Review of: "Theory of a Chemical Kinetic Approach for the Estimation of the Age of Fingerprints"

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Potential competing interests: No potential competing interests to declare.

Report on the manuscript: "Theory of a Chemical Kinetic Approach for the Estimation of the Age of Fingerprints", A. Gamarra et al.

Ref. Quesos-VFJR22.

General comments:

The manuscript presents a theoretical approach to determine the age of fingerprints based on the determination of the chemical oxygen demand (COD) and the assumption that this quantity varies according to a first-order rate law. The manuscript presents an interesting approach but also offers serious problems with regard to its practical implementation in forensic science so that major revision is recommended based on the following considerations.

General remarks:

I) The authors assume that the COD of the fingerprint decreases following a first-order rate law. However, the COD results from the superposition of the reactivity of several organic components of the fingerprint whose proportion may vary from one fingerprint to another. It is unclear if, effectively, a first-order rate law applies for the variation of COD in fingerprints. The authors mention (page 2, last line) several citations (refs. [6-9]) supporting this assumption, but more concretion is pertinent.

II) The authors should be aware that the graph in Figure 1 is, in principle, non-universal. The COD will depend on the chemical composition of the fingerprint and possibly of the substrate (wood, glass, metals, …) where the fingerprint is deposited, as well as the conditions of aging; i.e., that each individual fingerprint will produce a (lightly but significantly) different straight line. Then:

a) The method proposed by the authors implies that the COD of the problem fingerprint has to be determined several times at time intervals large enough to ensure that the graph in Figure 1 was satisfactory. This means that the COD assay has to be repeated several times on the same fingerprint at times comparable to the estimated age of the sample. Then, for a fingerprint aged 10 years, according to Figure 1, the assays should be repeated at least 10 and 20 years after the first assay. Obviously, this limits seriously the application of the method for forensic purposes.

b) These repeated assays should be performed ensuring that the aging of the fingerprint was under identical conditions than those previously experienced. This condition is not easy to satisfy.

III) The authors do not provide any detailed discussion of the experimental conditions in which the COD assay applies. In particular, what is the net amount of fingerprint sample needed. Since the assay has to be repeated several times, it could require un-accessible amounts of sample.

IV) The claim (page 3, last paragraph) that the COD reactants (H2SO4 and K2Cr2O7) are in large excess and this ensures the pseudo-first order conditions is irrelevant. In principle, the assay is performed on an aliquot of the fingerprint in a time considerably much shorter than the age of the fingerprint. The concentrations of the reactants could influence the aging if the fingerprint was stored in contact with the reagents solution.

V) The authors declare in the Conclusions section that “Of course to validate our theory we must engage in a series of experiments programed to demonstrate if our hypothesis is true or not.”. Although the mere presentation of the hypothesis is of interest, obviously, it would be better that the authors have performed some experimental work. To complete the ‘hypothetical’ communication, the authors should perform a reasonable analysis of errors. In short: what would be the estimated uncertainty in the age estimate starting from the uncertainty in the usual COD determinations?