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Review Article

NINHYDRIN-BASED FORENSIC INVESTIGATIONS I. FINGERPRINTS

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Abstract
Ninhydrin reagents are currently used for amino acid determination. However, ninhydrin reacts with amino groups of amino acids and other components of palmar sweat to develop Ruheman's purple. Therefore, it was used on a large scale to fingerprint development. Another recent application of ninhydrin is related to trace cyanide detection and determination. However, this simple compound may have multiple applications in peptide and protein research, in drug identification and detection or in heterocycle synthesis. Mainly, detection of finger marks with ninhydrin at a crime scene is of prime interest for forensic investigators. Herein, we review the most significant forensic applications of ninhydrin and its derivatives.

Keywords*: forensic science; ninhydrin; fingerprint reagents; cyanide determination; chemical processing; luminescence*

Introduction

Detection of finger marks at a crime scene is of prime interest for forensic investigators, mainly for identification purposes. They are left unintentionally by people at a crime scene are detected and lifted using various specific methods. Fingerprint detection and analysis for individual identification has undergone tremendous changes since its introduction to the investigation of crimes in 1892. The physically driven detection techniques, the chemically driven ones, and those based on nanostructured materials are all used in the field of forensic science. Thermal paper finds its extensive use in the modern day life and could act as a vital piece of physical evidence carrying latent finger marks (*Jasuja & Singh, 2009*). A simple method involves iodine fuming to develop finger marks which were not only permanent but also without any background coloration. This method does not involve any pre- or post-treatment of the substrate and was able to develop very old finger marks. In case of different types of thermal papers, presence of different substituents on leuco dye (lactone ring) structure results in development of different colored fingermarks upon reaction with iodine. Sebaceous material laden marks have been found to be more intensely developed as compared to eccrine marks, and the difference was more pronounced in case of aged fingermarks. Although a method to detect and extract latent fingerprint images without applying any powder or chemicals on the object was introduced (*Lin et al., 2006*), ninhydrin-based fingerprinting is still in use.

The use of cyanoacrylate ester adhesives in the development of latent fingerprints in the crime laboratory has proven to be highly efficient and simple (*Barber, 1985*).

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The mechanism is an anionic polymerization of alkyl 2-cyanoacrylate ester initiated by the weak bases such as water and amines present in the latent fingerprint residue. Various methods have been developed to accelerate the process of developing latent fingerprints with cyanoacrylate fumes. However, these methods require some caution on the part of the examiner due to the possibility of toxic fumes being produced by subjecting the cyanoacrylate to extreme conditions. Fingerprinting process has made great progress since the discovery that the latent finger marks can be visualized by ninhydrin (*Almog, 2001*). When a mass disaster happens, positive identification of multiple bodies becomes critically necessary (*Sloan, 1995*).

Ninhydrin is one of the most widely used reagents for chemical development of fingerprints on porous surfaces.

The detection is based on the reaction of ninhydrin with a monoacidic component of the fingerprint to form an intensively colored compound named Ruhemann's purple (*Petraco et al., 2006*).

The introduction of ninhydrin treatment for the visualization of latent fingermarks on porous surfaces revolutionized approaches to forensic fingermark examination (*Jelly et al., 2009*). Since then, a range of amino acid sensitive reagents has been developed and such compounds are in widespread use by law enforcement agencies worldwide. Ninhydrin reacts with amino groups of amino acids and other components of palmar sweat to develop Ruheman's purple. Full reaction may take several days or even weeks, but it can be accelerated by heat and moisture. The last formulation uses the solvent HFE7100 as the carrier (*Almog, 2001*).

This paper reviews the development and use of ninhydrin reagents for the detection of latent fingermarks as well as for other drug and poison determination.

Fingerprinting, science or art?

The role of the forensic scientist in the judicial system is of paramount importance (*Bono, 1981*). A clear understanding of ethical violations is essential to establish the extent to which justice is hindered by unethical conduct among forensic problems (*Saks, 1989*). Seven major classes of evidence of ethical conduct and examples of each are examiner: proficiency testing studies, self-reported surveys and focus groups, complaints to forensic science associations, court cases, content analysis of ethical codes, anecdotal data (news reports, the professional literature, and case studies), and circumstantial evidence.

Three main categories of ethical problems emerged from the data: problems of competency, individual misbehavior, and problems of practicing science in an adversary system. A lawyer refers to fingerprints of importance to the testifying expert (*Moenssens, 1975*).

His credentials are favored by attorneys and his books relating to fingerprints are frequently referenced in court. While the book has good chapters on history and classification, the chapter dealing with fingerprint comparisons lacks detail or specific guidelines and some viewpoints are debatable.

Fingerprints and the similar ridges on the palm of the hand and the sole of the foot have more uses than identification: they are also of value in anthropology, medicine and genetics (*Penrose, 1969*). A compilation has been prepared for the technicians interested in furthering their knowledge about the numerous ways latent prints can be detected (*Brooks, 1972*).

It was hypothesized that the nervous system might play a role in the timing or patterning of the formation of papillary ridges (*Morohunfola et al., 1992*).

Ridgeology is an evaluative method of friction ridge identification based on scientific principles and procedures, principles, and procedures that have been established and verified through years of research (*Ashbaugh, 1991*). A study of friction ridge impressions left in the wet clay and preserved in antique vases was carried out (*Astrom & Eriksson, 1980*). Ridgeology means a forensic identification science that is associated with all of the ridges on the volar areas and not just on the finger tips as dactyloscopy or fingerprint identification implies. A large body of research was dedicated to the inheritance of palmar lines (*Bansal et al., 1987; Jones, 1997; McBride, 1995; Penrose, 1963.*).

The types of visualization fluids tested may be used without altering latent fingerprints and are undetectable by conventional methods after evaporation (*Black, 1990*).

An apparently new form of complete absence of dermal ridge patterns was transmitted as an autosomal dominant trait through five generations in an Irish-American family (*Reed & Schreiner, 1983*). Affected individuals lacked dermatoglyphic patterns, sweat pores, and ability to sweat in the volar areas of the fingertips, palms, and soles.

A history of fingerprinting was introduced by various authors (*Acree, 1998*). H. Ancient finger prints were identified in clay (*Cummins, 1941*). Some authors referred to fingerprint identification since the beginning of the XX century (*Bateson, 1906; Blue, 1915*). The methods used for the recovery of fingerprints from the skin of crime victims have already been reviewed along with their effectiveness (*Allman & Pounds, 1991; Bobev, 1995*).

In the beginning, latent fingerprints were developed by dusting with powder such as amorphous carbon, fuming with iodine vapor, and treating with silver nitrate (*Shutler, 1980; Menzel, 1983*).

Then, criminalists used ninhydrin to develop latent fingerprints on paper (*Oden & von Hofsten, 1954*). The use of ninhydrin analogues (*Almog et al., 1982*), a combination of ninhydrin and trypsin (*Menzel et al., 1984*), ninhydrin and metal salts (*Everse et al., 1986; Stoilovic et al., 1986*), glues containing cyanoacrylate ester (*Kendall, 1982; Menzel et al., 1983*), various lasers and fluorescent dyes, (*Dalrymple et al., 1977; Menzel & Almog, 1985*) luminescent dusting powders or conventional latent print enhancing chemicals (*Menzel et al., 1983; Herod & Menzel, 1982; Mazzella & Lennard, 1995; Taylor & Douglas, 1997*) are the most significant developments in latent fingerprint identification. The complexation of Ruhemann's purple with metal ions enhances the sensitivity of the analyses by allowing estimation of the resulting chromophore by fluorescent, luminescent, phosphorescent, and laser techniques (*Friedman, 2004*).

The fundamental problems of retrieval of latent fingerprints from the skin are discussed together with the methods reported in the literature, which include electronography, iron powder-Dakty foil, iodine-silver plate transfer, Kromekote lift, and laser detection, along with several less frequently used techniques. The limited successes achieved with these reported methods during actual case works are discussed; they are limited because they are often found to refer only to idealized research conditions. At present, the use of high-powered light sources such as lasers seems to be the only technique that may be useful for revealing fingerprints on skin when investigating a case (*Allman & Pounds, 1991*). Nevertheless, the importance of standards in forensic science was outligned (*Almiral & Furton, 1998*).

A study of 102 female and 95 male same-sexed twin pairs was carried out to analyse the genetic component of

the variance of the a-b, b-c and c-d interdigital ridge counts by means of the Christian method (*Arrieta, 1992*). The a-b count in males seems to be more influenced by environmental factors than the other counts. For females, the three interdigital counts seem to have a strong genetic component influencing their phenotypic expression.

Incipient ridges may create certain disagreements among examiners as to their inclusion and value as part of the identification process (*Ashbaugh, 1992*). However, when understood and approached from their morphological structure and evaluated as to their significance in the spectrum of clarity, incipient ridges can be a vital factor in determining individuality. The differences in human dermatoglyphics seem to be of prenatal origins (*Babler, 1977*).

A lipid-specific method, which is sensitive, rapid and with a wide range of applicability for latent fingerprint detection was described that involves europium chelate luminescence (*Allred et al., 1997*).

Identification of fingerprints

Ninhydrin, the most productive means of latent print development on porous items (paper, unfinished wood, etc.), can be used as powder, bulk powder, or premixed liquid. The last one might be methanol and acetone-based 0.5% working solutions or heptane-based formulation, which minimizes the running of inks. Once thoroughly mixed, ninhydrin can be applied by sprayer or brush or by dipping the specimen.

Re-immersion of the ninhydrin treated item into a tray of the blank organic solvent, then subjecting to humidity, can increase the intensity of the purple dye. Metal salt treatments such as zinc chloride may be used to fluoresce and enhance the ninhydrin developed ridge detail.

The development of fingerprints by brushing on powder is a well known technique (*Thomas, 1978*).

The effects on the blood grouping of bloodstains subjected to the fingerprinting techniques commonly used (powders, chemicals, and laser) have been studied (*Bowen & Wickett, 1988*). After treatment for fingerprinting, the samples were grouped in the nine blood group systems routinely performed at Forensic Laboratory Edmonton. Some distortion or destruction of blood groups was detected; however, other techniques appeared to cause no changes.

Brandon *et al*., (*1997*) investigated cloned primates and the possibility of identical fingerprints.

Generally, chemical reagents for amino acids and possibly some other components in fingerprints producing visible latent fingerprints on surfaces such as cheques, paper documents, bank notes, etc. may react with blood and may be used for developing blood-contaminated fingerprints on porous and non-porous surfaces. Fingerprints developed with ninhydrin can be made fluorescent by application of zinc chloride. If used after DFO (1,8 Diazafluoren-9-one) additional fingerprints may be developed.

The mechanics of powder adhesion to fingerprints was reported along with two electrostatic methods of fingerprint development. In addition, the identification of a person depends on how many points are visible on the recovered fingerprint (*Thornton, 1977*).

Visualization of latent fingerprints produced by vapor phase fuming of dimethylaminocinnamaldehyde is often desirable due to its non-destructive characteristics, and various fuming techniques with varying effectiveness are available (*Brennan et al., 1995*). The quantification of fingerprint contrast is a relatively new concept in fingerprint enhancement research (*Vanderwee et al., 2011*). Subjective qualitative methods that are currently reported in the literature include: side-by-side assessment, assigning a score to a treatment based on visible

criteria and stating observed results without presenting supporting validation. These qualitative methods often do not state clearly the visual assessment parameters and produce a degree of ambiguity when defining the enhancement results (*Menzel, 1997*). The relative contrast index model was constructed to empirically quantify the difference in contrast between fingerprint ridges and valleys, using measurements gained from a microspectrophotometer.

Another technique describes dermal ridges on the dermal surface instead of the epidermal surface (*Okajima, 1975*).

Dermal ridges are observable by the metachromatic effect of the reagent with toluidine blue, which might suggest a close relationship between morphological characteristics and quantitative variations of biochemical components in the connective tissue. Dermatoglyphic features were recognized in fetuses from the 14th gestational week. Morphogenesis of dermal components--that is, grooves, primary and secondary dermal ridges, furrows, papillae, and sweat ducts--was examined at various gestational stages. The general law in the developmental sequence of the ridges in different volar areas was also confirmed.

Fingerprinting at crime scene

Several compounds of interest for developing fingerprints are shown in Fig. 1. Latent fingerprints on various items were developed by exposed them to fumes obtained by heating the solid polymer, polycyanoacrylate (*Almog & Gabay, 1986*).

The results are comparable in quality to those obtained by the regular Super Glue technique, based on the liquid cyanoacrylate monomer which is harder to handle. Without heating, the development process required much longer periods of time.

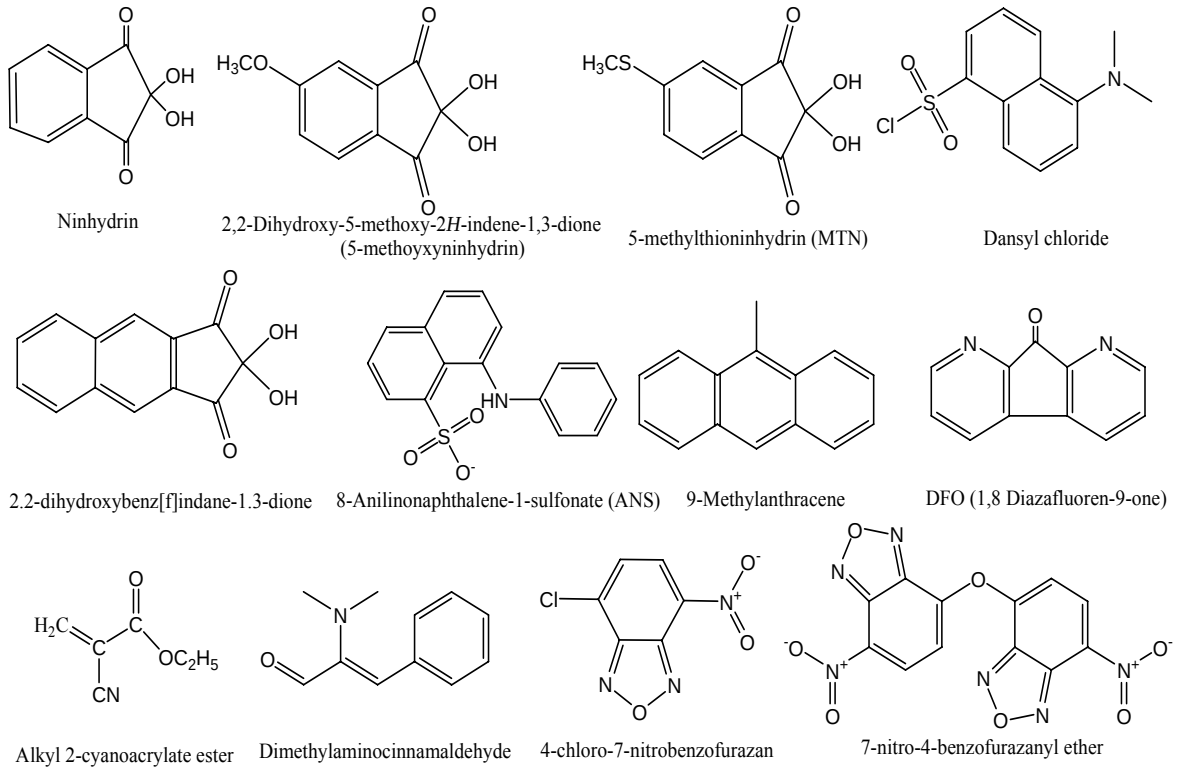


Fig. 1. Several compounds used in forensic investigations for fingerprint developing.

There is a substantial amount of published literature addressing forensic approaches to making such latent print examinations (*Smith et al., 1993; Batey et al., 1998*). While many latent fingerprints contain numerous points of comparison, and thereby pose no particular obstacle to the identification process, a number of the latent prints encountered in scene work posses less than ideal clarity. It is in the examination of this latter group of prints that even the most experienced examiner needs to have established a fundamental set of identification criteria that is framed in good basic forensic practices. A study conducted by the Knoxville Police Department and Oak Ridge National Laboratory has revealed a significant difference between the fingerprint sweat chemical compounds of pre-pubescent children and adults (*Bohanan, 1998*).

Several papers have been described research into the methods of developing latent fingerprints from the glass surface of unignited incendiary bottles and an optimization of the technique (*Shelef et al., 1996*).

Fingerprint mechanisms

The physical mechanisms of fingerprinting have been a particularly neglected field of study (*Theeuwen et al., 1998*). Little is known about the physical techniques of developing or detecting fingerprints have emerged since the widely used powdering method. Consequently, research on the fundamental physics of fingerprints including an investigation into the mechanism of powder adhesion to fingerprint deposits is currently being carried out by many fingerprint scientists (*Theeuwen et al., 1998*).

When explored the quality of ninhydrin-developed fingerprints on paper in two groups of individuals, both groups showed the expected bell-shape distribution, with the majority of the donors belonging to the central zone, defined as "average" or "good" (*Almog et al., 2011*).

Because the clearance rates for arson cases remain low due to fire's destructive nature, subsequent suppression, and a misconception by investigators that no forensic evidence remains (*Clutter et al., 2009*). Nevertheless, several research shows that fire scenes can yield fingerprints if soot layers are removed prior to using available fingerprinting processes. An experiment applying liquid latex to sooted surfaces was conducted to assess its potential to remove soot and yield fingerprints after the dried latex was peeled. Latent fingerprints were applied to glass and drywall surfaces, sooted in a controlled burn, and cooled. Liquid latex was sprayed on, dried, and peeled. Results yielded usable prints within the soot prior to removal techniques, but no further fingerprint enhancement was noted with ninhydrin.

Post mortem identification needs new methods for softening mummified fingers before taking up the finger marks (*Augibe & Costello, 1985*).

Attempt was made to correlate between a physiological feature, palmar moisture, and the fingerprint donorship. As a rule, high fingermark quality could be associated with sweating hands, but there were individuals with moist palms whose fingermarks had a low score and vice versa. This finding supports the logical but hitherto unproven assumption that besides the amount of palmar sweat, the other physiological factor governing the prints' quality is the total amount of substrate, amino acids in this case, in the latent deposits, which depends on the substrate concentration in the sweat.

The thermal development of finger marks on paper and similar surfaces by direct contact heating of the substrate using coated or ceramic surfaces at temperatures in excess of 230 ºC produces results superior to those obtained using hot air (*Song et al., 2011*).

Finger marks can also be developed in this way on other cellulose-based substrates such as wood and cotton fabric, though ridge detail is difficult to obtain in the latter case. The processes observed during the thermal development of finger marks can be reproduced simply by heating untreated white copy paper or filter paper, or these papers treated with solutions of sodium chloride or alanine. There is no evidence to suggest that the observed fluorescence of finger marks heated on paper is due to a reaction of finger mark constituents on or with the paper (*Song et al., 2011*). Thermal degradation of cellulose, a major constituent of paper and wood, is known to give rise to a fluorescent product if sufficient oxygen is available. However, the absence of atmospheric oxygen has only a slight effect on the thermal development of finger marks, indicating that there is sufficient oxygen already present in paper to allow the formation of the fluorescent and charred products. In a depletion study comparing thermal development of finger marks on paper with development using ninhydrin, the thermal technique was found to be as sensitive as ninhydrin for six out of seven donors.

When thermal development was used in sequence with ninhydrin and DFO, it was found that only finger marks that had been developed to the fluorescent stage (a few seconds of heating) could subsequently be developed with the other reagents. In the reverse sequence, no useful further development was noted for finger marks that were treated thermally after having been developed with ninhydrin or DFO. Aged finger marks, including marks from 1-year-old university examination papers were successfully developed using the thermal technique.

Latent fingerprints are made visible in a single step by in situ growth of gold nanoparticles on ridge patterns (*Hussain et al., 2010*). The chemicals, among the essential components of human sweat, found responsible for the formation and assembly of gold nanoparticles are screened and used as ink to write invisible patterns, using common ball pen and inkjet printer, which are then developed by selectively growing gold nanoparticles by soaking them in gold salt solution.

Factors which affect the recovery of latent prints on firearms were also studied (*Barnum, & Klasey, 1997*).

Genetics of fingerprint pattern

A genetic theory has been developed showing that the basic fingerprint pattern sequence is all ulnar loops and that a variety of genes cause deviations from this pattern sequence (*Slatis et al., 1976*). Genes that have been proposed include: (1) a semidominant gene for whorls on the thumbs (one homozygote has whorls on both thumbs, the other has ulnar loops on both thumbs and the heterozygote usually has two ulnar loops or one ulnar loop and one whorl; (2) a semidominant gene for whorls on the ring fingers which acts like the gene for whorls on the thumbs; (3) a dominant gene for arches on the thumbs and often on other fingers; (4) one or more dominant genes for arches on the fingers; (5) a dominant gene for whorls on all fingers except for an ulnar loop on the middle finger; (6) a dominant gene for radial loops on the index fingers, frequently associated with an arch on the middle fingers; and (7) a recessive gene for radial loops on the ring and little fingers. These genes may act independently or may show epistasis.

A few topics on the genetics of dermatoglyphics were discussed by Miller (*1958 & 1973*). He also studied post mortem identification of damaged friction ridge skin (*Miller, 1995*).

The process of ageing of fingerprints was studied and several factors affecting the process (chemical composition of a fingerprint trace, external influences and background material) are taken into account (*Baniuk, 1990*). The efficiency of the method and usefulness of the results obtained have also been invstigated.

Differences in the skin surface lipid content and the dynamic friction coefficient were investigated with respect to age, sex, and anatomical region (*Cua et al., 1995; Nicolaides, 1974*). Measurements were obtained on 11 anatomical regions, namely, the forehead, upper arm, volar and dorsal forearm, postauricular, palm, abdomen, upper and lower back, thigh, and ankle. Skin surface lipid content data were compared with measurements to determine the relative contribution of the former to frictional properties of skin. Skin surface lipid content was statistically lower on the forehead, dorsal forearm and postauricular area in females. Both parameters, however, show considerable regional variability. These data suggest that surface lipid content plays a limited role in frictional properties of skin.

Ninhydrin-developed fingerprints

In order to develop fingerprints a ninhydrin stock solution containing 25 g ninhydrin, 50 mL glacial acetic acid and 100 mL ethanol has to be prepared (*Frégeau et al., 2000*). Then, by dilution, a ninhydrin working solution is carried out (30 mL stock solution, 50 mL ethanol, and completion to 1 L with heptane).

Information about the mechanism of reaction between ninhydrin-positive compounds in fingerprints can ultimately help to design compounds with stronger chromo-fluorogenic properties in aid of detecting fingerprints at crime scenes (*Petraco et al., 2006*). The three most accepted mechanisms of formation have been considered using ab initio quantum mechanical calculations. At relatively high temperature (~ 100 ºC) all three mechanisms are energetically feasible (Fig. 2). However since it is recommended that forensic analyses be performed at room temperature, a revised mechanism is proposed for the formation of Ruhemann's Purple under these conditions.

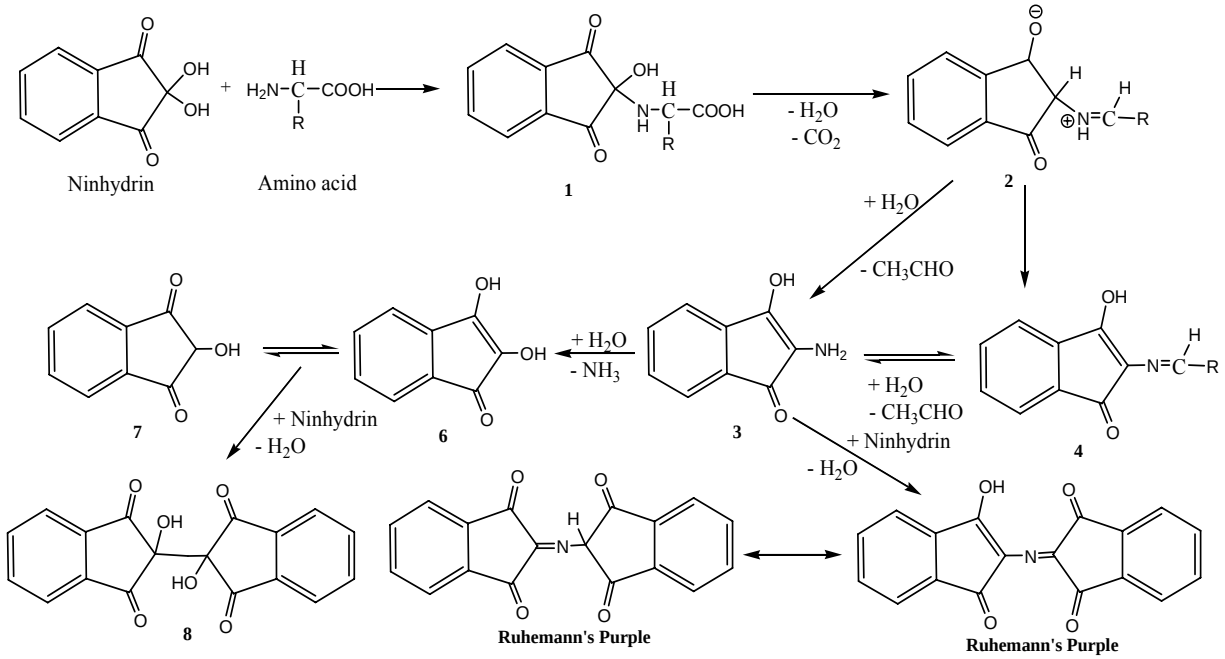


Fig. 2. Ruhemann's Purple-based mechanism of fingerprint development with ninhydrin.

Fluorescing chemicals

Certain fluorescing vapor-phase chemicals were used and their advantages for the development of latent fingerprints discussed (*Almog & Gabay, 1980*). For example, latent fingerprints are detectable by their inherent luminescence under laser illumination (*Salares et al., 1979*). Less that on-fifth of 240 samples each containing four prints on paper gives luminescent prints. Similar results were obtained for 120 samples each containing one print on glass. Forty-one of the samples showing no luminescence were sprayed, approximately one month after deposition, with a solution containing the fluorescent tag in agent 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole (NBD chloride). After treatment with NBD chloride, 37 of these samples gave luminescent prints, many of which were intensely luminescent and contained good ridge detail (*Almog & Gabay, 1980*).

In another study, five 7-nitro-4-benzofurazanyl ethers have been examined as potential fluorigenic reagents for latent fingerprints on paper (*Almog, J., et al. 1987*). All developed latent fingerprints with high sensitivity, similar to that of the parent compound 4-chloro-7-nitrobenzofurazan. The amino acid reagent 1,8-diazafluoren-9-one (DFO) produces a highly fluorescent species with latent fingerprints on paper (*Pounds et al., 1990*). Spectral characteristics of the fluorescent fingerprint show excitation (approximately 470 nm) and emission (approximately 570 nm) maxima in the visible part of the spectrum. Some printing inks fluoresce under these conditions and would therefore hinder fingerprint detection but optical brighteners present in paper do not interfere.

Ninhydrin luminescence

The development of fluorogenic ninhydrin reagents enhanced the application area of ninhydrin (*Wimalasena et al., 2003*), especially their use in forensic science (*LaPorte & Ramotowski, 2003*; *Schwarz & Frerichs, 2002*).

Fluorescent fingerprints visualized by DFO revealed more fingerprint detail than ninhydrin, the standard method for such surfaces.

Fingerprint development techniques may use blue-green laser light but suffer from high background fluorescence on substrates such as cardboard, wood, leather, and some metals and plastics (*Burt & Menzel, 1985*). These substrates tend to exhibit little or no fluorescence under ultraviolet light, prompting us to search for procedures that yield visible fluorescence under this illumination. Specifically, chemical development with dansyl chloride and vapor staining with 9-methylanthracene were found to be useful when dealing with these substrates.

A method based on the use of 1,8-diazafluoren-9-one (DFO) in the dry state was developed for latent print visualization on papers (*Bratton & Juhala, 1995*). The procedure provides the same fluorescence intensity as conventionally prepared DFO with ink run, damage to papers, or background induced fluorescence due to the DFO solution.

8-Anilinonaphthalene-1-sulfonate (ANS) has shown itself to be a valuable and sensitive reagent method for the detection of latent and greasy prints on porous surface (*Cheng, 1988*). The working solution is sprayed onto the porous surface where latent or greasy prints are suspected and the prints show bright yellow fluorescence against dark background under ultraviolet illumination. The advantage of this method seems to be its rapid reaction, no heat needed, high sensitivity, no unpleasant odor, simplicity, and convenience in processing.

Fingerprints developed with ninhydrin form stable, colored complexes when treated with various metal salts (*Stoilovic, 1986*). Many of these colored complexes can be used to increase the sensitivity of detection of latent prints because of photoluminescent properties

The intensity of this photoluminescence is increased at low temperatures and this is a common characteristic of each of the complexes formed with salts of the second (b) group of the Periodic Table. Spectral characteristics of these Group IIb metal complexes and the influence of environmental factors on their formation were studied. These data have helped determine optimal conditions for the enhancement of ninhydrin developed fingerprints. Taking into account spectral characteristics, solubility, versatility, stability, and reproducibility, the use of the cadmium nitrate tetrahydrate complex is advocated for general use for fingerprint enhancement. The use of zinc nitrate is favored if toxicological considerations are paramount, but ninhydrin development has to be carefully controlled if optimal results are to be obtained. Limited applications for mercuric complexes are found when a red shift is desired to remove background effects.

Trypsin has been applied to latent prints two weeks to two months old to eliminate the background problems that had been encountered with old prints (*Everse, 1986*).

Zinc chloride treatment of latent prints previously exposed to ninhydrin enhances their detection upon laser examination. Thus, a detection improvement is observed when ninhydrin-treated latent fingerprints are sprayed with a solution of zinc chloride and subsequently subjected to argon laser examination (*Herod & Menzel, 1982; Menzel et al., 1990*). However, zinc chloride reaction occasionally fails to occur. In fact, high humidity and elevated temperature, particularly the former, are needed. Cadmium nitrate, although it produces weaker fluorescence than zinc chloride, may be useful. Reaction conditions are much the same as those for zinc chloride.

Ninhydrin-treated latent fingerprints not discernible in the conventional way can show fluorescence in the red and near-infrared spectral regions when subjected to continuous-wave dye laser illumination at about 580 nm, thus becoming amenable to development (*Herod & Menzel, 1982*). In order to increase luminescence and image enhancement benzo(f)ninhydrin and tris(2,2'-bipyridyl) ruthenium (II) chlorid hexahydrate as a staining dye for time-resolved imaging were introduced (*Menzel & Almog, 1985; Menzel, 1988*).

Ninhydrin derivatives used in fingerprinting

"Dual fingerprint reagents" are chemical formulations which produce with latent fingerprints in a single step, impressions that are both colored and fluorescent (*Almog et al., 2008*). By mixing the solutions of two commercially available ninhydrin analogues, 5-methoxyninhydrin (MN) and 5-methylthioninhydrin (MTN) with zinc or cadmium salts results in a dual reagent. This mixture is much more sensitive than the parent dual reagent, ninhydrin/$ZnCl_2$. The main advantage of this formulation is its usage at room temperature, with no need to cool the sample to liquid nitrogen temperature.

At 0.05 % concentration, which is 10-fold lower than the common ninhydrin working solution, MTN/$ZnCl_2$ is as sensitive as DFO in the fluorescence mode and considerably more sensitive in the color mode. MTN is also slightly cheaper than DFO.

In an attempt to design new reagents for the chemical development of latent fingerprints, a number of ninhydrin analogues were synthesized and their reactions with latent fingerprints on paper were studied (*Almog et al., 1982*). The ring-fused and substituted ninhydrins developed latent fingerprints with a sensitivity similar to that of ninhydrin.

The most promising of the group was 2.2-dihydroxybenz[f]indanc-1.3-dione, which developed latent fingerprints as dark green images with excellent resolution.

Eleven vicinal triketones and one vicinal tetraketone were reacted with amino acids in solution and with latent fingerprints on paper to give colored products of forensic interest (*Almog, 1987*).

Benzo[f]ninhydrin was compared to ninhydrin for fingerprint development on paper (*Almog et al., 2000*). The performance of ninhydrin was slightly better than that of benzo[f]ninhydrin. The significant advantages of the benzo[f]ninhydrin over ninhydrin were the much stronger fluorescence it gave after treatment with zinc salts and a slightly quicker reaction under ambient conditions.

The effectiveness of the fluoreogenic reagent NBD chloride has been compared with the popular colour reagent ninhydrin for the development of fingerprints on paper (*Stoilovic et al., 1984*). NBD Chloride was found to be more sensitive than ninhydrin for moderately old fingerprints (39 months) and never inferior to ninhydrin in all other cases. A qualitative evaluation technique was used to establish the relative efficiency of each method. This is based on the number of points of identification, assessed on a 14 scale, where 4 represents a court worthy print (> 12 points) and 1 represents a print containing no points.

The detection of latent finger marks on thermal paper by dry contact with 1,2-indanedione, which reacts with the amino acids present to give colored, photoluminescent prints was recently described (*Patton et al., 2010*).

Different treatment paper reagent formulations and treatment times were investigated.

The conditions which provided the best performance used treatment papers prepared from an acid-free fluorous solution containing 1,2-indanedione and zinc chloride, with a contact time of 48 h.

The dry contact approach was compared to current methods used by law enforcement agencies within Australia.

Most thermosensitive surfaces of thermal paper turn black when they come into contact with polar organic solvents such as are used in ninhydrin petroleum benzin solution (*Schwarz & Klenke, 2010*). This dark staining reduces the contrast between the developed fingerprint and the background to such an extent that the identification process becomes very difficult. Integrating polyvinylpyrrolidones (PVP) into a ninhydrin solution prevents the black staining, and the developed fingerprints appear in clear contrast to the background. The new ninhydrin solution containing PVP is considered successful compared to the two-step ninhydrin-acetone washing method for thermal paper which is popular in Germany (*Schwarz & Klenke, 2010*).

An efficient application of nano-technology to fingerprint visualization is the possibility of more selective binding of gold nanoparticles (NP) to fingerprint material (*Almog, J., Glasner, 2010*). Ninhydrin and 1,2-indanedione containing loosely bound thiol groups, such as thiohemiketals (THK) of ninhydrin, and thioketals of 1,2-indanedione were prepared and tested as potential fingerprint reagents. By reacting ninhydrin with various thiols we were able to produce a series of novel THK, bearing the SR group always at C2. Ninhydrin THK reacted with amino acids to produce the expected Ruhemann's purple, and they also developed latent fingermarks on paper in a similar manner to ninhydrin.

Ketals and thioketals derived from 1,2-indanedione reacted neither with amino acids nor with latent fingermarks. The thiols which are formed on the ridges as byproducts of the reaction with amino acids will be tested for their potential as stabilizers for gold NP that will become covalently bound to the fingerprint ridges.

5-Methoxy-2,2-dihydroxy-1,3 indanedione (5-methoyxyninhydrin) can be used as a developer of latent fingerprints on

paper (*Almog & Hirshfeld, 1988*). Visible development closely resembles that achieved with ninhydrin, whereas the fluorescence after zinc chloride treatment is considerably stronger than that of ninhydrin developed prints, particularly when excited by the green line of the copper-vapor laser.

The ninhydrin method suffers form several disadvantages because the reaction is slow and requires heat for complete development (*Sasson, 1978*). Sometimes the method is misleading because of background reactions and not all individuals excrete sufficient perspiration to leave latent prints identifiable with ninhydrin. Therefore, the ninhydrin kit was replaced by a 4-dimethylamino-cinnamaldehyde reagent (*Sasson, 1978*).

Ninhydrin positive substances

Ninhydrin can easily react with amino groups in organic compounds, which are consequently named ninhydrin-positive substances. Ninhydrin can be utilized in place of the traditional Kjeldahl method for the determination of the protein content of beer or wine (*Abernathy et al., 2009*). The assay only measures alpha amino acids and ammonia so other nitrogen sources are not detected, resulting in a 30% reduction in total protein of a variety of beers compared to the Kjeldahl method, which measures nitrogen from all sources.

The polymer-salt rich environment of aqueous two-phase systems disturbs standard protein quantification methods, like UV measurement or Bradford assay. Therefore, the influence of high polyethylene glycol and phosphate salt concentrations on the readings of three colorimetric protein assays: Bradford, DC (Bio-Rad) and ninhydrin assay was investigated (*Gonzalez-Gonzalez et al., 2011*). The ninhydrin assay displays minimal protein-to-protein variation and high sensitivity.

Amino acids and peptides separated by chromatography and electrophoresis on thin layers of cellulose or silica gel can be located by spraying them with either ninhydrin, fluorescamine, or o-phthaldialdehyde (*Schiltz et al., 1977*). o-Phthaldialdeyhde and ninhydrin were used for amino acid detection in the 50-200-pmol range and were superior to fluorescamine.

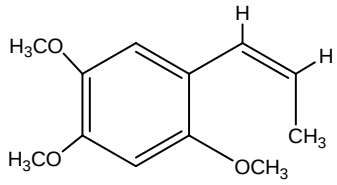
Ninhydrin and fluorescamine, on the other hand, were better for the detection of peptides. A method is described for the elution of peptides from thin layers with 6 N HCl. Most small peptides were recovered in yields of at least 80%, ninhydrin-reacted peptides in somewhat lower yields.

The polypeptides in a hydrolysate obtained by acidic hydrolysis of wool were determined by the ninhydrin reaction and biuret reaction (*Zhao et al., 2009*). The hydrolysis degree of wool keratin was about 33%.

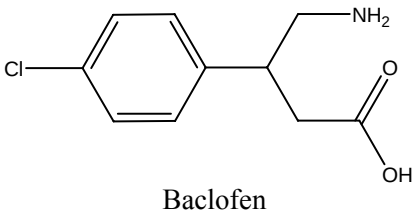
Carcass decomposition results in the release of nitrogenous compounds into associated soil. The current study investigated the release of ninhydrin reactive nitrogen (NRN) following burial (similar to 40 cm depth) and decomposition on the soil surface. Also investigated was the lateral extent of NRN in grave soil. NRN concentration increased significantly in grave soil collected from the center of graves (similar to 20 cm depth) during the initial two months of burial. A similar finding was also observed in the base of the grave during the initial six months of burial. However, no change in NRN concentration was observed 60 cm from buried carcasses. Carcasses decomposing on the soil surface were associated with higher NRN during the initial 97 days of decomposition. Therefore, the analysis of soil NRN can be a presumptive evidence for grave soil within two months postmortem following burial and up to 97 days postmortem on the surface.

Various compounds react with ninhydrin to yield colored or fluorescent derivatives that can be used for analytical purposes. These compounds may interfere with the fingerprinting or not, depending on the reaction conditions.

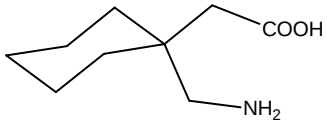
For example, β-asarone (1,2,4-trimethoxy-5-prop-1-enyl-benzene) is such a ninhydrin positive substance (*Oswald et al., 1969*).



β-Asarone



Baclofen



Gabapentin

Gabapentin in pure form as well as in their pharmaceutical formulations was analyzed with a ninhydrin-based spectrophotometric method (*Siddiqui et al., 2010*). Gabapentin reacts as n-electron donor with ninhydrin, whereas pi-acceptors are 2,3,5,6-tetrachloro-1,4-benzoquinone, chloranilic acid, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, tetracyanoethylene or 7,7,8,8-tetracyanoquinodimethane. The obtained complexes are measured at 568, 230, 314, 304, 335 and 439 nm for ninhydrin, chloranil, and chloranilic acid, DDQ, TCNE and TCNQ respectively.

A UV/VIS derivative spectrophotometry method for the determination of caffeine and B vitamins in energy drinks after solid phase extraction has been developed (*Pieszko et al., 2010*). Caffeine has been determined in the mixture with B2 vitamin with zero-crossing technique from the I derivative spectra (λ 266.8 nm), and B3 in mixture with B-6 vitamin from the II derivative spectra (λ 280.1 nm). B-12 vitamin has also been determined in a three-component mixture with vitamins B-3 and B-6. Taurine in drinks has been determined from the basic spectra after derivatization with ninhydrin (λ 570 nm).

Aminothiols give weak purple-colored reactions with ninhydrin. Using a D-penicillamine paradigm, adsorption of this compound via a disulfide bond onto thiol-reactive solid prior to ninhydrin reaction allowed spectrophotometrical monitoring of the supernatant at 570 nm (*Rojanarata et al., 2010*). Compared with off-solid method, this approach expanded the linear concentration range to 50-600 μg mL^{-1} and enhanced the sensitivity so that D-penicillamine with the concentrations of less than 100 μg mL^{-1} could be accurately measured by using a second-order polynomial calibration curve. Additionally, this assay was unaffected by disulfide adduct interference, highlighting its potential for the analysis of D-penicillamine as well as other aminothiols.

The determination of formaldehyde with a chemiluminescence method has been described (*Dong, Y., Fu, 2010*). The method is based on the CL-emitting reaction between ninhydrin and potassium permanganate in hydrochloric acid medium, enhanced by formaldehyde.

The changes in the amino acid content of the digestive-gland gonad complex (DGG) of Biomphalaria glabrata snails as a function of estivation was determined by high performance thin-layer chromatography-densitometry using also ninhydrin (*Vasta et al., 2010*). Amino acids were extracted in ethanol-water (70:30) and determined on silica gel or cellulose layers developed with either 2-butanol-pyridine-glacial acetic acid-deionized water (39:34:10:26) or 2-butanol-pyridine-25%

ammonia-deionized water (39:34:10:26). Separated zones were detected by postchromatographic derivitization with ninhydrin and quantified by visible mode slit-scanning densitometry at 610 nm. Alanine, arginine, glycine, leucine/isoleucine, lysine, serine, and valine were unequivocally identified in chromatograms. This method might have several new forensic applications.

Baclofen in tablet reacts with ninhydrin reagent in aqueous solution producing a colored product, which can be spectrophotometerically determined (*Hosseinimehr et al., 2010*).

Ultrasonic resonator technology (URT) was compared with the well established UV-Vis/ninhydrin assay to estimate protease activities in defined buffer systems (*Born et al., 2010*). Hydrolysis of casein was measured using subtilisin, trypsin, halophilic protease from Haloferax mediterranei and Bacillus lentus alkaline protease. Sensitivity, reproducibility, working range as well as the limit of detection and the limit of quantification were comparable for both methods. The quantification of protease activity by URT was possible when the product concentration measured by the UV-Vis/ninhydrin assay was correlated to the corresponding ultrasonic velocity signals.

A densitometric method for analysis of four alpha-aminocephalosporins, such as cefaclor monohydrate, cefadroxil monohydrate, cefalexin anhydrous, and cefradine anhydrous, both in bulk drugs and in formulations was developed and validated (*Saleh et al., 2010*). The detection was made after spraying with ninhydrin reagent.

Organic azides can be visualized on TLC plates, based on triphenylphosphine-mediated reduction of azides to the corresponding amines which give contrasting color spots with ninhydrin (*Cegielska, B. & Kacprzak, 2009*).

Anchored amine materials can be assayed with ninhydrin as a rapid laboratory determination of available surface amines (*Scruggs et al., 2009*). The assay agreed well with expected values for aminopropyltriethoxysilane grafted onto commercial silica.

Ninhydrin was successfully used for determining the biogenic amines histamine (*Friedman & Noma, 1981*), and phenylethylamine (F*riedman & Noma, 1986*), lysine (*Finley & Friedman, 1973*), tryptophan (*Friedman & Cuq, 1988*), nonprotein amino acids (*Bell, 2003*), etc. Ninhydrin is also widely used with paper and silica gel plates (*Laskar et al., 2001*).

The detection of fraudulent addition of rennet whey to fluid milk can be done by the acidic ninhydrin spectrophotometric method (ANSM) for quantitative determination of free and bound sialic acid of milk glycoprotein (*Fukuda et al., 2004*).

The ninhydrin reaction facilitated the analysis, isolation, and characterization of many antibiotics, bacterial toxins, and microbial products containing ninhydrin-reactive amino groups (*Frutos et al., 2000; Gallo-Martinez et al., 2002; Jeannotte et al., 2003*). A qualitative test useful in the identification of *Streptococcus agalactiae*, *Campylobacter jejuni*, *Gardnerella vaginalis*, *Listeria* sp. and other aerobic bacteria is based on the hydrolysis of sodium hippurate. The presence of the enzyme hippurate hydrolase is visualized by the color formed when ninhydrin reagent oxidizes the amino acid produced during hippurate hydrolysis.

Some ninhydrin reactions do not involve formation of Ruhemann's purple and they are used to measure cysteine, protein-bound tryptophan, pipecolic acid, and sialic acid (*Friedman, 2004*).

Aldehydes and primary amines react with ninhydrin to afford highly fluorescent ternary products (*Samejima et al., 1971*). Starting from ninhydrin several compounds such as quinoxaline, guanide, or dimethyldihydroresorcinol ones have been prepared (*MacFadyen, 1950*).

Casework investigations

Fingerprinting with or without ninhydrin reagent solved a large number of cases of murder (*Tiller & Tiller, 1992; Acree, 1998b*, *Adair, 1998*). Alphonse Bertillon, one of the most noted criminalists at the turn of the century, introduced his system of classification for anthropometry measurements (Rhodes, 1956). While Alphonse opposed using fingerprints to replace the "Bertillon" measurements, he adopted their use and is credited with the first criminal identification resulting from a cold search of the files.

The history of fingerprints from ancient usage to the time of the book's writing was presented by Browne and Brock (*1954*).

In addition to the historical story with reference to the early pioneers of the science, the authors include many factual stories of cases solved.

Positive identification of multiple bodies was carried out by handled enforcement agency in the case of the largest airline disaster in the United States in 1993 (*Sloan, 1995*).

In addition, the survival of physical evidence from a scavenged grave was also investigated (*Adair, 1998*).

The usage of forensic evidence was presented in the history of Sir Harry Oakes (*Bocca, 1959*).

Cyanide detection and determination with ninhydrin

Cyanide also reacts with ninhydrin in alkaline solution to form a red- or blue-colored product with a λ_{max} of 485 or 590 nm, depending oh solution Ph (*Drochioiu, 2002a; Drochioiu, 2002b*). This reaction can be used to measure low levels of cyanide in industrial effluents (*Nagaraja et al., 2002*). Nevertheless, the process whereby the colored compounds is formed from ninhydrin remained obscure.

Therefore, all the compounds involved in cyanide reaction with ninhydrin were synthesized, isolated and characterized and a new mechanism of reaction was advanced (*Drochioiu et al., 2004*). The reaction was proposed also for cyanide determination in blood and other body fluids (*Drochioiu & Mangalagiu, 2002*). A review on cyanide determination refers to the forensic usage of ninhydrin (*Drochioiu et al., 2007*). However, there is no review on the application of ninhydrin to cyanide detection.

Toxicological aspects of ninhydrin

Ninhydrin is considered as a non-toxic compound. However, ninhydrin is an irritant if inhaled or if it comes in contact with your skin (*Soost et al., 2010*). For example, allergic, immunoglobulin E (IgE)-mediated rhinitis caused by ninhydrin was diagnosed earlier in a woman working as a laboratory technician in a forensic laboratory (*Piirilä et al., 1997*). The ninhydrin specific IgE was lower, but the histamine challenge test still showed slight bronchial hyper-responsiveness (PD_{15} 0.70 mg).

It was recommended the cessation of allergen exposure in occupational allergic rhinitis, in order to prevent asthma.

At present, there is a the strong interest in the forensic chemistry and law enforcement communities in developing alternatives to the current generation of ninhydrin like chemicals for the detection and development of latent fingerprints (*Petraco et al., 2006*).

Conclusions

In spite of many physical methods to extract fingerprints, ninhydrin is most useful. In addition, it has more applications in cyanide determinations. Other research revealed several novel properties of these techniques. For example, moistened hands do not necessarily allude to high quality fingerprints: the relationship between palmar moisture and fingerprint donorship.

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