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Evaluation of alternative powders for Forensic Papilloscopy

R.G. Ferreira[a,*], A.A. Okuma[a], L.M. Costa[a]

[a] *CEFET-MG, Centro Federal de Educação Tecnológica de Minas Gerais, Belo Horizonte (MG), Brasil*

**Endereço de e-mail para correspondência: rafahh97@gmail.com. Tel.: +55 37 99992-1044.*

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Resumo

As impressões papilares têm sido uma das provas mais importantes para a identificação de indivíduos durante uma investigação criminal. No entanto, as substâncias utilizadas para a revelação de impressões papilares na Papiloscopia Forense são, geralmente, tóxicas. Assim, este trabalho visou reduzir o risco a que os profissionais da área estão expostos, mediante utilização de reveladores eficientes, menos tóxicos e economicamente viáveis. Além disso, os estudos foram direcionados para a visualização de impressões papilares latentes depositadas em diferentes materiais com superfícies não porosas, tais como fórmica bruta, madeira envernizada, metal bruto, metal galvanizado e vidro, de modo a encontrar reveladores mais adequados que proporcionem uma boa resolução de imagem. Para este estudo, foi feita uma pesquisa na literatura de substâncias corantes não tóxicas apropriadas para o desenvolvimento de impressões papilares pelo método de aplicação de pó, além de uma caracterização por espectrofotometria UV-Vis dos seus compostos corantes. Nesse contexto, este trabalho apresenta o estudo do potencial de aplicação dos corantes alimentares e produtos naturais em pó de beterraba vermelha, hibisco, algas Spirulina, índigo carmim e tartrazina em investigações criminais.

Palavras-Chave: Impressões papilares; Corantes alimentícios; Química verde; Método do pó; Espectrofotometria.

Abstract

Fingerprints and other ridge skin impressions has been one of the most important evidences for identifying individuals during a criminal investigation. However, the substances used for fingerprint and other ridge skin impressions revelation in Forensic Papilloscopy are usually toxic. Thus, this work aimed to reduce the risk to which professionals in the area are exposed, through the use of efficient, less toxic and economically viable revealers. Furthermore, the studies were directed to the visualization of latent fingerprints and other ridge skin impressions deposited on different materials with non-porous surfaces such as rough Formica, varnished wood, raw metal, galvanized metal and glass, in order to find more appropriate developers that provide good image resolution in spite of the surface. For this study, a search was made in the literature for non-toxic dyeing substances appropriate for fingerprint and other ridge skin impressions development by the powder method, in addition to a UV-Vis spectrophotometry characterization of its dye compounds. In this context, this work presents the study of the potential for implementation of the food dyes and natural products powders red beet, hibiscus, algae Spirulina, indigo carmine and tartrazine in criminal investigations.

Keywords: Fingerprints; Food dyes**;** Green Chemistry; Powder method; Spectrophotometry.

1. INTRODUCTION

Papilloscopy has been an important branch of forensic science for many years and even today is one of the most widely used human identification techniques, along with DNA. This science analyzes, in particular, fingerprints and other ridge skin impressions, which are considered perennial, immutable and unique, and therefore, are fundamental physical evidence in solving crimes [1-2].

In crime scenes it is common to find latent prints, i.e. invisible to the naked eye. In these cases, techniques are used to develop these fingerprints, such as the powdering method, which has been used for over a century. This technique is based on the adherence of powder to the substrates present in the fingerprints, enabling the visualization of its lines [2-3].

Regular powders are usually composed of a pigment and a binder. Some of the most commonly used pigments are carbon black, talc, kaolin, aluminum, titanium dioxide, among others, and some binders are iron, lycopodium, corn starch, rosin and gum arabic. There are also metallic powders, containing meshed metals and luminescent powders, containing organic compounds that fluoresce or phosphoresce under UV light [4-5].

However, a problem related to the powders is the fact that most of them present high toxicity, causing them to represent a risk to the professionals involved and to the environment [6]. For instance, International Agency for Research on Cancer (IARC) published a work about the carcinogenic risks related to Carbon black, titanium dioxide and talc [7].

Consequently, many studies are being conducted to find non-toxic substances that can replace the toxic papilloscopic developers with products that better fit the principles of Green Chemistry. A few examples are powders made from plants like turmeric and gambir and with synthetic food and festival colors [3,5,8]. In this type of work it is common that prevention, use of safe solvents and auxiliaries, design for energy efficiency, use of renewable feedstocks and inherently safe chemistry for accident prevention are often the main principles of green chemistry exploited [9].

In this context, the present work aiming to test some products and dyes that are part of the daily life of the population (mostly from vegetable origin) [10] as alternatives for papilloscopic developers and also characterize their dye compounds by UV-Vis Spectrophotometry. The advantage of using food colorants or food products as papilloscopic developers is that they are not only low cost but also do not pose high toxicity like the substances currently used.

2. MATERIALS AND METHODS

The materials and methods used for characterizing the dye compounds present in the powders through the spectrophotometry technique [11] and for developing fingerprints using the powders are discussed in the following sections.

2.1. Dye characterization

The compounds were characterized in three stages. First, we conducted a solid-liquid extraction from powdered products using ultrasound irradiation [12]. For indigo carmine, tartrazine, and red beet, we used distilled water at room temperature, while for hibiscus and spirulina algae, we used Ethanol Absolute 99.8%, Certified AR for Analysis, as solvents.

Secondly, a centrifugation of the extracts obtained was performed for the removal of solids that could interfere with the analysis. For this, microtubes and an Eppendorf 5410 centrifuge were used.

Finally, the solutions containing the samples of the synthetic and natural dyes were analyzed by spectrophotometric analysis in the UV-Vis region, using a Varian Cary 50 spectrophotometer and quartz cubes of 1 cm optical length, scanning at 250-700 nm.

The results obtained were processed in the Origin software for the generation of the absorption spectra and subsequent interpretation and discussion.

2.2. Fingerprint development

This study collected a total of 300 fingerprints from ten donors, aged 19 to 65, with each donor providing 30 fingerprints. All donors signed an informed consent form. The volunteers were asked to touch oily body parts, such as forehead and nose, and then press their fingertips, now containing sebum, on the indicated surfaces. Different fingers were used in taking the prints.

Typically, powder application involves brushing, but this method can potentially damage the fingerprint [13]. Therefore, to avoid damaging the fingerprints, the method used was the deposition of the powders on the surfaces carrying the latent fingerprints, in the horizontal position, and the gentle removal of excess powder by tapping, in upright position.

The powders of natural products, such as red beet (*Beta vulgaris esculenta*), hibiscus (*Hibiscus sabdariffa*), and spirulina algae (*Spirulina plantesis*), were sourced from the local market. Additionally, food dyes like indigo carmine and tartrazine were purchased from NEON Comercial Reagentes Analíticos LTDA.

Five types of non-porous surfaces were used in this work:

- Rough Formica
- Varnished wood
- Raw metal
- Galvanized metal
- Glass

Before each experiment, the surfaces were cleaned using ethyl alcohol, and gloves were worn to prevent contamination from other fingerprints.

3. RESULTS AND DISCUSSION

The results of the characterization of the dye compounds present in the powders using spectrophotometric techniques and the fingerprint developments made with the powders are in the following topics. Besides that, a topic discussing some of the Green Chemistry principles that are present in this work was included.

3.1. Dye characterization

The results obtained for the characterization of the colorants of each product will be discussed separately in the following sections.

All molecular structures of the powder components were created by the authors using ChemSketch software.

3.1.1. Beta vulgaris esculenta

Red beet, a reddish purple vegetable, has as dyes a mixture of betacyanins (betanin and its epimer isobetanin) and betaxanthins (vulgaxanthin I, vulgaxanthin II and indicaxanthin), Figure 1.

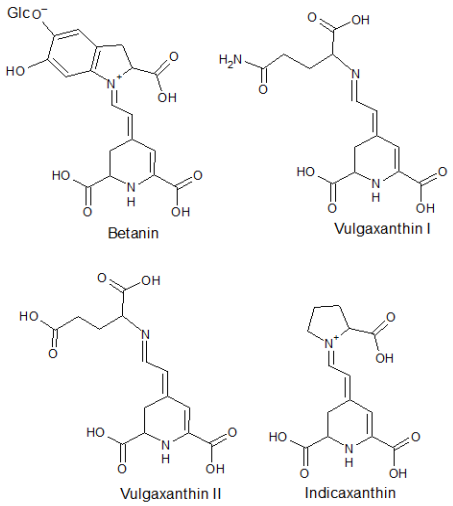

Figure 1. Betacyanins and betaxanthins found in red beet.

Betalains have conjugated double bonds, and betalamic acid, their common base, exhibits phenolic characteristics. These factors explain why these substances exhibit maximum absorption in the UV-Vis region [14].

The absorption spectrum of the red beet is shown in Figure 2.

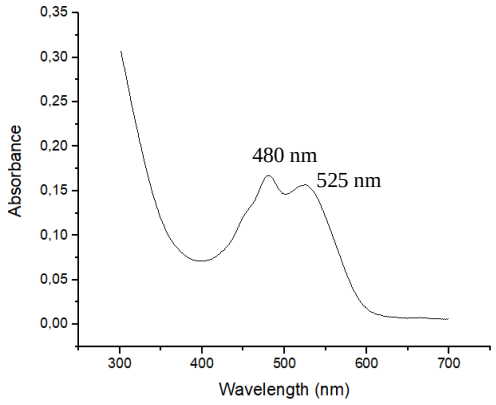

Figure 2. Absorption spectrum of red beet.

Betacyanins are purple-red pigments, which is why their spectrophotometric analysis reveals a maximum absorption peak around 535-540 nm. In contrast, betaxanthins are yellow pigments with a maximum absorption range between 476 and 478 nm [15]. The absorption spectrum of the beet sample presented two overlapping bands, the first with maximum absorption at 480 nm, relative to betaxanthins, and the second at 525 nm, relative to betacyanins. This result was expected, given the absence of prior compound separation and the potential interference of solvent polarity in the spectrophotometric analysis of polar organic compounds [16].

3.1.2. Hibiscus sabdariffa

Hibiscus Sabdariffa is a reddish plant widely used in commerce. The dyes present in it are anthocyanins, which fall into the flavonoid class. The main anthocyanins found are delfinidin-3-O-sambubioside and cyanidin-3-O-sambubioside, as shown in Figure 3, but other anthocyanins are also present in smaller quantities [17].

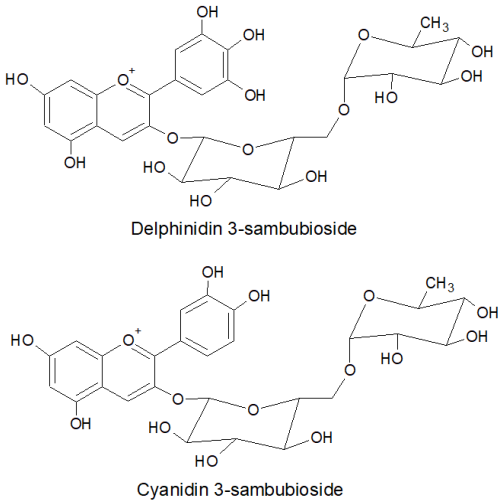

Figure 3. Main anthocyanins of *Hibiscus Sabdariffa*.

From the absorption spectrum of hibiscus, shown in Figure 4, two peaks can be seen, one with maximum absorption at 546 nm and the other at 327 nm.

According to the literature, the anthocyanins of *Hibiscus Sabdariffa* typically exhibit maximum absorption at around 530 nm and 540 nm. Therefore, the peak observed at 546 nm likely corresponds to a mixture of anthocyanins responsible for the color, and the slight variation could be attributed to the polarity of the solvent or the composition of the anthocyanin mixture itself, as no specific tests were conducted to identify the individual components [18-19].

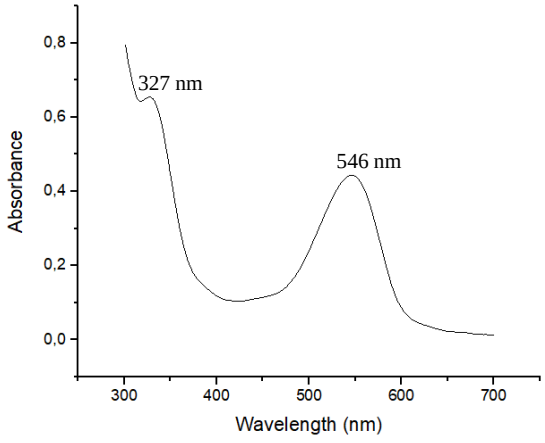

Figure 4. Absorption spectrum of hibiscus.

The peak at 327 nm is associated with the presence of compounds known as hydroxycinnamates found in the cell wall of plants, including hibiscus. In the literature, these compounds are reported to exhibit absorption between 320 and 330 nm [20]. Both maximum absorptions in the visible region can be justified by the presence of aromatic rings and conjugated double bonds in the anthocyanin and hydroxycinnamate molecules.

3.1.3. Spirulina plantesis

Spirulina is an algae that presents several photosynthetic pigments, the main ones being chlorophyll a, carotenoids (as lutein and *β*-carotene) and ficobiliproteins (as phicocyanine and aloficocianine). This justifies the presence of several bands in the absorption spectrum, since all of these absorb light in the visible region because of their chromophores, such as unsaturation and carbonyl, in chlorophyll a, conjugated double bonds, in carotenoids, and carboxyl, carbonyl and unsaturation, in ficobiliproteins [21]. The absorption spectrum of spirulina algae is presented in Figure 5.

In the spectrum of the Spirulina algae extract (Figure 5), bands with maximum absorption at 666, 618, 430, 416, and 336 nm can be observed, along with shoulders at approximately 588, 471, and 386 nm.

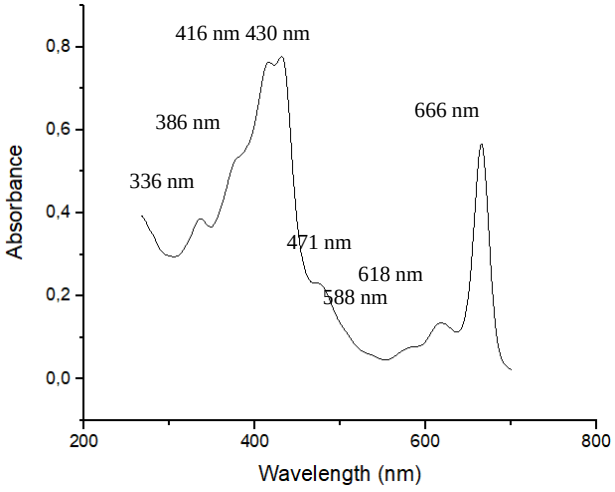

Figure 5. Absorption spectrum of spirulina algae.

The maximum absorption observed at 618 nm can be associated to the presence of phycocyanin, a blue color pigment, since it absorbs between 611 nm and 622 nm. The maximum absorption at 666, 430, 416 and 336 nm can be associated to chlorophyll a, since it normally presents absorption in two regions of the spectrum, red and violet. It's possible that the characteristic carotenoid bands have overlapped because they are less intense, and the shoulder at 471 nm may be related to their presence. Carotenoids typically absorb in the 400 to 500 nm range, with a maximum around 472 nm, although it is not possible to confirm this from this spectrum alone [22-23].

3.1.4. Indigo carmine

Figure 6 displays the absorption spectrum of indigo carmine.

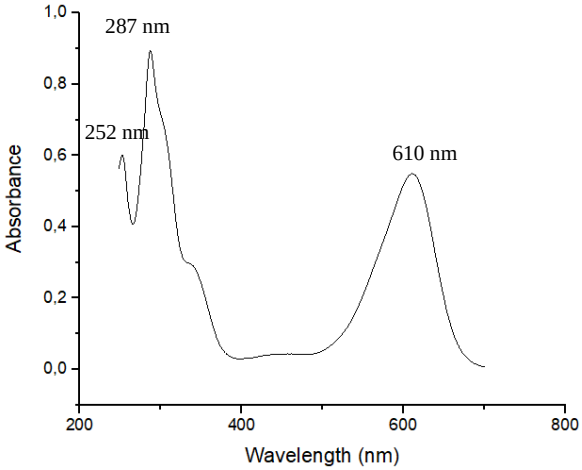

Figure 6. Absorption spectrum of indigo carmine.

Indigo carmine, Figure 7, is a dye that presents very characteristic peaks, being reported in the literature maximum absorbance values of 250, 287 and 610 nm by Wang and collaborators (2017) and 250, 290 and 610 nm by Ortiz and collaborators (2016). In the obtained spectrum (Figure 6), bands with maximum absorbance at 252, 287, and 610 nm were recorded, consistent with the literature [24-25].

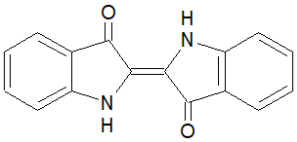

Figure 7. Chemical structure of Indigo carmine.

Indigo carmine absorbs in the UV-VIS region due to the presence of aromatic rings, a carbonyl group, and an amino group in its structure (chromophores). Its color is associated with absorption at 610 nm, which corresponds to the characteristic region of orange, whose complementary color is blue. The absorption bands at 287 and 252 nm in the ultraviolet region are attributed to the amino group and the carbonyl group, respectively [25].

3.1.5. Tartrazine

The absorption spectrum of tartrazine is shown in Figure 8.

The tartrazine has characteristic peaks in the ultraviolet and visible regions. The authors Oancea and Meltzer (2013) and Gobara and Baraka (2014) have reported characteristic absorption bands for tartrazine with maxima at 428 and 257 nm. The absorption spectrum obtained for the tartrazine sample showed absorption

bands with maxima at 427 and 258 nm, which match the literature [26-27].

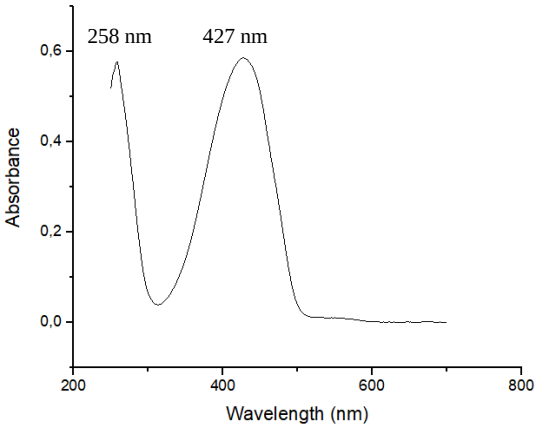

Figure 8. Absorption spectrum of tartrazine.

In the spectrum of tartrazine, the maximum absorption band at 258 nm is characteristic of individual aromatic rings, while the maximum absorption at 427 nm is associated with the groups N=N, C=N and C=O, related to the yellowish color of the dye [27]. The chemical structure of tartrazine is shown in Figure 9.

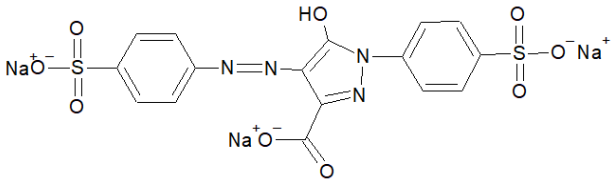

Figure 9. Chemical structure of tartrazine.

3.2. Fingerprint development

The results obtained from the experiments with the fingerprints are shown in the Figures 10-14.

It was observed that the differences in the quality of the latent fingerprints developed are associated with four main factors: the size of the grains, the contrast of color with the surface, the purity of the powders and the roughness of each surface.

Concerning the grain characteristics, it was noted that the finest powders (Spirulina algae, indigo carmine and tartrazine) adhered better to the components of the latent digital than the powders with coarser particles, such as Hibiscus powder and red beet powder. According to the literature, particles with a diameter of around 10 μm are considered ideal for strong adhesion [13]. Furthermore, more uniform powders have been found to yield better results. Grains with varying sizes and colors can interfere with the quality of fingerprint development [28]. Red beet and hibiscus were visually the least homogenous powders in color and size This, in combination with the adhesion factor, made it more challenging to reveal, but still achievable with some positive results.

Regarding the surfaces, it is important that the powder has good contrast with the background color to improve the visualization of fingerprint lines [29]. As can be seen in Figure 10, the color of the Formica is similar to the color of hibiscus and red beet, making visualization difficult. In the case of varnished wood, there was also a problem with the visualization of fingerprints developed with red beet, hibiscus, and tartrazine, as shown in Figure 11, because the contrast was not ideal. Moreover, surface roughness interfered with the results, as some grains can get trapped in the interstices of the structure [30]. Therefore, the rougher and more irregular the surface, the less clear the impression revealed by the dust method. This can be observed when comparing the fingerprints revealed on raw metal, as shown in Figure 12, which is the roughest surface in the work, with those on galvanized metal (Figure 13) and glass (Figure 14), which are the two smoothest surfaces.

In addition to this, there are still some factors to consider in every research involving volunteers, such as the conditions to which each person is subject. Variables such as age, gender, metabolism, diseases, and external substances that the person may have come into contact with on the day of the experiments also influence the results, as they affect the composition of the fingerprint [4].

Fig. 10. Fingerprints developed on rough formica with different powders: [a] red beet; [b] hibiscus; [c] spirulina algae; [d] indigo carmine; [e] tartrazine.

Fig. 11. Fingerprints developed on varnished wood with different powders: [a] red beet; [b] hibiscus; [c] spirulina algae; [d] indigo carmine; [e] tartrazine.

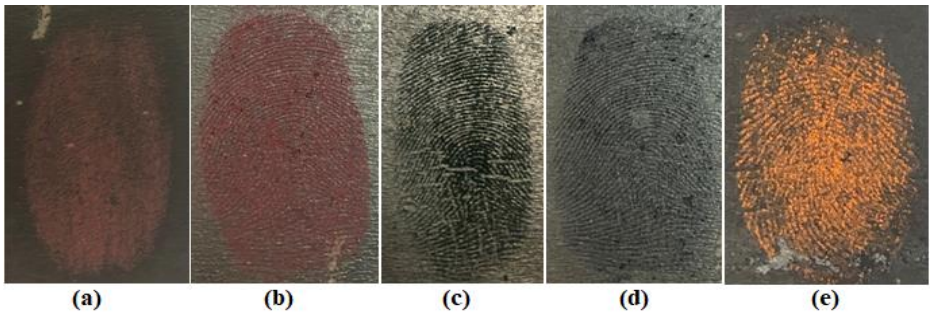

Fig. 12. Fingerprints developed on raw metal with different powders: [a] red beet; [b] hibiscus; [c] spirulina algae; [d] indigo carmine; [e] tartrazine.

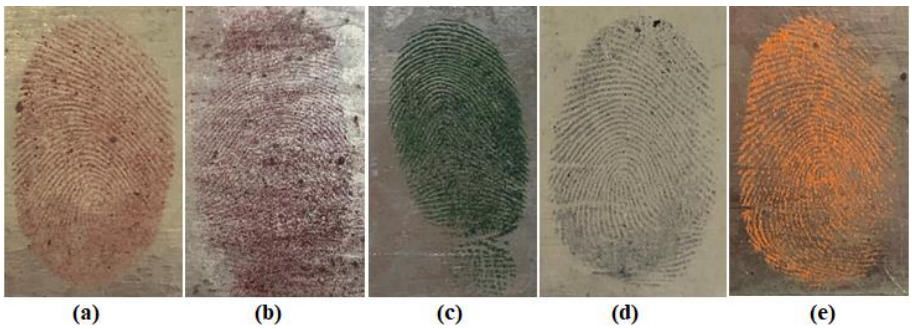

Fig. 13. Fingerprints developed on galvanized metal with different powders: [a] red beet; [b] hibiscus; [c] spirulina algae; [d] indigo carmine; [e] tartrazine.

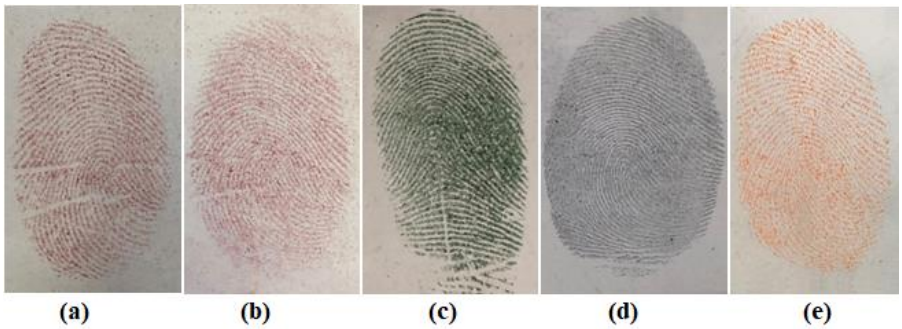

Fig. 14. Fingerprints developed on glass with different powders: [a] red beet; [b] hibiscus; [c] spirulina algae; [d] indigo carmine; [e] tartrazine.

3.3. Green Chemistry

The first of the 12 principles of Green Chemistry demonstrated in this work is prevention, as it has produced no waste that requires treatment or cleaning. In this project, the samples used for UV-Vis spectrophotometric characterization were all prepared using distilled water or ethyl alcohol, adhering to the principle of using safe solvents and auxiliaries [9,31].

Furthermore, the application of ultrasound as an energy source in the pigment extraction process aligns with the principle of energy efficiency. Additionally, the use of some natural products that are technically and economically viable is in line with the principle of utilizing renewable feedstocks [9,31].

Finally, this work primarily focuses on ensuring inherently safe chemistry to prevent accidents. The main objective of the project is to replace the currently used

powders by papilloscopists with less toxic alternatives, thereby reducing the risks they face [9,31].

4. CONCLUSION

It can be concluded from the present study that the powders made from food dyes and natural products such as red beet, hibiscus, algae spirulina, indigo carmine, and tartrazine can be used as a greener alternative to the current fingerprint and other ridge skin impressions developers used in criminal investigations. In addition, it was possible to characterize the dye compounds present in each of the powders used in this research by spectrophotometry in the UV-Vis region.

Furthermore, based on all the tests conducted, it is possible to conclude that finer and more uniform powders develop higher-quality fingerprints. Besides that, it was demonstrated that there is an importance in having good contrast between the color of the powder and the color of the surface, and the powder technique yields better results on smoother surfaces.

Moreover, the authors are aware of the importance of green chemistry and believe it is important to emphasize that this work is aligned with it, as it encompasses the following principles: prevention, the use of safe solvents and auxiliaries, design for energy efficiency, the use of renewable feedstocks, and inherently safe chemistry for accident prevention.

In conclusion, the authors believe that this work serves as a foundation for future research aimed at replacing toxic papilloscopic developers with products that better adhere to the principles of Green Chemistry.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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