) Asano, K. G.; Bayne, C. K.; Horsman, K. M.; Buchanan, M. V. Chemical Composition of Fingerprints for Gender Determination. *J. Forensic Sci.* **2002**, *47*, 805−807.
(39) Hemmila, A.; McGill, J.; Ritter, D. Fourier Transform Infrared Reflectance Spectra of Latent Fingerprints: A Biometric Gauge for the Age of an Individual. *J. Forensic Sci.* **2008**, *53*, 369−376.
(40) Hazarika, P.; Russell, D. A. Advances in Fingerprint Analysis. *Angew. Chem., Int. Ed.* **2012**, *51*, 3524−3531.
(41) Ifa, D. R.; Manicke, N. E.; Dill, A. L.; Cooks, R. G. Latent Fingerprint Chemical Imaging by Mass Spectrometry. *Science* **2008**, *321*, 805−805.
(42) Ruhemann, S. CXXXII. Cyclic Di- and Tri-Ketones. *J. Chem. Soc., Trans.* **1910**, *97*, 1438−1449.
(43) Odén, S.; Hofsten, B. V. Detection of Fingerprints by the Ninhydrin Reaction. *Nature* **1954**, *173*, 449−450.
(44) Friedman, M. Applications of the Ninhydrin Reaction for Analysis of Amino Acids, Peptides, and Proteins to Agricultural and Biomedical Sciences. *J. Agric. Food Chem.* **2004**, *52*, 385−406.
(45) Almog, J.; Glasner, H. Ninhydrin Thiohemiketals: Basic Research towards Improved Fingermark Detection Techniques Employing Nano-Technology. *J. Forensic Sci.* **2010**, *55*, 215−220.
(46) Schulz, M. M.; Brune, V.; Maierthaler, M.; Graw, M. Visualization of Latent Biological Traces via 5-Methylthioninhydrin (5-MTN) Staining for Forensic DNA Typing. *Forensic Sci. Int. Genet. Suppl. Ser.* **2011**, *3*, e530−e531.
(47) Almog, J.; Hirshfield, A.; Frank, A.; Grant, H.; Harel, Z.; Ittah, Y. 5-Methylthio Ninhydrin and Related Compounds: A Novel Class of Fluorogenic Reagents. *J. Forensic Sci.* **1992**, *37*, 688−694.
(48) Reagents for Analysis of Low Molecular Weight Amines; http://www.invitrogen.com/site/us/en/home/References/Molecular-Probes-The-Handbook/Fluorophores-and-Their-Amine-Reactive-Derivatives/Reagents-for-Analysis-of-Low-Molecular-Weight-Amines.html (accessed Jan 9, 2013).
(49) Jelly, R.; Lewis, S. W.; Lennard, C.; Lim, K. F.; Almog, J. Lawsone: A Novel Reagent for the Detection of Latent Fingermarks on Paper Surfaces. *Chem. Commun.* **2008**, 3513−3515.
(50) Stoilovic, M. Improved Method for DFO Development of Latent Fingerprints. *Forensic Sci. Int.* **1993**, *60*, 141−153.
(51) Pounds, A. C.; Grigg, R.; Mongkolaussavaratana, T. The Use of 1,8-Diazafluoren-9-one (DFO) for the Flourescent Detection of Latent Fingerprints on Paper. A Preliminary Evaluation. *J. Forensic Sci.* **1990**, *35*, 1−7.
(52) Grigg, R.; Mongkolaussavaratana, T.; Pounds, C. A.; Sivagnanam, S. 1,8-Diazafluorenone and Related Compounds. A New Reagent for the Detection of α-Amino Acids and Latent Fingerprints. *Tetrahedron Lett.* **1990**, *31*, 7215−7218.
(53) Latent Prints in the 1933 Hamm Kidnapping; http://www.fbi.gov/news/stories/2003/september/hamm090803 (accessed Jan 9, 2013).
(54) Sirchi. Overview of Latent Print Development Techniques; http://www.sirchie.com/Assets/Manuals/pdf/LP%20Dev%27mt%20Tech_TB02-102ENG-REV2E.pdf. TB02-102ENG-REV1 2009, 1−20.
(55) Crown, D. A. The Development of Latent Fingerprints with Ninhydrin. *J. Crim. Law, Criminol. Police Sci.* **1969**, *60*, 258−264.
(56) O'Neill, M. E. The Development of Latent Fingerprints on Paper. *J. Crim. Law Criminol.* **1937**, *28*, 432.
(57) National Institute of Justice. The Fingerprint Sourcebook; http://www.nij.gov/pubs-sum/225320.htm (accessed Jan 9, 2013).
(58) Rawji, A.; Beaudoin, A. Oil Red O versus Physical Developer on Wet Papers: A Comparative Study. *J. Forensic Identif.* **2006**, *56*, 33−54.
(59) Cantu, A. A. Nanoparticles in Forensic Science. *Proc. SPIE 7119* **2008**, 71190F.
(60) Lee, H. C.; Ramotowski, R.; Gaensslen, R. E. *Advances in Fingerprint Technology*, 2nd ed.; CRC Press: Boca Raton, FL, 2001.
(61) Leben, D. A.; Ramotowski, R. S. Evaluation of Gun Blueing Solutions and Their Ability to Develop Latent Fingerprints on Cartridge Casings. *FDIAI News* **1997**, 10−11. https://www.fdiai.org/Newsletter%20Archives/Newsletters/Jan1997/Jan1997leben&ramotowski.pdf.
(62) Bhaloo, Z. M.; Yamashita, B.; Wilkinson, D.; NicDaeid, N. The Recovery of Fingerprints from Fired Cartridge Cases: A Comparison of Current Methods of Development with an Electrostatic Deposition Technique. *Identif. Can.* **2010**, *33*, 88−102.
(63) Kristof, M. Discovery of Super Glue; http://www.kristofcreative.com/creative-resources/great-ideas/discovery-of-super-glue/#axzz2ZQpQ4IGI (accessed Jul 18, 2013).
(64) Wargacki, S. P.; Lewis, L. A.; Dadmun, M. D. Understanding the Chemistry of the Development of Latent Fingerprints by Superglue Fuming. *J. Forensic Sci.* **2007**, *52*, 1057−1062.
(65) Czekanski, P.; Fasola, M.; Allison, J. A Mechanistic Model for the Superglue Fuming of Latent Fingerprints. *J. Forensic Sci.* **2006**, *51*, 1323−1328.
(66) Coulier, P.-J. Les vapeurs d'iode employées comme moyen de reconnaître l'altération des écritures. *L'Année Sci. Ind.* **1863**, *8*, 157−160.
(67) Teitelbaum, R. C.; Ruby, S. L.; Marks, T. J. On the Structure of Starch-Iodine. *J. Am. Chem. Soc.* **1978**, *100*, 3215−3217.
(68) Mashiko, K.; Miyamoto, T. Latent Fingerprint Processing by the Ruthenium Tetroxide Method. *J. Forensic Identif.* **1998**, *48*, 279−290.
(69) Centoricka, M.; Rone, B. Development of Latent Fingerprints on Various Surfaces by Using the RTX Method. *Probl. Forensic Sci.* **2002**, *51*, 155−157.
(70) Mashiko, K.; German, E. R.; Motojima, K.; Colman, C. D. RTX: A New Ruthenium Tetroxide Fuming Procedure. *J. Forensic Identif.* **1991**, *41*, 429−436.
(71) Trapecar, M.; Balazic, J. Fingerprint Recovery from Human Skin Surfaces. *Sci. Justice* **2007**, *47*, 136−140.
(72) Beaudoin, A. New Technique for Revealing Latent Fingerprints on Wet, Porous Surfaces: Oil Red O. *J. Forensic Identif.* **2004**, *54*, 413−421.

(73) Guigui, K.; Beaudoin, A. The Use of Oil Red O in Sequence with Other Methods of Fingerprint Development. *J. Forensic Identif.* **2007**, *57*, 550−581.
(74) Beaudoin, A. Oil Red O: Fingerprint Development on a 21 Years Old Cold Case. *J. Forensic Identif.* **2011**, *61*, 50−59.
(75) Beaudoin, A. Fingerprint Staining Technique on Dark and Wetted Porous Surfaces: Oil Red O and Rhodamine 6G. *J. Forensic Identif.* **2012**, *62*, 315−329.
(76) Wood, M. A.; James, T. ORO. The Physical Developer Replacement? *Sci. Justice* **2009**, *49*, 272−276.
(77) Trozzi, T. A.; Schwartz, R. L.; Hollars, M. L.; Leighton, L. D.; Schehl, S. A.; Trozzi, Y. E.; Wade, C. Processing Guide for Developing Latent Prints. U.S. Department of Justice, Federal Bureau of Investigation, Laboratory Division: Washington, DC, 2000http://www.onin.com/fp/fbi_2000_lp_guide.pdf.
(78) Chesapeake Bay Divison, International Association for Identification. Latent Fingerprint Processing Techniques—Selection and Sequencing Guide.
(79) Arrowhead Forensics. http://www.crime-scene.com/store/latent.shtml. Processing Chemicals. Arrowh. Forensic Cat., Lenexa, Kansas.
(80) Schiemer, C.; Lennard, C.; Maynard, P.; Roux, C. Evaluation of Techniques for the Detection and Enhancement of Latent Fingermarks on Black Electrical Tape. *J. Forensic Identif.* **2005**, *55*, 214−238.
(81) Struwe, L. Gentain Violethttp://gentian.rutgers.edu/GentianViolet.htm (accessed Jul 18, 2013).
(82) Tucker, G. W. A Modified Crystal Violet Application Technique for Black Electrical Tape. *J. Forensic Identif.* **1990**, *40*, 148−150.
(83) WonderHowTo. How to Use gentian violet to reveal latent fingerprints; http://science.wonderhowto.com/how-to/use-gentian-violet-reveal-latent-fingerprints-302460/ (accessed Feb 4, 2014).
(84) Becue, A.; Moret, S.; Champod, C.; Margot, P. Use of Stains to Detect Fingermarks. *Biotechnol. Histochem.* **2011**, *86*, 140−160.
(85) Sodhi, G. S.; Kaur, J. Powder Method for Detecting Latent Fingerprints: A Review. *Forensic Sci. Int.* **2001**, *120*, 172−176.
(86) Francese, S.; Bradshaw, R.; Flinders, B.; Mitchell, C.; Bleay, S.; Cicero, L.; Clench, M. R. Curcumin: A Multipurpose Matrix for MALDI Mass Spectrometry Imaging Applications. *Anal. Chem.* **2013**, *85*, 5240−5248.
(87) Burns, D. S. Sticky-Side Powder: The Japanese Solution. *J. Forensic Identif.* **1994**, *44*, 133−138.
(88) Jones, B. J.; Reynolds, A. J.; Richardson, M.; Sears, V. G. Nano-Scale Composition of Commercial White Powders for Development of Latent Fingerprints on Adhesives. *Sci. Justice* **2010**, *50*, 150−155.
(89) Nelson, J. Homemade Solution for Processing Latent Prints on the Adhesive Side of Tape. *THE PRINT* **1998**, *14*, 1−2.
(90) Cucè, P.; Polimeni, G.; Lazzaro, A. P.; De Fulvio, G. Small Particle Reagents Technique Can Help to Point out Wet Latent Fingerprints. *Forensic Sci. Int.* **2004**, *146* (Suppl.), S7−S8.
(91) Material Safety Data Sheet. Small Particle Reagent—Dark. Sirchie Finger Print Lab. http://www.sirchie.com/Assets/msds/spr100.pdf.
(92) Kabklang, P.; Riengrojpitak, S.; Suwansamrith, W. Latent Fingerprint Detection by Various Formulae of SPR on Wet Non-Porous Surfaces. *J. Sci. Res. Chula. Univ.* **2009**, *34*, 59−64. http://forensic.sc.mahidol.ac.th/proceeding/50_Phatwalan.pdf.
(93) Misner, A. H. Fingerprint Detection Using Vacuum Metal Deposition. Forensic Science and Identification Services, 2003.
(94) Thomas, G. L. The Physics of Fingerprints and Their Detection. *J. Phys. E: Sci Instrum.* **1978**, *11*, 722−731.
(95) Tang, H.-W.; Lu, W.; Che, C.-M.; Ng, K.-M. Gold Nanoparticles and Imaging Mass Spectrometry: Double Imaging of Latent Fingerprints. *Anal. Chem.* **2010**, *82*, 1589−1593.
(96) Fraser, J.; Sturrock, K.; Deacon, P.; Bleay, S.; Bremner, D. H. Visualisation of Fingermarks and Grab Impressions on Fabrics. Part 1: Gold/zinc Vacuum Metal Deposition. *Forensic Sci. Int.* **2011**, *208*, 74−78.
(97) Hazarika, P.; Jickells, S. M.; Wolff, K.; Russell, D. A. Imaging of Latent Fingerprints through the Detection of Drugs and Metabolites. *Angew. Chem., Int. Ed.* **2008**, *47*, 10167−10170.
(98) Leggett, R.; Lee-Smith, E. E.; Jickells, S. M.; Russell, D. A. Intelligent" Fingerprinting: Simultaneous Identification of Drug Metabolites and Individuals by Using Antibody-Functionalized Nanoparticles. *Angew. Chem., Int. Ed.* **2007**, *46*, 4100−4103.
(99) Hazarika, P.; Jickells, S. M.; Wolff, K.; Russell, D. A. Multiplexed Detection of Metabolites of Narcotic Drugs from a Single Latent Fingermark. *Anal. Chem.* **2010**, *82*, 9150−9154.
(100) Hazarika, P.; Jickells, S. M.; Russell, D. A. Rapid Detection of Drug Metabolites in Latent Fingermarks. *Analyst* **2009**, *134*, 93.

DOI: 10.1021/ed400597u
J. Chem. Educ. 2015, 92, 497−504