B164 Fingerprint Aging Mechanism Determination Through Electrochemistry

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After attending this presentation, attendees will understand the great potentialities offered by electrochemical techniques in the fascinating and highly challenging research field of fingerprint age determination. Currently, a reliable, quantitative, and reproducible technique for determining the age of fingerprints found at the crime scene is still lacking, although it is considered one of the major challenges for future forensic science innovation.[1,2]

This presentation will impact the forensic science community by demonstrating a quantitative determination of the fingerprint aging mechanism through Electrochemical Impedance Spectroscopy (EIS) measurements. Prior to a reliable method for fingerprint age determination being effectively developed, a deeper understanding of the aging mechanism is necessary as research efforts must be refocused on the fundamental understanding of the fingerprint itself.[3]

This study seeks to accurately investigate the fingerprint aging mechanism on selected metallic substrates, namely AISI316L stainless steel, aluminum (6082), and brass. The chemical as well as the physical modifications which a fingerprint undergoes over time will surely affect the electrochemical response of the system, constituted by the print residue and the substrate on which it has been deposited.

As recently recommended by the International Fingerprint Research Group (IFRG), natural "ungroomed" marks were tested in order to evaluate the proposed technique for actual scenarios.[4] A three-electrode cell was employed for the EIS measurements, using the metallic substrate bearing the fingerprint as the working electrode, a platinum foil as the counter electrode, and $Ag/AgCl/KCl_{sat}$ as the reference electrode. The impedance spectra were acquired in the 100kHz÷100mHz frequency range (ω), applying a sinusoidal potential wave (0V bias, 10mVrms of amplitude). In this way fingerprints were monitored over a time period of 45 days.

The equivalent circuit used to fit the experimental impedance data collected at different aging times was a Randle's one R(QR), consisting of an ohmic resistance, mainly ascribed to electrolyte (i.e., 0.2 M Na2SO4) solution, in series with the parallel combination of the double-layer capacitance (C_{dl}) and the charge transfer resistance (R_{ct}) of the reaction activated during the slight polarization applied to the substrate. The double-layer arrangement of the systems investigated in this study differs from an ideal capacitor, thus a Constant Phase Element (CPE) whose impedance contribution is reported in Equation 1 has been used to replace C_{dl}.

Equation 1: $Z(w)=Y_0(jw)^{-n}$. Y_0 represents a constant with dimension $F×s^{n-1}$, ω is the applied frequency, while *j*=Ö-1and 0<n<1. The EIS results showed that the fingerprint mainly affects the capacitance of the double layer formed at the metal substrate/electrolyte interface: the fingerprint aging process has, as its main effect, a decrease of the active area of the metal substrate (due to the spreading of the fingerprint on the metal surface), a phenomenon which leads to a decrease of the capacitance of the electric double layer, directly correlated with the ageing process, through a 3-parameters exponential decay equation of the type in Equation 2.

Equation 2: $y=y_0+ae^{-bx}$. Similarly to what observed for the Y_0, the exponent n reported in Equation 2 also undergoes an exponential decay during the aging of the fingerprint. This latter behavior can be correlated to a variation in the roughness of the fingerprint-substrate system, in accordance to literature data.[5] On the contrary, the R_{ct} value does not significantly change during the aging process: this result suggests that the only faradaic reaction activated during the slight polarization applied to the substrate is the oxidation of the metallic substrate (hypothesis confirmed by the high R_{ct} values obtained, which are consistent with the passive behavior of the metals used when exposed to the selected electrolyte).

In conclusion, EIS allowed this study, for the first time, to quantitatively clarify the aging mechanism of fingerprints on metallic substrates, smoothing the way for reliable fingerprint age determination studies and for considering the possibility of easily coupling EIS to further electrochemical-based techniques (this latter aspect being the main focus of current research).

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