Forensic Science International 254 (2015) 205–214

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Evaluation and comparison of 1,2-indanedione and 1,8-diazafluoren-9-one solutions for the enhancement of latent fingerprints on porous surfaces

Valentina D'Elia [a,b,1,*], Stefano Materazzi [c], Gianpaolo Iuliano [d], Luca Niola [d]

[a] Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, University of Alcalá, Ctra. Madrid-Barcelona Km. 33.6, 28871 Alcalá de Henares, Madrid, Spain
[b] University Institute of Research in Police Sciences (IUICP), University of Alcalá, Alcalá de Henares, Madrid, Spain
[c] Department of Chemistry, University of Rome "La Sapienza", P.le Aldo Moro 5, 00185 Rome, Italy
[d] Sezione di Impronte e Dattiloscopia, Reparto Carabinieri Investigazioni Scientifiche, 00191 Rome, Italy

ARTICLE INFO

Article history:
Received 5 May 2015
Received in revised form 20 July 2015
Accepted 21 July 2015
Available online 30 July 2015

Keywords:
Latent fingerprints
Porous surfaces
1,8-diazafluoren-9-one
1,2-indanedione
IND–Zn

ABSTRACT

1,2-indanedione (1,2-IND) and 1,8-diazafluoren-9-one (DFO) are used in the forensic field to enhance latent fingerprints deposited on porous surfaces due to the formation of fluorescent products by reacting with the amino acids present in the papillary exudate. The study was carried out in collaboration with the Fingerprints and Photography Section of the Carabinieri Scientific Investigation Department (RIS) of Rome, in which laboratories, until now, DFO has been the most used because of its excellent enhancing properties, even if it is more expensive and relatively toxic in comparison with the 1,2-IND.

The aim of this work was then to evaluate and to compare the effectiveness of three solutions of 1,2-IND in different formulations and a DFO solution employed as single enhancing treatments, in order to assess whether it was possible to replace a reagent with the other obtaining equally satisfying results.

In this case, white office paper was selected as deposit surface since it also permitted one to observe those reaction products that appear visible to a naked eye. Beside to a qualitative study of the visual characteristic of the enhanced fingerprints, further quantitative studies were conducted on the intensity of fluorescence of the products and on the consumption of amino acids during the reaction. The analyses, which at first were conducted on standard samples, were then repeated on real samples to validate the results obtained.

The DFO confirmed its excellent enhancement properties, but also one of the three solutions of 1,2-IND showed comparable properties in terms of enhanced fingerprint definition and stability over time from the completion of a crime. As a result, we proved that a selected 1,2-IND formulation may replace with satisfactory achievements the DFO solution currently employed, providing also advantages from the point of view of safety and cost savings.

1. Introduction

Latent fingerprints refer to fingerprints not observable to a naked eye. These are often found on a crime scene on objects commonly handled or accidentally touched during a crime. Enhancement techniques are chosen according to the time passed from the deposit of fingerprints and to the characteristic of the deposit surfaces. The paper, like all the porous surfaces, absorbs very quickly the hydrosoluble component of the sweat, while the liposoluble part remains on the surface for 12–24 h. Only a small amount of secretion remains on the substrate for a longer period. Both 1,2-indanedione (1,2-IND) and 1,8-diazafluoren-9-one (DFO) react with the amino acids present in papillary exudate giving fluorescent products, even if in some cases it is possible to observe the enhanced fingerprint in the visible range too.

The 1,2-IND was synthesized for the first time in 1997 in the University of Pennsylvania by professor Madeleine Joullié and her coworkers as intermediary for the preparation of analogous of ninhydrin, already used as reagent for the enhancement of fingerprints on porous surfaces. The reaction between this molecule and the ones of amino acids leads to the formation of

* Corresponding author at: Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, University of Alcalá, Ctra. Madrid-Barcelona Km. 33.6, 28871 Alcalá de Henares, Madrid, Spain. Tel.: +34 918854971.
E-mail address: valentina.d@uah.es (V. D'Elia).
[1] Website: www.inquifor.com.

http://dx.doi.org/10.1016/j.forsciint.2015.07.036
0379-0738/

a molecule called Joullié's Pink (JP). As it says the name, the molecule of JP has a pale pink color, but shows an intense luminescence if illuminated with green light (480–560 nm). However, some studies showed that latent fingerprints treated only with 1,2-IND tend to deteriorate in few days, losing both their color and their fluorescence. Instead, when fingerprints already treated with 1,2-IND were further treated with metallic salts as zinc or cadmium chloride, an increase of the fluorescent intensity of the product was observed. Moreover, the product assumed a darker color in the visible increasing the contrast with the substrate. This phenomenon is also verified when salts of zinc are directly added to the solution, in fact, in such cases fingerprints employ weeks or months before losing their color or their luminescence [1]. On the base of the studies conducted until now, the role of the metallic salts in the reaction of the 1,2-IND has not been entirely clarified, although it seems that this reaction proceeds through a mechanism similar to that of the Strecker degradation. Since previous studies [2,3] had shown that, by adding $ZnCl_2$, the product of the reaction became darker and more luminescent, initially it was supposed that the role of Zn^{2+} was only to form a complex with the JP. Anyway, following studies [4] underlined that, actually, these changes in color and intensity of fluorescence were not particularly evident. More recently [5,6], instead, it was found that an elevated concentration of $ZnCl_2$, contrarily than previously observed, leads to a decrease of the luminescence and the color intensity of the product of the reaction. In consideration of these results, it seemed probable that Zn^{2+} ions work as catalysts in the form of Lewis acid [7]. Furthermore it was noted that the zinc, by stabilizing the fluorophore obtained as product of the reaction, increases the period of permanence of the fingerprints on the substrate. Nevertheless, it is always preferable to prepare the solution of 1,2-IND just before its use because the presence of $ZnCl_2$ directly in the solution could cause a decrease of the shelf-life of the reagent from 1 year (IND) to 3 months (IND–Zn). Moreover, it is preferable to avoid the use of alcoholic solvents because they bring to the formation of hemiketals which reduce the reactivity of the 1,2-IND with the amino acids [1,8]. The ideal carrier solvent should be volatile enough to quickly evaporate, but also non-toxic, non-inflammable and non-polar, to avoid smears of inks eventually present on a porous substrate. Initially chlorofluorocarbons were used, mainly CFC-113, but since they contributed to the increase of the depletion of atmospheric ozone, they were soon replaced by hydrofluoroethers. Among these, the more common is the HFE-7100 (mixture of 1-methoxy-nonafluorobutane and 1-methoxy-nonafluoroisobutane) used as valid alternative to the petroleum ether that is cheaper but toxic and highly flammable [9]. In addition to the carrier solvent, polar solvents such as ethylacetate, dichloromethane, ethanol or methanol are often needed in the formulations of the reagent since they ensure the permanence in solution of the same reagents. Also the addition of acetic acid to the solution has been debated: in most of the studies conducted [6,9,10] it is recommended not to use it, because it has a negative effect on the definition of the enhanced fingerprints and causes a deterioration of the mixture with the consequent decrease in the solution shelf-life. Other research groups, instead, used acetic acid asserting that it is a very important component in the solutions of 1,2-IND [1]. All researcher, however, agree that working solutions should be stored in dark bottles since they are susceptible to photochemical degradation, which would occur upon a possible exposure to sunlight. Finally, it should be considered that the reaction between the 1,2-IND and the α-amino acids may be affected by the constituents of the paper, but also by humidity and environmental conditions. Therefore, a 1,2-IND solution that works very well under certain conditions could not to be the best under different conditions. Basing on this information, it does not exist a specific optimal formulation for the 1,2-IND and this variability is the main reason for which different formulations have been investigated.

The DFO was synthesized for the first time in 1950 by Druey and Schmidt, but it was introduced as a reagent for the enhancement of the latent fingerprints from Pounds and Grigg in 1989 [11]. It reacts with the amino acids contained in the natural secretions giving a pale red/magenta product, which has also a strong luminescence at room temperature without need of further treatment (such as the addition of metal salts). In order to start the reaction, it is necessary to apply heat using an oven or a hot plate at temperatures that go from 100 to 180 °C and for times not exceeding 20 min. Indeed, a prolonged heating at high temperatures and especially in case of high humidity, could have adverse effects on the luminescence of the fingerprints treated. It was observed that, by subjecting the fingerprints developed with DFO to a further treatment with ninhydrin, there is not a great improvement in the visualization of the fingerprints already enhanced, but it is possible that other fingerprints are highlighted. This observation suggests that probably the DFO does not consume all of the amino acids present in the exudate and this can be due to an incomplete or slow reaction and to the fact that the reagent does not react with some types of amino acids, so it is often recommended to perform anyhow a treatment with ninhydrin [12,13]. Unlike what has been described for the 1,2-IND, the presence of methanol in the DFO solution proved to be of fundamental importance, not only because it ensures the permanence of the reagent in solution within the non-polar solvent, but also because it reacts with the same DFO forming hemiketals. A thorough study demonstrated that by replacing the methanol with ethanol, the sensitivity of the reagent decreased, while by replacing it with the t-butyl alcohol, no fingerprints are displayed. This variability in the performance of the reagent could be explained by considering that the three alcoholic solvents have different polarities: the t-butyl alcohol in fact has a stereochemistry that inhibits the formation of hemiketals, which are fundamental for the progress of the reaction of the DFO [12]. The first formulations of DFO, similarly to what it was seen for the 1,2-IND, contained CFC-113 as carrier solvent, which was subsequently replaced by the HFE-7100 for the same reason mentioned above. Currently, in some formulations, together with the HFE-7100, also the HFE-71DE (mixture of 1-methoxy-nonafluoro-butane and 1-methoxy-nonafluoro-isobutane with 1,2-dichloroethylene) is present. According to some studies, the latter solvent is able to improve the performance of the reagent because the trans-1,2-dichloroethylene may contain traces of HCl able to catalyze the reaction [12]. However, since it is a highly toxic and flammable solvent, its use is avoided in most laboratories [1,6,12]. DFO solutions, like 1,2-IND ones, should be stored in dark glass bottles, since they are sensitive to photochemical degradation, and possibly in the refrigerator. Depending on storage conditions, the shelf-life of this reagent ranges from 3 to 6 months. The humidity of the environment and the specific porous surface on which fingerprints are deposited are two factors to be considered, but their influence is not decisive for the visualization of fingerprints as for the 1,2-IND. In fact, when fingerprints developed with the DFO are not properly stored, it is possible a decrease of the luminescence as result of the absorption by the substrate of environmental humidity, but the luminescence can be completely restored by heating again for a few minutes.

2. Experimental

2.1. Chemicals

The 1,2-IND and the DFO were both provided by Sirchie (Youngsville, NC, USA); $ZnCl_2$, ethanol, glacial acetic acid, petroleum ether and methanol were supplied by Merck (Rome, Italy); ethyl acetate was provided by VWR BDH Prolabo (Milan, Italy);