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Theory of a Chemical Kinetic Approach for the Estimation of the Age of Fingerprints

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Abstract

Fingerprints are one of the most important forms of physical evidence in forensic investigations worldwide. The age of a fingerprint is the time at which a latent fingerprint was deposited. Unfortunately, there is a lack of reliable methods to determine the age of fingerprints. This is due to the fact that fingerprint composition changes in time through complex chemical, biological and physical processes. Chemical kinetics is the study of reaction rates and the effects of concentration, temperature, pressure and other physical factors on these rates. It establishes quantitative relationships, called rate laws, between the concentrations of reagents, products and time. Therefore, chemical kinetic rate laws allow us to determine the concentration of a given reagent at any time or the time corresponding to a given concentration. In this work we propose to use a chemical kinetic approach to investigate the age of fingerprints by measuring the evolution in time of all of their components at once. To this end, we propose to measure the time evolution of a lumped parameter, the Chemical Oxygen Demand – COD of the fingerprint. This parameter is a measure of the whole composition of the fingerprint.

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Introduction

In this section we closely follow the seminal work of Dr. Josep De Alcaraz- Foussoul[1] who was the first to emphasize the importance of the gathering and determination of the age of fingerprints in the criminal justice systems. Fingerprints

remain the basic tool for identification of suspects at crime scenes. There have been developed sophisticated method for visualizing latent fingerprints. However, as Dr. De Alcaraz- Foussoul and Gadd et. al, [2], comment, no reliable method has been developed for determining the age of latent fingerprints. This means that “while fingerprints can be identified and associated with suspects, potentially guilty perpetrators have to be released and innocent victims unnecessarily implicated because investigators lack a robust method of assessing the time the trace (fingerprint) was deposited at a scene. The most common situation occurs when a suspect has legitimate accesses to a scene before or after the actual crime. The inability to date the moment the fingerprint was deposited often nullifies otherwise strong items of evidence or implicates innocent persons. As a consequence, in the UE alone, “the implementation of a reliable method of age estimation of fingerprints could represent an estimated 2.3 billion Euro savings “, [1].

A number of authors have worked in the issue:[3][4][5]. As a rule they use sophisticated instrumental methods to follow the variation in concentration, i.e.the time evolution of one or two of the main components of fingerprints, such as: squalene or cholesterol. With their measured values over time, they drawn evolution curves and from these they try to estimate the age when they were deposited, with a very low accuracy. This lack of accuracy and precision constitutes a serious limitation because, while measurements in natural sciences might have some allowance for limited reproducibility and accuracy, criminalistics investigations require absolute reproducibility and non-variability in terms of the results. It should be kept in mind that a significant percentage of innocents have been incriminated and incarcerated based in erroneous fingerprint identification. Evidence is not only a scientific but a legal issue. To the best of my knowledge, no one approached the problem in a physicochemicaly rigorous way, that is to say, through the formulation of chemical kinetic models of the time evolution of the fingerprints. There are advantages in measuring the COD of a fingerprint instead of separately determining the evolution of one or more of the organic components of it. For example, to measure the Chemical Oxygen Demand of a material we do not need to determine the concentration of specific substances rather, we measure the effect of a combination of substances, as a consequence the analytical process is much simplified. Measurement of COD requires a very simple instrumentation that can be operated by persons with a minimum scientific training and that would be beneficial for criminal investigations , providing rapid results and giving immediate information. Substituting sophisticated and expensive instrumentation with simple equipment is a very important trend in modern forensic science.

The COD Test

By definition, COD is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a very strong chemical oxidant. The COD test uses a strong chemical oxidant in a solution of a very strong acid and heat to oxidize organic carbon to CO_2 and H_2O.

Proposed Rate Law for the Removal of the Cod of Fingerpints

A number of authors, [6][7][8][9], reported that the consumption of the COD of substrates as complex as waste waters

coming from slaughterhouses, domestic waste waters and a variety of other origins, obeys a first order rate law. That is, a first order kinetics. This means that the rate of decomposition of the sewage is proportional to the lumped concentration of the components of the waste. In our case the reagent is the COD of the fingermark.

In a first-order reaction the reaction rate is proportional to the first power of the concentration of one of the reacting substances. Therefore, for constant volume, irreversible, reactions carried out isothermically, the rate law will be

$$\text{rate} = -\frac{dC}{dt} = --\mathbf{dc/dt} = \mathbf{KC} \qquad (1)$$

Where

K = rate constant, has the dimension of a reciprocal of time

t = current time, in hours

In our case C refers to the COD of the fingerprint

C = COD of the fingerprint **at elapsed time t**

$C_{\mathbf{tod}}$ = COD of **the fingerprint at the time of deposition,** tod, which we take as a constant

Eq. (1) is the differential form of the rate law. It is an ordinary differential equation of the first degree.

The chief significance of having a reaction rate law such as (1) is that they provide a satisfactory framework for the interpretation of and evaluation of experimental kinetic data.

In our case, the concentration of the oxidants used to determine the COD (sulphuric acid and potassium dichromate) is orders of magnitude higher than the concentrations of the organic components of the fingerprints. When one reactant is in such a very large excess, the amount of this material that can be consumed by reaction is negligible compared to the total amount of organic matter present. **Under these circumstances, the concentration of the reactant in excess may be regarded as essentially constant throughout the course of the reaction and therefore, we can, safely assume that the rate will be proportional to the COD of the fingerprints**. That is to say, the reaction will be **first order in COD.**

Eq. (1) is easily integrated between the limits: $C_{\mathbf{tod}}$ and C_t for C and between t and $\mathbf{t_{tod}}$, **the time of deposition of the fingerprint.** After some simple algebraic steps we will have

$$\ln\left(\frac{C_{tod}}{C_t}\right) = -k * \left(t - t_{tod}\right) \qquad (2)$$

$$\ln C_t - \ln C_{tod} = -k * t + k * t_{tod}$$

$$\ln\left(\frac{C_{tod}}{C_t}\right) = k * t - k * t_{tod} \qquad (3)$$

And this is the equation of a straight line y = mx + b, with slope = k and intercept = - $\mathbf{k}^{*}\mathbf{t}_{\mathbf{tod}}$ on the time axis.

Therefore, a plot of $\ln\left(\frac{C_{tod}}{C_t}\right)$ versus time would give a straight line with intercept = - k$\mathbf{t}_{\mathbf{tod}}$ on the x axis, at a point located at a **distance** = k*$\mathbf{t}_{\mathbf{tod}}$ time units from the origin.

Actually we don´t know the concentration of the fingerprint at the tod: C_{tod}. However, we can determine the time of plot deposition **from the of equation (3),** if the concentration of the COD of the fingermark decreases linearly with time.

Effectively, since C_{tod} is constant and C_t **decreases** in time, $\ln\left(\frac{C_{tod}}{C_t}\right)$ will increase in time, see Figure 1. To estimate the time of deposition of the fingermark we have to proceed as follows. Our first sample (taken at time t) and its COD will provide us with a first point in a semi logaritmic coordinate system $\ln\left(\frac{C_{tod}}{C_t}\right)$ versus time. Therefore, if (as we postulate) the COD of the fingerprints decreases following a first order rate law, then the following values of the COD have to settle after the first on a line , as in the Figure 1.

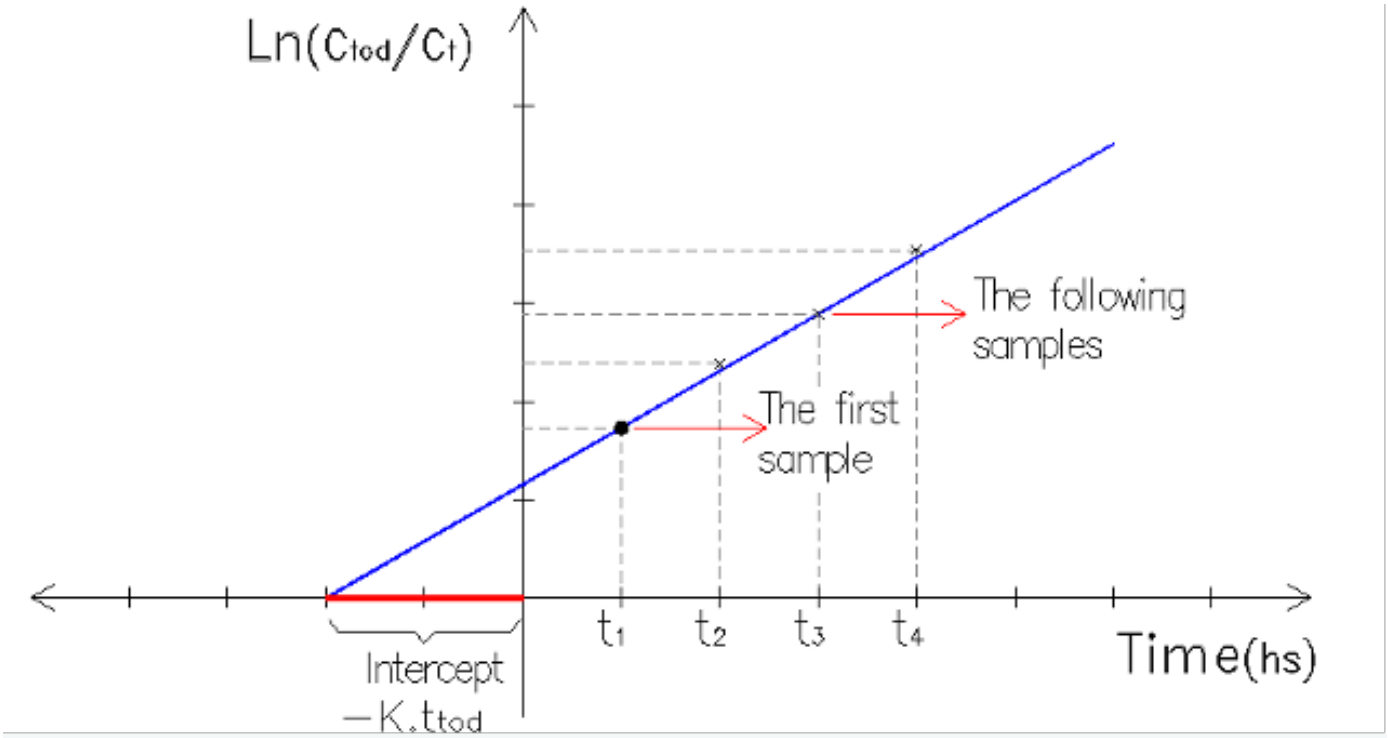

Figure 1. Plot of $\ln(C_{tod}/C_t)$ versus time

If the straight line intercepts the negative side of the time axis on a certain point = - kt^*_{tod}, we will have

Intercept on the time axis = = - kt^*_{tod} (4)

and therefore

t^*_{tod} = Absolute value of the measured intercept on the time axis/ - K , (5)

see Figure 1.

Conclusion

In this piece, we engage in a though exercise and present what, to the best of our knowledge, is the first well founded mathematical model of the time evolution of fingerprints left at crime scenes. Its main advantage, in comparison with the other, essentially empirical, approaches described in the literature, is that it provides us with a formula to estimate the age of fingerprints. The main hypothesis of the model is that the lumped composition of the fingerprints, measured by their COD, evolves following a first order rate law. Of course to validate our theory we must engage in a series of experiments programed to demonstrate if our hypothesis is true or not. However, no matter the results of such an experimental program, our approach remains valid because, as any material system that changes by chemical reactions, the chemical evolution of fingerprints must follow some form of chemical kinetic rate law. If experiments demonstrate that the proposed first order rate law does not applies, the problem will be to empirically found the right rate law. While we developed a

program for the experimental testing of the theory for simple, almost ideal conditions: fingerprints deposited on glass, it is beyond our possibilities- by lack of resources- to implement a program to test the theory for the much more complex cases encountered in field conditions. We will appreciate collaborating with forensic scientist interested in joint research projects to advance this interesting field.

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