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Latent Fingerprint Detection Using a Scanning Kelvin Microprobe

ABSTRACT: Electrochemical interactions between latent human fingerprints and metal surfaces in ambient air are investigated using a scanning Kelvin microprobe. Inorganic salts present in sweat deposited at fingerprint ridges locally depassivate the metal surface producing a Volta potential decrease of greater than 200 mV. Volta potential patterns may persist for months and prints may be visualized by potential mapping, even when overcoated with a polymer layer. Because the Volta potential differences are produced by involatile salts they persist when the organic components of the fingerprint residue have been volatilized by heating to 600°C.

KEYWORDS: forensic science, latent fingerprint, print visualization, metal surface, electrochemical mechanism, scanning Kelvin microprobe

Numerous methods have been described for the development of latent fingerprints on metal surfaces (1–3). Techniques such as powder dusting (4), cyanoacrylate fuming (5), and exposure to ruthenium tetroxide (6) tend to detect one or other of the organic components (fat, amino acids, or proteins) present in fingerprint ridge deposits. Conversely, aqueous electroplating solutions (3), and aqueous redox reagents such as selenous acid (3), ammoniacal silver nitrate, (7–9) palladium salts (10), gold salts (11), and gun blueing mixtures (7,9,12), react electrochemically with the metallic surface exposed between ridge deposits. Consequently, it has been reported that aqueous reagents are most effective when visualizing sebaceous prints and tend to work less well with ecrine prints due to the substantial water solubility of ecrinic deposits (8). In this paper we show how latent fingerprints deposited on metallic surfaces may be visualized directly, without development or any other form of perturbation, by Volta potential mapping using a scanning Kelvin microprobe (13,14). We propose that the observed Volta potential patterns arise primarily as a result of electrochemical interactions (13,14) occurring between the metal surface and water soluble but nonvolatile, inorganic salts (such as NaCl) present in fingerprint deposits. Furthermore, we test this hypothesis by heating samples to volatilize the organic fraction of the print residue. We also investigate the possibility of exploiting the purely potentiometric nature of the scanning Kelvin microprobe to visualize latent prints present beneath intact insulating films such as paint, oil, or grease. The primary aim of our work was to obtain ad-

ditional insight into the mechanisms by which human fingerprints interact with metal surfaces. However, the findings obtained suggest that the scanning Kelvin microprobe may itself be suitable for further investigation as a potential forensic tool when latent prints are located on a relatively small area of metal surface.

Experimental Details

Materials

Samples of 1 mm thick iron foil, purity 99.5%, were obtained from Goodfellow metals Ltd. Samples of 1 mm thick brass foil, 37% zinc and 63% copper, were obtained from Advent Research Materials Ltd. Prior to fingerprint deposition, iron metal samples were abrasively cleaned and polished using aqueous slurries of 6 μm followed by 1 μm polishing alumina (Buehler Ltd). Cleaned iron samples were rinsed with distilled water, followed by acetone, and allowed to dry in air. Brass samples were used as supplied. Fingerprints were deposited using a constant pressure from the right forefinger after freshly washing the hands with soap and water. Sebum rich prints were deposited as above but after rubbing the side of the nose with the finger tip.

Methods

The scanning Kelvin microprobe apparatus used in this work is shown schematically in Fig. 1. The vibrating reference probe assembly was mounted in a fixed position above the moving test sample. The reference probe itself consisted of a 125 μm diameter gold wire, which was vibrated along the vertical axis using a moving coil electromechanical actuator. The probe vibration frequency was 280 Hz and the vibration amplitude was 50 μm peak-to-peak. Reference probe vibration amplitudes were checked using stroboscopic observation in conjunction with a traveling microscope. The experimental arrangement was such that the tip of the vibrating reference probe was held at earth potential and positioned inside a stainless steel environment chamber, which was also at earth potential. The electromechanical actuator and vibrator drive electronics were positioned outside the environment chamber in order to ensure effective electrostatic and magnetic shielding of both the reference probe and sample. Vibration was conducted to the probe tip via a 50 mm long glass push rod.

Positioning and scanning of the test sample was carried out using a micromanipulation stage consisting of three orthogonally arranged (x,y,z), stepper motor driven, linear bearings (Time and Precision Ltd.). The probe was held at a constant height of 100 μm above the sample surface and scanned in a raster of parallel lines 100 μm apart. Kelvin probe measurements were made once every 100 μm to generate a regular array of values. To perform each mea-
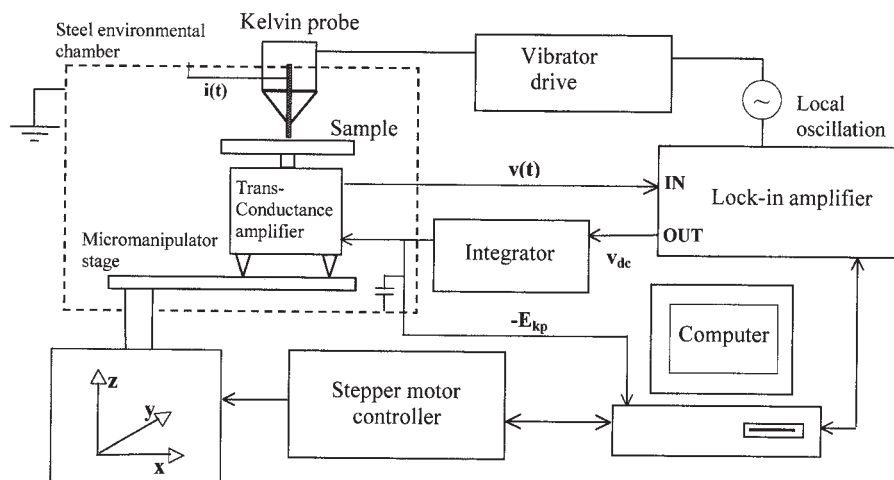
FIG. 1—*Schematic representation of the major components of the scanning Kelvin microprobe apparatus.*

surement the ac current, $i(t)$, generated in the external circuit connecting the sample and vibrating probe (see following section), was amplified and converted into an ac voltage signal, $v(t)$, using a dc biased transimpedance amplifier circuit. The $v(t)$ signal was detected using a lock-in amplifier (Perkin Elmer model 7260). The dc output of the lock-in amplifier, v_{dc}, was transmitted to a feedback system based on an integrator circuit which controlled the dc bias, E, applied to the sample via the transconductance amplifier so as to automatically null $i(t)$. The magnitude of the dc bias (equivalent to $-E_{kp}$ as defined in the following section) applied via the integrator, was digitized and logged. Probe scanning and data logging were all carried out automatically under microcomputer control. All scans were performed in ambient air (nominal temperature 22°C, R.H 45%).

Results and Discussion

When the electrical potential of a metallic body is referred to, it is usually the Galvani, or inner, potential determined by the Fermi level of electrons within that body which is meant. At distances $>10~\mu m$ from the metal surface, potential falls away with increasing distance as determined by the laws of electrostatics. However, between approximately 0.1 μm and 10 μm from the metal surface there exists a region where potential is approximately independent of distance; this is known as the Volta, or outer, potential of the metal. In vacuum, the Volta potential reflects the extension of electronic wavefunctions beyond the surface, a tendency related to the work function of the metal. If the metal is in contact with a solution of electrolyte, adsorbtion of ions in the electrical double layer also affects the Volta potential, which corresponds approximately to the potential at the inner Helmholtz plane (15).

As the name suggests, the scanning Kelvin probe (SKP) technique is based upon the vibrating capacitor method pioneered by Lord Kelvin (16), for the measurement of metallic work functions. The theory underlying Kelvin probe measurements has been described in detail elsewhere (13,14) but may be summarized as follows. The vibrating probe tip and sample surface form the two plates of a parallel plate capacitor, while the space between them, typically air or a combination of air-gap and nonconducting material, constitutes the dielectric. If a Volta potential difference (ΔV) exists between the probe and the sample surface, the periodic change in capacitance caused by probe vibration, generates an al-
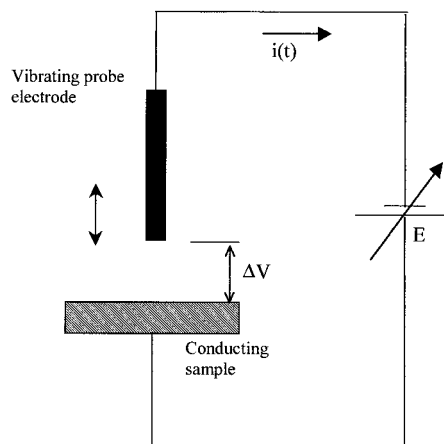

FIG. 2—*Schematic diagram illustrating the principle of operation of the Kelvin probe for measuring surface Volta potential differences. Volta potential difference, ΔV; Kelvin probe current signal,* i(t)*; externally applied dc bias voltage,* E.

ternating current in the external circuit shown in Fig. 2. The time-dependent value, $i(t)$, of this current is given by Eq. 1:

$$i(t) = \varepsilon\varepsilon^0 A~\Delta V\{d_1\omega\cos(\omega t)/(d_0 + d_1\sin(\omega t))\} \qquad (1)$$

where ε is the permitivity of free space, ε^0 is the dielectric constant of the inter-electrode medium, A is the effective probe tip area, d_1 is the probe vibration amplitude, d_0 the mean probe-surface distance, ω the angular frequency of probe vibration, and t is time. The Kelvin probe measurement is made by current nulling, i.e., a d.c. bias voltage (E in Fig. 2) is adjusted until ΔV, and hence the magnitude of $i(t)$, is zero. Under null-current conditions the experimentally measured parameter $E_{(i=0)}$ is equal and opposite to the value of ΔV which would exist if the Galvani potentials of the probe and sample were identical, i.e., if E were zero. It is customary to refer to the quantity $-E_{(i=0)}$ as the Kelvin probe potential (E_{kp}). We have used a gold vibrating probe, so that in our work E_{kp} is equivalent to the Volta potential of the sample surface relative to that of gold at the same Galvani potential.

When measurements are performed on pristine surfaces under vacuum, E_{kp} is determined only by the difference in work functions

between the probe and test sample surfaces. Scanning Kelvin probe microscopes, having lateral resolutions of 100 nm or better, have recently been developed for the study of metal structures and dopant profiles on semiconductor surfaces (17–19) under high vacuum. In contrast to these systems, which are typically used to image areas of a few microns square, the SKP apparatus described here to image fingerprints scans much larger areas (up to 5 cm by 5 cm) and has a lateral resolution of ~125 μm. Our apparatus is based on instrumentation developed to study metallic corrosion occurring under thin films of electrolyte (13,14) and electrolyte droplets (20).

Any metal surface exposed to moist air will acquire a so-called humidity layer of adsorbed water molecules, the thickness of which increases with relative humidity (13,21). If any environmentally derived electrolyte (ionic salts) are associated with this humidity layer, E_{kp} values will tend to deviate from those determined purely on the basis of work function differences as a result of ionic adsorbtion and electrochemical redox reactions associated with corrosion processes occurring at the sample surface. The relationship between E_{kp} and redox activity has been discussed in detail elsewhere (13). However, for our purposes the most important finding is that E_{kp} measured through an adsorbed electrolyte film directly reflects the electrochemical open circuit potential, or free corrosion potential (E_{corr}), of the metal surface in relation to that electrolyte. So that,

$$E_{kp} = E_{corr} + C \qquad (2)$$

where C is a constant determined by the probe material and the potential drop at the electrolyte-air interface (13). For any freely corroding metal, M, the value of E_{corr} is determined by the relative facility of the anodic oxidation process (Eq 3) and the cathodic reduction process, which under aerobic conditions is typically oxygen reduction (Eq 4).

$$M \rightleftharpoons M^{n+} + ne^- \qquad (3)$$

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad (4)$$

It is well known that when a metal surface is covered with an insoluble (passive) oxide film, reaction (3) is inhibited and the metal will exhibit more positive E_{corr} values than when the same metal is actively corroding to a soluble oxidation product (22), as shown schematically in Fig. 3. Thus, when a single metal surface is covered by a thin film of adsorbed electrolyte, regions of that metal surface covered with a passive oxide film will typically exhibit significantly higher E_{kp} than those where the passive film has broken down.

Many metals spontaneously develop passive surface films, which may range from nanometers to several microns in thickness, when exposed to moist air. However, so-called aggressive ions, such as chloride (Cl⁻), tend to break down passive films and activate metal surfaces through the formation of soluble metal choride complexes (22). Consequently, the chloride rich inorganic salts present in the aqueous component of fingerprint secretions will tend to cause local depassivation of a metal surface in areas where secretions are deposited. Thus, when a Kelvin microprobe is scanned over a latent fingerprint, it is to be expected that ridges will be disclosed as regions of lower E_{kp} against the background of passive metal.

That this is actually the case is clearly illustrated in Fig. 4a, where a latent fingerprint, freshly deposited on a polished iron surface, has been visualized by mapping E_{kp} at a resolution of 10 data points per mm along both x and y axes. The interpolated greyscale
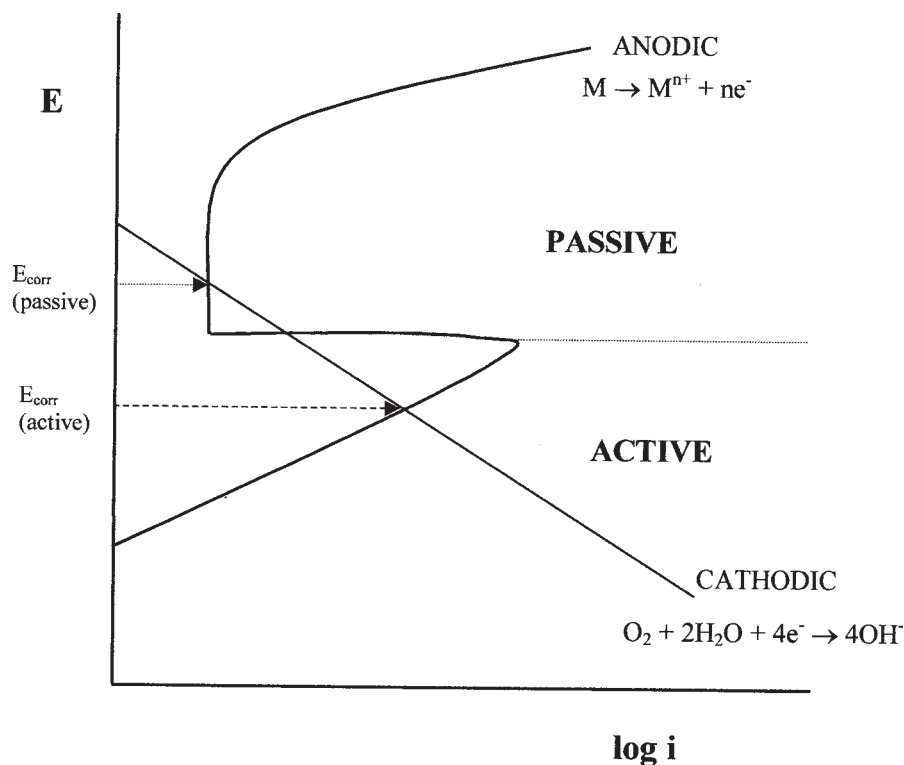

FIG. 3—*Evans, potential (E)–log current modulus (i) diagram showing the effect of a passive-active transition on the free corrosion potential (E_{corr}) of a metallic surface. Under free corrosion conditions the E_{corr} corresponds to that potential where the anodic and cathodic currents are equal and opposite.*
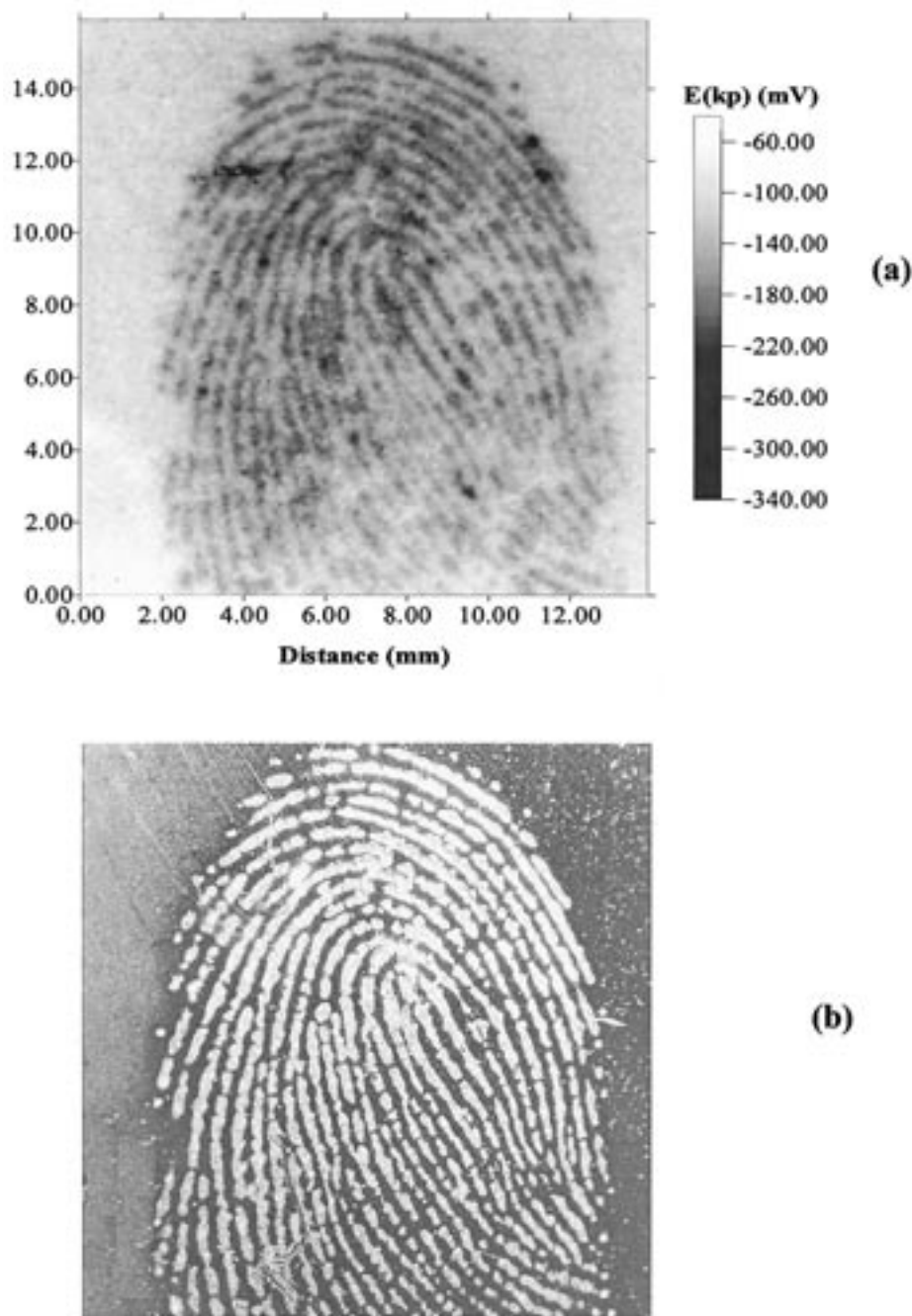
FIG. 4—(a) *The E_{kp} pattern produced by fingerprint deposited on an iron surface, as imaged by the Scanning Kelvin microprobe using a resolution of 10 points per mm. (b) A photographic image of the same area taken under illumination at a 30° angle of incidence.*

image, produced from the matrix of E_{kp} values, has been generated using commercially available cartography software (Surfer™, Golden Software). The ridge detail and characteristic right hand loop pattern of the sample fingerprint are clearly visible and exactly match the photographic image shown in Fig. 4b, which was obtained using glancing angle illumination. It can been seen from Fig. 4a that E_{kp} values in ridge regions may be up to 280 mV lower than the background. When samples were stored in ambient air this E_{kp} pattern was still clearly detectable one month after the fingerprint was applied. Visual evidence of corrosion could be detected two to three weeks after initially depositing the fingerprint.

Further tests have shown that fingerprints deposited on a range of other metals, such as copper, aluminum, nickel and titanium and various alloys including brass, can also be efficiently visualized in this way.

Since the Kelvin probe measurement is made under null-current conditions, E_{kp} is independent of the dielectric constant of the medium lying between the vibrating probe and sample surface. This property has been exploited in work using the SKP technique as a tool for investigating localized corrosion phenomena occurring beneath polymer coatings applied to metal substrates (23–25). It has been shown that electrochemically determined

Volta potential differences occurring over the metal surface can be mapped through a continuous polymer film. The technique should therefore be capable of detecting a latent fingerprint pattern under similar circumstances. The ability of the SKP to detect Volta potential distributions associated with fingerprint patterns overcoated with intact, insulating films was assessed by applying prints to iron substrates as above and then applying a range of polymer based coatings. The E_{kp} pattern shown in Fig. 5a was obtained after spray painting over a freshly deposited fingerprint with a commercially available clear cellulosic lacquer (plasticoat), to give a film thickness of 20 μm. The line plot in Fig. 5b illustrates the variation of E_{kp} over a cross section of the fingerprint pattern indicated by the dashed line in Fig. 5a. The sample

was stored in ambient air and the E_{kp} patterns in Fig. 5 were still clearly detectable one month after the substrate was overcoated. Other metal surfaces, including brass and copper, printed then overcoated with various pigmented and clear paint systems gave similar results, although application of coatings by brushing led to some smearing of the Volta potential pattern.

If Volta potential differences are induced by inorganic salts, the SKP should allow print visualization in situations were fingerprinted surfaces have been subjected to elevated temperatures, causing volatilization of the organic component of the residue. We used a Gleeble electric welding simulation apparatus (26,27) to heat print-bearing 1 mm thick sheet brass samples through a preprogrammed temperature-time profile by passing large tran-
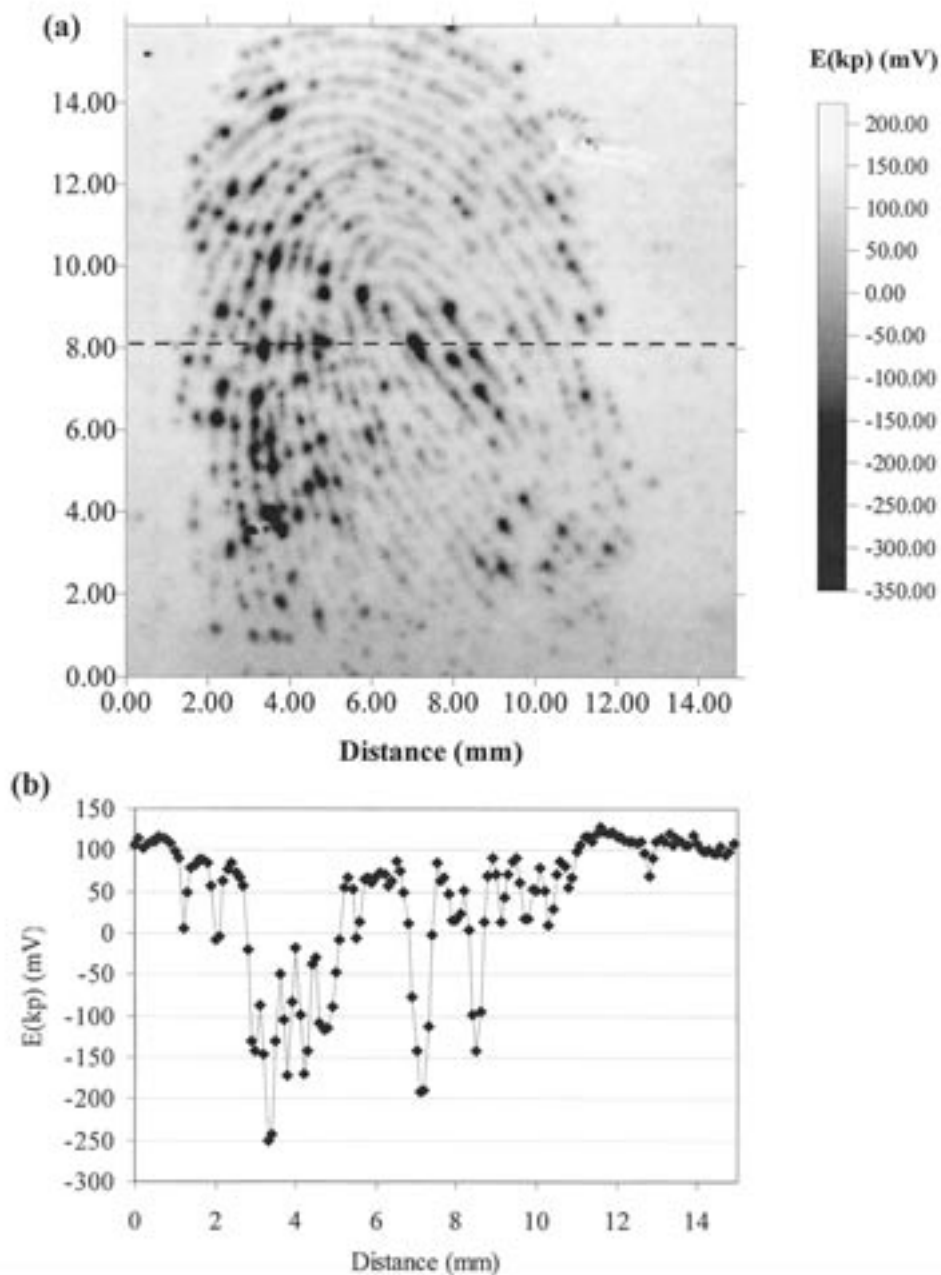

FIG. 5—(a) The E_{kp} pattern produced by fingerprint deposited on an iron surface and overcoated using a spray applied cellulosic lacquer of 20 μm thickness. (b) A plot of E_{kp} versus distance along the broken line in 4(a) showing the characteristic Volta potential profile across the ridges of a latent print.
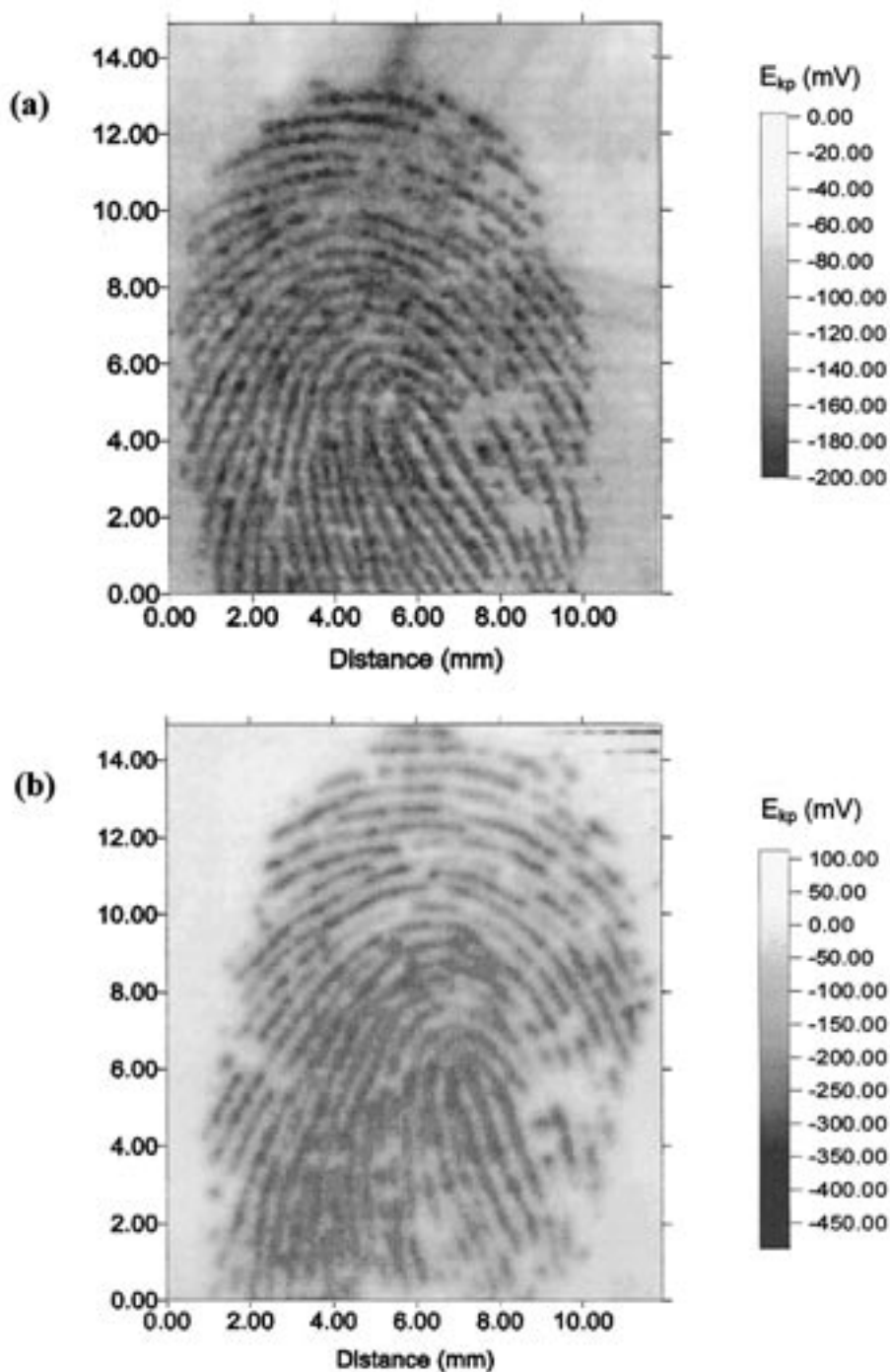
FIG. 6—*A comparison of* E_{kp} *patterns produced by a sebum rich fingerprint deposited on brass before* (a) *and after* (b) *being subjected to a rapid heating-cooling cycle employing a peak temperature of 600°C.*

sient dc currents controlled by temperature feedback. A heating rate of 200°C/s was used to attain target temperatures between 400 and 600°C in room air. Samples were then allowed to cool naturally in air (exponential cooling with a half life of 3 s). Figure 6 shows typical data, obtained from four day old sebum-rich prints visualized by SKP a) before and b) after heating to 600°C. It is evident from Fig. 6b that the fingerprint pattern is clearly visualized by E_{kp} mapping even after heating. Since the organic substances contained in the fingerprint are likely to have been

vaporized at 600°C, the observation that patterns remain detectable is consistent with the hypothesis that the Volta potential changes detected by the Kelvin probe are produced by nonvolatile salt deposits.

Although all the experiments outlined here were performed on planar samples, many real samples would obviously be nonplanar. Nonplanar samples can also be scanned provided the surface profile is known and used to control probe position. Surface profiling may be carried out using conventional mechanical or optical meth-

ods. However, recent work (28) has demonstrated that surface profiling is possible using the SKP itself by exploiting the fact that harmonic distortion in the Kelvin probe current [$i(t)$ in Eq (1)] is dependent on probe to sample distance. Similarly, real samples may exhibit irregular surface textures and contamination by pre-existing organic and/or inorganic films. Preliminary studies carried out by ourselves suggest that surface texture is not necessarily problematic provided the texture does not, of itself, produce a spreading (blurring) of the print deposit. However, the development of Volta potential differences may be suppressed by preexisting surface contamination if this prevents access of fingerprint salt deposits to the metal surface.

Rubbing freshly deposited fingerprints with a dry cloth may produce smearing of the resulting Volta potential variations or prevent their appearance altogether. However, once patterns of surface depassivation are well established (typically after several days) rubbing with a dry cloth has relatively little effect. Water or polar organic solvents tend to be more injurious and can destroy Volta potential patterns by redistributing salt deposits and inducing more general depassivation of the metal surface.

Conclusions

We have demonstrated that on metallic surfaces, such as iron or brass, the electrolytes present in latent fingerprint ridge deposits induce localized Volta potential variations that may be visualized directly using a scanning Kelvin microprobe (SKP). The observed Volta potential variations probably result from electrochemical depassivation of the metal surface by chloride ions and may persist for periods greater than one month when the metal is in contact with room air. They also persist when metal (brass) surfaces are heated to 600°C implying that the electrolytes concerned are primarily comprised of nonvolatile inorganic salts (such as NaCl). Once developed, Volta potential patterns are substantially unaffected by organic contamination superimposed by, for example, spray painting. However, contamination of the metal surface prior to print deposition may interfere with the development of Volta potential patterns if contaminants prevent print residue electrolytes from contacting the metal surface.

Further work will obviously be necessary to determine whether the above findings are primarily of theoretical interest or whether the SKP is capable of being developed as a practical forensic tool. Nevertheless, the SKP possesses features which suggest that it is worthy of further investigation. The SKP is completely nonperturbing and does not require exposure of the print to radiation, vacuum or any other destructive agency, which could prove advantageous in situations where the fingerprint must be preserved for future extraction of genetic materials. Furthermore, because the Volta potential changes detected by SKP are primarily induced by nonvolatile inorganic salts it may be possible able to detect prints in instances where the organic components of the residue are scanty or have been lost as a result of exposure to high temperatures. Finally, because the SKP measurement is purely potentiometric it may be possible to visualize fingerprints which have become overcoated or contaminated with insulating films such as paint, oil or grease.

Regardless of whether the SKP itself proves to be of practical usefulness it is to be hoped that the findings presented here will contribute to the physico-chemical understanding of fingerprint deposits and facilitate the rational design of reagents and techniques for forensic fingerprint visualization on metallic surfaces.

References

1. Lee HC, Gaensslen RE, editors. Advances in fingerprint technology. New York; Elsevier, 1991.
2. Hazen RJ. Significant advances in the science of fingerprints. In: Davis GG, editor. Forensic Science. 2nd. Washington DC: American Chemical Society, 1986;229–312.
3. Bentsen RK, Brown JK, Dinsmore A, Harvey KK, Kee TG. Post firing visualisation of fingerprints on spent cartridge cases. Science and Justice 1996;36:3–8.
4. James JD, Pounds CA, Wilshire B. Flake metal powders for revealing latent fingerprints. J. Forensic Sci 1991;36:1368–74.
5. Sampson WC. An inquiry into the methodology of preserving and developing latent prints on expended cartridge casings. J Forensic Ident 1993;43:4–12.
6. Mashiko K, German ER, Motojima, Colman CD. A new ruthenium tetroxide fuming procedure. J Forensic Ident 1991;41:429.
7. Migron Y, Hocherman G, Springer E, Almog J, Mandler D. Visualization of sebaceous fingerprints on fired cartridge cases: A laboratory study. J Forensic Sci 1998;43:543–8.
8. Reed R. Development of latent prints on brass with silver nitrate. Ident News 1985;35(7):11.
9. Schutz F, Bonfanti M, Champod C. La revelation des traces papillaires sur les douilles par les techniques de etching et de blueing et comparison avec la deposition multimetallique. Can Soc Forensic Sci J 2000;33:65–81.
10. Migron Y, Mandler D. Development of latent fingerprints on unfired cartridges by palladium deposition: A surface study. J Forensic Sci 1997;42:986–92.
11. Saunders GC, Cantu AA. Evaluation of several techniques for developing latent fingerprints on unfired and fired cartridge cases. Proceedings, of the International Symposium on Fingerprint Detection and Identification; 26–30 June 1995; Neurim. Israel: 155–60.
12. Cantu AA, Leben DA, Ramotowski R, Kopera J, Simms JR. Use of acidified hydrogen peroxide to remove excess gun blue from gun blue-treated cartridge cases and to develop latent prints on untreated cartridge cases. J Forensic Sci 1998;43:294–8.
13. Yee S, Oriani RA, Stratmann M. Application of a Kelvin microprobe to the corrosion of metals in humid atmospheres. J Electrochem Soc 1991;138:55–60.
14. McMurray HN, Worsley DA. Scanning electrochemical techniques for the study of localised metallic corrosion. In: Compton RG, Hancock G, editors. Research in chemical kinetics, Vol. 4. Oxford: Blackwell Science, 1997:149–202.
15. Brett CMA, Oliveira Brett AM. Electrochemistry: principles, methods and applications. Oxford; Oxford University Press, 1993.
16. Thompson W, (Lord Kelvin). Contact electricity of metals. Philos Mag 1898;42:82–101.
17. Nonnenmacher M, O'Boyle MP, Wickramasinghe HK. Kelvin probe force microscopy. Appl Phys Lett 1988;58:2921–3.
18. Henning AK, Hochwitz T, Slinkman J, Never J, Hoffmann S, Kaszuba P, et al. Two-dimensional surface dopant profiling in silicon using scanning Kelvin probe microscopy. J Appl Phys 1995;77:1888–96.
19. Chavez-Pirson A, Vatel O, Tanimoto M, Ando H, Iwamura H, Kanbe H. Nanometer-scale imaging of potential profiles in optically excited n-i-p-i heterostructure using Kelvin probe force microscopy. Appl Phys Lett 1995;67:3069–71.
20. Chen C and Mansfeld F. Potential distribution in the Evans drop experiment. Corros Sci 1997;39:409–13.
21. Leng A, Stratmann M. The inhibition of the atmospheric corrosion of iron by vapour phase inhibitors. Corrosion Sci 1993;34:1657–83.
22. Trethewey KR, Chamberlain J. Corrosion for science and engineering. Harlow, England; Longman Scientific, 1995.
23. Stratmann M, Streckel H, Feser R. A new technique able to measure directly the delamination of organic polymer films. Corrosion Sci 1991;32:467–70.

24. Furbeth W, Stratmann M. Investigation of the delamination of polymer films from galvanized steel with the scanning Kelvin probe. Fresenius J Anal Chem 1995;353:337–41.

25. Leng A, Streckel H, Stratmann M. The delamination of polymeric coatings from steel. Part 1: Calibration of the Kelvinprobe and basic delamination mechanism. Corrosion Sci 1999;41:547–78.

26. Ferguson H. Metalworking process simulations save production headaches. Metal progress 1986;130:37–40.

27. Ferguson H. The physical simulation of continuous steel processes. J Metals 1988;40:14–6.

28. Cheran LE, Liess HD, Thompson M. Scanning Kelvin microprobe in the tandem analysis of surface topography and chemistry. Analyst 1999; 124:961–70.

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