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Temporal Estimation of Latent Fingerprint Analysis: Development of Spectroscopic and Spectrometric Methods with Multivariate Approaches for Forensic Routine.

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Introduction

Fingerprints are a complex biological matrix and it composition can varies greatly depending on the donor and also extrinsic factors[1]. The age of latent is one of the most challenging problems in forensics[2]. The fingermark aging can be defined as the relative or absolute attribution of its age, consisting mainly of determining the time interval that separates the elements analyzed to the current date or determining the relative order of elements in the past, called chronology of events[3]. The development of suitable methods of detecting fingermarks aging may represent an improvement in criminal procedures[4]. In this sense, this doctoral research aim to develop a method using infrared spectroscopy with the use of chemometric tools and a mass spectrometry method with chemical imaging of samples for application in forensic routine.

Experimental section

Review Papers: A bibliographical survey on the subject was carried out, which resulted in two systematic review articles, the first focus on analytical methods applied to fingermark and the second focus on the most important components present fingermarks. The reviews analyzed papers from the last decade and were organized in tables by theme and relevance. **Spectroscopy Method**: Latent fingermarks were collected from three Caucasian female donors. The deposition protocol comprised the collection of the fingermark of the right thumb on a reflective microscope slide provided by Agilent Technologies, previously cleaned with ethanol, exerting a force between 1.0 and 1.5 kg for 15 seconds. Two samples were collected, one from the right thumb and other from the right index finger. The monitored times in the analysis were: hour zero, 3 days, 4 days, 5 days and 6 days. The analyzes were performed on the Cary 630 FTIR Spectrometer (Agilent Technologies) and the results were analyzed using Matlab® software. **Mass Spectrometry Method:** Latent fingermarks were collected from two donors, one male and one female, from the thumb of the dominant hand. The collection was carried out on the same day, repeating the procedure 8 times for each donor (16 analyses), with intervals of 30 minutes between collections. Analyzes were performed at 8 times (0, 1, 2, 7, 15, 21, 30, 50 days) with MALDI source in FT-ICR Mass Spectrometry equipment, (Bruker Daltonics), using 2 $mg.mL^{-1}$ CHCA as matrix.

Results and Discussion

Review Papers: The review was published in the Journal of Forensic Sciences[5] and the main results were: 62% of the selected articles used mass spectrometry as the principal or associated technique for fingerprint analysis, followed by 16% for spectroscopic methods. Also, it is possible to observe a growing use of chemical imaging in this field. The fingermark components review is in the final stage, but it can say that there are important components that can be found in this samples, such as squalene, cholesterol and other fatty acids, as well as contaminants that are strongly present and it can be an important accessory factor to help in fingermark aging surveys. **Spectroscopy Method:** Fingermark Analysis by Fourier Transform Micro Infrared Spectroscopy Using Chemometric Tools was published in the Brazilian Journal of Analytical Chemistry[6] and had as main results: even with different donors, the IR spectrum was similar, although humans did not secrete fatty acids in the hands, these are the most predominant signals on the spectrum; the chemometric analysis made it possible to differentiate sex

donors, as well as aged samples. **Spectrometry Methods:** The results are being processed for a better evaluation, but, it was possible to perform chemical imaging from the collected spectra data from the monitored ions until 50-day aged samples.

Conclusions

From the review studies, the development and advancement of analytical techniques for fingermark analysis is undeniable, a fact that was possible to prove in practice with the developed methods of FTIR and MALDI. The studies carried out allowed separating samples by time, enabling a technique suggestion for temporal estimation of this forensic evidence. These studies need to continue for to apply in the routine of forensic laboratories.

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