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Development of a printed quality control test strip for the analysis and imaging of fingermark composition

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ABSTRACT

In the last decade, there have been many scientific developments regarding the use of mass spectrometry to analyse the composition of fingermarks. In this context, the development of a dedicated quality control test strip would benefit the forensic community by providing a way to assess the reproducibility of the measures as well as to perform inter-laboratory comparisons. To accomplish this goal, the use of a chemical printer offers the possibility of combining a visual template with artificial fingerprint secretions. The design of the quality control test strip as well as the preliminary assessment of its performance with fingermark detection reagents and matrix-assisted laser desorption-ionisation combined with mass spectrometry imaging (MALDI-MSI) are presented in this paper. The chosen template combines two geometric patterns intended to help assess the chemical analysis (full square) and imaging (lined square) capabilities of the instrument. The artificial secretion is composed of two distinct solutions: artificial sweat and artificial sebum. The printing reproducibility and chemical homogeneity of the quality control test strips were assessed in two ways: (1) using MALDI-MSI, the printed pattern was analysed and the *m/z* values compared to the reference list based on the artificial secretion composition, and (2) using two common fingermark detection techniques, the printed pattern was processed using an amino acid reagent (ninhydrin) and a lipid stain (Oil Red O). Overall, the results highlight the potential of a printed quality control test strip for the assessment of the quality of fingermark detection techniques as well as the possibility of performing quality monitoring of mass-spectrometry-based techniques over time.

1. Introduction

Fingermarks are one of the most ancient methods of individualisation and are still commonly found in crime scenes or on related items. To date, many techniques have been developed to detect fingermarks [1], but there are still a significant number of fingermarks that remain undetected or unexploited due to their poor quality [2]. Consequently, the development of new methods to improve fingermark detection is of particular interest in the academic field as well as among government institutions. In the last decade, a considerable number of analytical techniques were developed for fingermark analysis, including a wide range of mass-spectrometry-based techniques [3]. Among those techniques, matrix-assisted laser desorption-ionisation combined with mass spectrometry imaging (MALDI-MSI) appears the most promising, with more than 35 publications on it during the last decade [1,3,4].

MALDI-MSI relies on the desorption, ionisation and vaporisation of the analytes contained in a specific sample followed by the detection and characterisation of the mass-to-charge ratio (*m/z*) of each molecule detected.

Practically, the analysed specimen is put on a glass slide and coated with a dedicated matrix. The matrix then absorbs the laser wavelength and allows the ionisation of the analytes. The produced ions are then detected by a mass spectrometer, which records the *m/z* values and the signal intensities corresponding to each pixel of the scanned area. Hence, each pixel is associated with a spectrum, which contains all of the ions detected at the pixel coordinates. In imaging mode, the difference of intensity between pixels allows for the reconstruction of the spatial distribution of each type of ion [5]. For readers interested, additional information about MALDI-MSI can be found in the literature [6,7]. In the context of fingermarks, MALDI-MSI allows for the simultaneous detection and mapping of

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numerous compounds present in the secretion residue, hence enabling imaging of the ridge pattern and the acquisition of chemical information linked to fingermark composition. The technique is currently recognised as a Category C technique by the Home Office [8], which means that MALDI-MSI is at "a development stage exhibiting potential as an effective fingermark recovering process".

In the literature, MALDI-MSI has been successfully applied to the detection of various contaminants (e.g., explosives, drugs, condom lubricants) initially present on the fingertips [4,9–13], the reconstruction of the ridge pattern [13–25] and the differentiation of individuals [5]. Recently, the technique has also provided valuable information when applied to fingermarks related to actual cases [26]. Overall, recent scientific developments are promising but raise the question of the reliability of the method. Indeed, in every validation process, analytical standards are used to ensure the validity of the technique. However, no quality control test strip has been mentioned so far regarding the analysis of fingermarks with MALDI-MSI or other mass-spectrometry-based techniques.

The lack of standardisation in the fingermark detection field has been highlighted for several years now [27,28]. In 2014, the International Fingerprint Research Group (IFRG) published guidelines for researchers willing to work with fingermarks [29]. These recommendations apply mostly to fingermark detection techniques, but they also highlight the necessity of implementing standardised quality control in order to guarantee the consistency of the results and the ability to compare research between laboratories.

Some studies have already contributed interesting leads towards the development of a reproducible quality control test strip for mass spectrometry techniques. In 2009, Schwarz et al. [30] described a printed test strip created with a modified inkjet printer and an artificial solution of amino acids. This quality control test strip was designed to be used in routine work to assess the validity of the amino acid reagents before their use. Regarding mass-spectrometry-based techniques, the composition of a quality control test strip needs to be more complex to cover the wide range of *m/z* analysed (e.g., 50–2000), including not only amino acids but also triglycerides, free fatty acids and cholesterol. The optimal composition of a quality control test strip must be based on the mass range selected for the mass spectrometry analysis and must be adapted if needed depending on the range and type of molecules targeted. Time is also an important parameter to consider for the design of the quality control test strip. The verification of the different *m/z* and their intensities must be fast and efficient and should not take more than one hour.

To date, commercially available fingermark simulants have been proved to be unsuitable for mimicking fingermark residue, mostly due to their chemical composition [31,32]. Currently, the most complete formulation mimicking a natural fingermark is that published by Sisco et al., which combines an artificial sweat solution (19 compounds) with an artificial sebum emulsion (23 compounds) [33]. In their article, the authors suggest the use of stamps to apply the artificial residue on surfaces of interest, mostly due to the creamy nature of the final emulsion. However, the amount of solution transferred onto such stamps is not entirely reproducible and induces a great deal of variability, which is not suitable for quality control test strip. Pipetting was another solution suggested in the literature, but it also has some major drawbacks, such as the poor reproducibility and homogeneity of the depositions [31], as well as a limited spatial distribution (spots). Thus far, printing an artificial emulsion seems to be the best method to obtain a reproducible and homogenous quality control test strip for fingermark detection techniques. Similar to the method in Schwartz et al., the modification of an inkjet printer can allow for the accomplishment of this goal. However, this implies that only thin, flat and flexible substrates can be used (such as office paper), as well as non-viscous or overly volatile solutions [30,31]. An alternative could consist of using a chemical printer (such as the Dimatix Materials printer from Fujifilm). Such a device has been successfully tested by Janssen-Bouwmeester et al. [34] as well as by Jeanneret et al. [35] with artificial sweat to develop amino acid reagent test strips. The main advantages of a chemical printer over a modified inkjet printer are the possibility of printing on surfaces of different thicknesses and rigidities as well as the possibility of using chemicals that are not suitable for modified inkjet printers. Regarding the design of the printed control itself, many patterns have been tested, such as spots, full squares, full circles, lined circles or fingermark reproductions [34,35].

To attempt to rectify the lack of quality control test strip in the context of fingermark research and especially for mass-spectrometry-based analysis, the present study aims to create a printed quality control test strip that may be used for two purposes: (1) to monitor the quality over time of mass-spectrometry-based techniques such as MALDI-MSI to guarantee the consistency of the results and (2) the validity of fingermark detection reagents before their use. To accomplish this goal, it was decided to use a combination of both eccrine- and sebum-based secretions that would be printed on paper using a chemical printer. The pattern of the quality control test strip has been designed to assess both the chemical analysis and imaging capabilities of mass-spectrometry-based instruments with imaging capabilities such as MALDI-MSI. The artificial secretions used in this study are derived from those in Sisco et al. [33] and have been adapted to fit the mass range of the instrument as well as to be time efficient. It is expected that this research will promote the adoption of dedicated quality control test strip in fingermark research and hence facilitate comparison between studies performed in different laboratories.

2. Materials and methods

2.1. Materials

Acetonitrile (ACN), trifluoroacetic acid (TFA) and ultrapure water (H_2O) were purchased from Biosolve. The chemicals used to create the artificial solutions are referenced in Tables 1 and 2. They were all purchased from Merck/Sigma-Aldrich. The maximum purity was ordered for each compound (varying between 96% and 99%).

Hexane, 2-propanol, sodium hydroxide (NaOH), hydrochloric acid (HCl), methanol, ethyl acetate, petroleum ether, Oil Red O and

Table 1
Chemical composition of the Sisco artificial sweat [33]. (*) compound also present in the simplified artificial sweat. Abbreviation: ambient temperature (AmbT).

Chemicals	Quantity (mg)	Storage
Inorganic Salts		
Potassium chloride	1400	AmbT
Sodium chloride	1300	AmbT
Sodium bicarbonate	250	AmbT
Ammonium hydroxide	175	Fridge
Magnesium chloride	40	AmbT
Amino Acids		
Serine	275	AmbT
Glycine	135	AmbT
Ornithine	110	AmbT
Alanine	80	AmbT
Aspartic acid	40	AmbT
Threonine	40	AmbT
Histidine*	40	AmbT
Valine	30	AmbT
Leucine	30	AmbT
Other		
Lactic acid	1900	AmbT
Urea	500	AmbT
Pyruvic acid	20	Fridge
Acetic acid	5	AmbT
Hexanoic acid	5	AmbT

Table 2
Chemical composition of the Sisco artificial sebum [33]. (*) compounds also present in the simplified artificial sebum. Abbreviation: ambient temperature (AmbT).

Chemicals	Quantity (mg)	Storage
Free Fatty Acids		
Hexanoic acid	50	AmbT
Heptanoic acid	50	AmbT
Octanoic acid	50	AmbT
Nonanoic acid	50	AmbT
Dodecanoic acid*	50	AmbT or Fridge
Tridecanoic acid	50	Freezer
Myristic acid*	50	AmbT
Pentadecanoic acid	50	AmbT
Palmitic acid	55	AmbT
Stearic acid	55	Fridge
Arachidic acid*	50	AmbT
Linoleic acid	55	Freezer
Oleic acid*	55	AmbT
Triglycerides		
Triolein*	275	Freezer
Tricaprylin*	20	AmbT
Tricaprin*	20	Freezer
Trilaurin*	20	Freezer
Trimyristin*	20	Freezer
Tripalmitin*	20	Freezer
Other		
Squalene*	120	Fridge
Cholesterol*	30	Freezer
Cholesterol n-decanoate	40	AmbT
Cetyl palmitate	155	AmbT

α-cyano-4-hydroxycinnamic acid powder (α-CHCA) were also obtained from Merck/Sigma-Aldrich.

Ninhydrin crystals were purchased from BVDA (Netherlands). Liquid red food colouring (composition: E120, water and E202) from Hobby Décor was purchased at Manor (Switzerland).

The chemical printer (Dimatix Materials Printer DMP-2850), dedicated cartridges, cleaning pads and syringe needles were purchased from Fujifilm USA. Syringes of 3 mL were purchased from VWR. Superfrost Plus glass microscope slides (75 ×25 x 1 mm) were obtained from Thermo Fisher Scientific. White colour copy paper (A4, 200 gm^2, 21 ×2 9.7 cm) was obtained from Mondi (United Kingdom). The pH meter and electrode InLab Expert was bought from Mettler Toledo.

2.2. Instrumentation

2.2.1. Chemical printer

The printing of the quality control test strips was conducted on a piezoelectric printing system, Dimatix Materials Printer DMP-2850 from Fujifilm USA [36]. The Dimatix Drop Manager window was used to control the printer and set the different printing parameters.

Regarding the cartridge settings, for both the artificial sweat and sebum, the substrate thickness (cartridge height) was set to 300 µm, the DI Water waveform was used and the cleaning cycle Purge 1.0 s was applied at the start of each printing cycle. No cleaning was performed during printing or while idle. For the artificial sweat layer, if more than six patterns were printed in a row, a Purge 1.0 s cleaning cycle was conducted every four minutes during printing to prevent the nozzles from clogging.

The cartridge and the paper to be printed were kept at ambient temperature (21–25 °C). Finally, the other parameters were set as follows: template dimensions – 80 × 51 mm, drop spacing – 10 µm, one printed layer for each solution. No heating was applied to the substrate or the cartridge.

2.2.2. MALDI-MSI

All of the analyses were conducted on the hybrid mass spectrometer MALDI Linear Trap Quadrupole (LTQ) Orbitrap XL from Thermo Fisher Scientific, which was equipped with a linear trap and coupled to an Orbitrap [37]. The ion source was an azote (N_2) laser with a wavelength of 337 nm, a spot size of 50 × 60 µm and a laser repetition rate of 60 Hz with a pulse duration of 3 ns. The instrument was used in positive ionisation mode. The number of laser shots was set to 4 with an energy of 4 µJ. The analysed masses ranged from 100 to 2000 *m/z*, hence encompassing many polar molecules, including lipids, amino acids, proteins and peptides. The spatial and spectral resolutions were set to 100 µm and 60'000, respectively. The plate had a raster movement. Automatic gain control and automatic spectra filtering were disabled. The Tune Plus window from Thermo Fisher Scientific [37] was used to control the instrument and acquire the data. The instrument was used in imaging mode and set to acquire a square area of several mm^2 (between 10 and 20). By doing so, it was possible to gather information over a section in an acceptable scanning time of a few minutes.

2.3. Method

2.3.1. Artificial sweat

The artificial sweat solution was prepared following the recipe from Sisco et al. [33]. The 19 compounds presented in Table 1 were dissolved in 990 mL of deionised water. The solution was sonicated for 15 min. The pH of the solution was adjusted to 5.5 by adding saturated NaOH solution and/or HCl > 99%. Deionised water was then added to bring the solution to a final volume of 1 L. The solution was then sonicated for 15 additional minutes.

A small amount of red food colouring was added to the solution (6 mL to 1 L of solution) in order to visually check the pattern once printed. The resulting artificial sweat solution was transferred into a brown bottle, its cap covered with Parafilm, and stored in a fridge (4 °C).

Regarding the mass range of the MALDI-MS instrument, only histidine could be detected. Therefore, a solution of histidine was created. For this simplified artificial sweat, 40 mg of histidine was diluted into 1 L of deionised water. Similar to the artificial sweat solution, 6 mL of red food colouring was then added to the solution. No pH adjustment was made. The resulting solution was stored similarly to the artificial sweat.

The concentration of the obtained solutions was labelled C_0 and was used to prepare dilution series using deionised water.

2.3.2. Artificial sebum

The Sisco artificial sebum was prepared following the recipe from Sisco et al. [1]. The 23 chemicals presented in Table 2 were combined in a 20 mL amber vial.

The vial was sonicated for approximately 10–15 min to ensure the melting and mixing of all of the compounds.

At ambient temperature, the resulting artificial sebum was creamy. To ensure its printability, the prepared sebum (total weight of 2780 mg) was dissolved with 2780 µL of a 1:1 mix of hexane and 2-propanol. The concentration of the obtained solution thus obtained was labelled C_0 and was used to prepare dilution series using the hexane:2-propanol mixture.

All of the dilutions were made from the C_0 artificial sebum solution. The solvent was the same mix of 1:1 hexane and 2-propanol.

The solution was put into 20-mL amber vials, its cap covered with Parafilm, and stored in a fridge (4 °C).

Regarding the MALDI-MSI range of analysis, a simplified sebum solution was prepared. In this simplified formulation, 12 compounds representative of each chemical category were mixed: four fatty acids, six triglycerides, cholesterol and squalene (see Table 2).

2.3.3. Template design and printing protocol

To fulfil the objectives of this study, an ad hoc pattern was designed using the printer software. The pattern included three

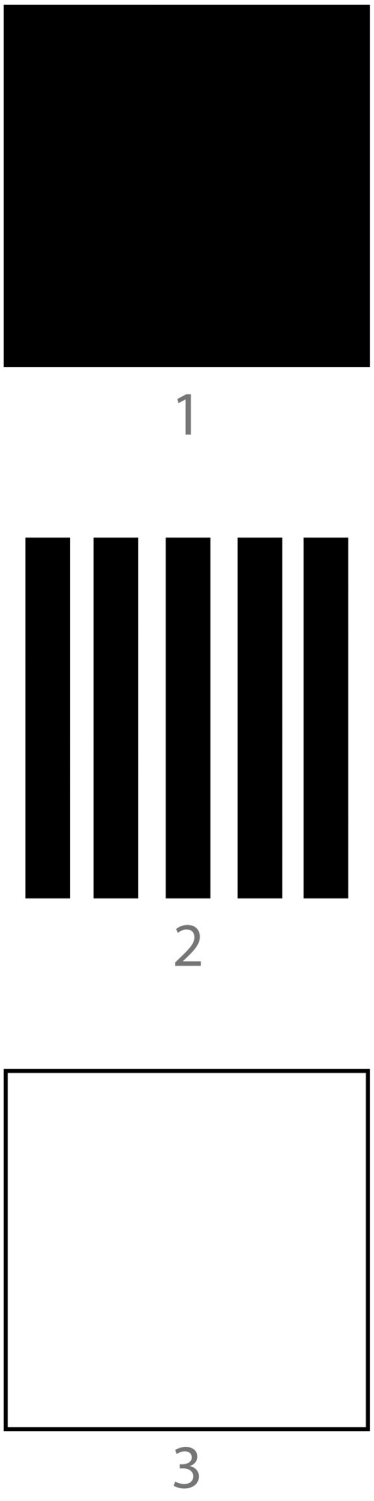

Fig. 1. Pattern of the printed quality control test strip.

distinctive parts (Fig. 1): (1) a full square, used to assess the detection capabilities of the mass spectrometry technique; (2) a lined square, used to check the imaging capacities of the instrument and (3) a blank square, in which nothing was to be printed so that it could be used as an analytical blank (i.e., substrate only).

Printing an actual emulsion remains a technical challenge. For this reason, the artificial sweat and sebum were printed successively as two superimposable layers. For each pattern printing, one cartridge was used for each artificial solution. The second layer was printed a few minutes (5–10 min) after the first one.

The cartridge parameters are presented in Table 3.

Regarding the substrate settings, the thickness was set to 300 µm.

2.3.4. Ninhydrin and Oil Red O

Ninhydrin was prepared according to Champod et al. [38]: 4 g of ninhydrin was dissolved in 20 mL of methanol and 10 mL of acetic acid. Once the dilution was complete, 70 mL of ethyl acetate and 900 mL of petroleum ether were added to the solution. The working solution was stored in an amber bottle and kept away from light. The following application protocol was carried out: each printed template was briefly immersed in the working solution, air dried a few seconds and placed in a humidity chamber (80 °C and 65% relative humidity) for 10–20 min. The reliability of the working solution was tested beforehand with a commercially available amino acid test strip (SEMA GmbH, Germany).

The Oil Red O recipe was adapted from Beaudoin [39]: 385 mL of methanol was mixed with 115 mL of a sodium hydroxide solution (4.6 g NaOH in 115 mL distilled water). Then, 0.77 g of Oil Red O was added to the mixture. Finally, the working solution was filtered and stored in an amber bottle away from light.

No buffer rinsing was carried out [40].

The following application protocol was carried out: each printed template was immersed in an adequate volume of working solution kept under orbital shaking for 30 min. To avoid excessive methanol evaporation during the detection process, the dish was covered with a glass plate. After 30 min, the templates were removed from the solution and rinsed in deionised water for 10–20 s. Finally, they were dried in an oven (50 °C) for 30 min. The reliability of the working solution was tested beforehand using sebum-rich fingermarks deposited on white paper (the same as used for the quality control test strip).

The ninhydrin and Oil Red O processed items were observed under white light and recorded using a Canon EOS 6D camera equipped with a 50-mm macro lens.

2.3.5. Conservation time

In order to assess the conservation time of the printed quality control test strip, four patterns were printed with the optimal concentration determined for each artificial solution (Sisco's solutions that were one year old, freshly prepared Sisco's solutions and simplified solutions).

Each quality control test strip printed was cut into three parts and developed with solutions of ninhydrin and Oil Red O. For each solution, each printed test strip was analysed on four different days spread over one month (1 day old, 3 days old, 1 week old and 3 weeks old) in order to observe the evolution of the pattern over

Table 3
Dimatix cartridge parameters.

Waveform	Cartridge	Cleaning Cycles
Waveform model: DI Water Jetting voltage: 25.00 for all the jets Tickle control: 23 kHz	Cartridge temperature: Ambient Meniscus vacuum: 4.0 Jets to use: 16 Cartridge print height: 1.0 mm	Start of printing: Purge 1.0 s During printing: None End of printing: None While idle: None

time. Each printed test strip was stored at ambient temperature in the dark.

2.3.6. MALDI-MSI

Since the original sweat and sebum solutions from Sisco et al. were highly concentrated, the concentrated solutions and dilution series were considered to determine the optimal concentration for MALDI-MSI analysis.

1.5 µL spots of each concentration were manually deposited on MALDI glass slides for each artificial solution.

Once the best values for manual deposition were determined, the selected concentrations were printed to check if the optimal values remained the same or needed to be adapted for the printing process.

1.5 µL spots were also deposited manually on both glass slides and paper with the optimal concentration selected for the printing process in order to investigate the influence of the substrate on detection.

The optimal concentration values determined for printing and manual deposition were applied for both Sisco's formulations and the simplified ones, as the simplified formulations respect the quantities defined by Sisco et al. [33]. As described in the instrumental section, all of the printed test strips as well as the manual spots were aged for 24 h before being analysed by MALDI-MSI.

Regarding the assessment of the reproducibility of the quality control test strip, up to two test strips were analysed per week with the MALDI-MSI instrument, for a total of 12 weeks.

All of the analysis were done in imaging mode, which meant that 100–150 pixels of the full square pattern were acquired. Thus, the intensity values reported for each selected compound were average intensity values of the *m/z* of interest over all of the pixels analysed. When two test strips were analysed in a week, the mean of the intensities was taken for the histograms.

2.3.7. Data processing

The data obtained from the MALDI-MSI were first visualised using XCalibur software (Thermo Fisher Scientific; version 3.1). Then, they were extracted and exported using ImageQuest software (Thermo Fisher Scientific; version 1.1.0).

Regarding the spectral analysis, the peak picking and the generation of intensity tables were performed with homemade R code using the MALDIquant and MALDIquantForeign packages. Peak picking is an approach that allows peak detection in one or several spectra. Only the peaks characterised by an intensity and width above the minimum values set are selected. Then, for each sample, the intensities of each *m/z* for each pixel were gathered in a.csv file.

For the MALDI-MS imaging, the final images were generated through MSiReader software (FTMS Laboratory for Human Health Research – NS State University, USA) [41].

The characterisation of compounds was achieved by precisely matching the mass values using the free online database Metlin (https://metlin.scripps.edu) [42]. The mass error was set to 10 ppm.

3. Results

3.1. Compound selection and adducts

The *m/z* of the compounds present in the solutions of Sisco et al. were searched in the acquired MALDI-MS spectra. The goal was to select enough compounds that were representative of the artificial solutions to best cover the mass range analysed (*m/z* 100–2000) with the instrument in this study. After analysing the MALDI-MS spectra of the Sisco's eccrine and sebum solutions, 13 compounds were retained (Table 4) to create the simplified solutions that corresponded best to the mass range of the MALDI-MS instrument.

For amino acids, only histidine could be detected as the other amino acids were below the mass range analysed (< *m/z* 100).

Table 4
Compounds selected for the simplified quality control test strip with their corresponding mass over charge (*m/z*) and associated adduct.

Compounds	*m/z*	Adduct type
Amino Acid		
Histidine	156.08	[M+H]
Free Fatty Acids		
Oleic acid	283.26	[M+H]
Arachidic acid	311.29	[M-H]
Dodecanoic Acid	201.18	[M+H]
Triglycerides		
Triolein	907.77	[M+Na]
Tricaprylin	493.35	[M+Na]
Tricaprin	577.44	[M+Na]
Trilaurin	661.54	[M+Na]
Trimyristin	745.63	[M+Na]
Tripalmitin	829.73	[M+Na]
Others		
Squalene	433.38	[M+Na]
Cholesterol	369.35	[M+H-H_2O]

Regarding free fatty acids, oleic acid and arachidic acid were selected because of their high intensity in the spectra as well as their non-complex adducts. Dodecanoic acid was also kept as it is part of the free fatty acid that has been previously detected by MALDI-MSI in several studies [17]. For triglycerides, all of them were highly detectable. The selected compounds were an adequate representation of the analysed mass range to estimate the capacity of the instrument to detect this class of compounds within a reasonable time of analysis.

Overall, the selected compounds, considered for the simplified solutions, offered a broad overview of the *m/z* analysed in the mass range selected and could be easily fragmented for identification. Indeed, most of them had also been previously identified with MALDI-MSI in positive mode.

3.2. Dilution choices

The analysis of the dilution series showed that for the eccrine solution, the undiluted (C_0) solution provided the best and most reliable signal. Indeed, with increasing dilutions, the *m/z* of interest (156.08) was not detected, which meant that the limit of detection (LOD) had been reached. These results were applicable both for the manual spots and the printed test strip (Fig. 2).

Regarding artificial sebum, a dilution of C_{500} permitted us to obtain a high and reliable chemical profile intensity for the manual spotting deposition method (Fig. 3).

For the printed test strip, due to the printing process, C_{500} and higher dilutions did not allow for the detection of the majority of the compounds. Therefore, the dilution C_{100} was chosen as the optimal dilution for this substrate, in terms of chemical profile intensity, and was used for the quality control printing on paper (Fig. 3).

Similar results were obtained using the simplified solutions (results not shown) corroborating these conclusions.

3.3. Substrate influence: porous versus non-porous

Since the artificial sebum and sweat spots were deposited on MALDI glass slides and the test strips were printed on paper, the substrate influence was further investigated. Many studies have shown that it is possible to recover fingermarks by MALDI-MSI analyses on various surfaces such as paper and glass [4]. To have representative results, the experiment was repeated on eight different days distributed equally through three months, using the same artificial solutions.

The results depicted in Fig. 4 illustrate that for the same concentration of the artificial solutions (C_{500}), there was a small difference between glass and paper substrates for amino acids

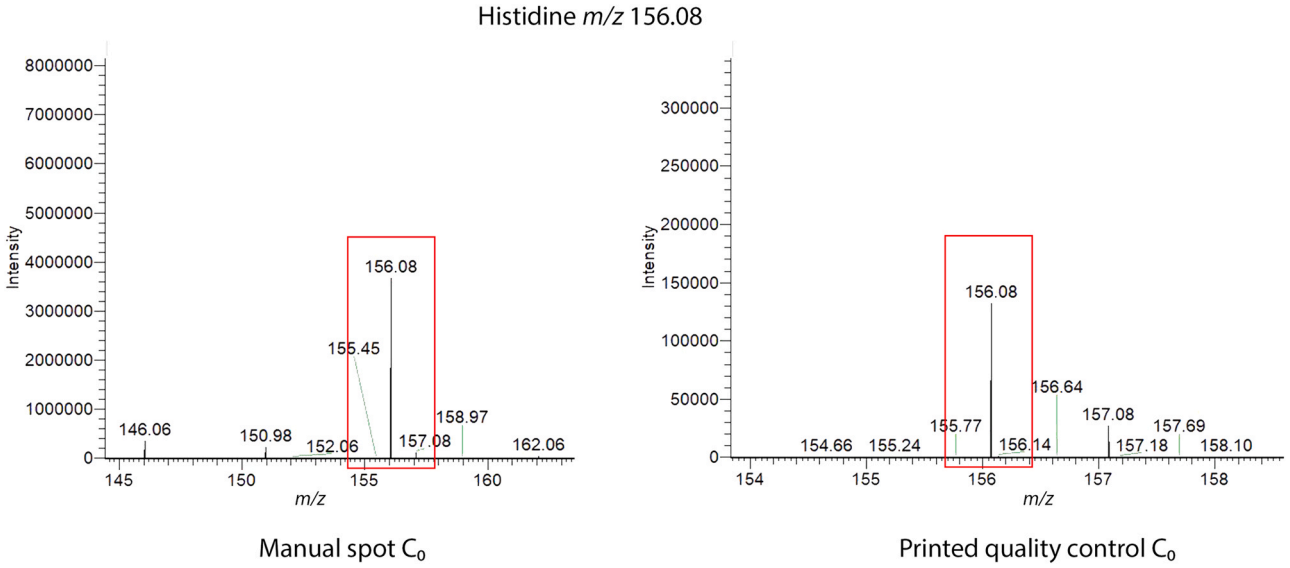

Fig. 2. Intensity of the histidine signal (red box) obtained when analysing a manual spot (left) and a printed quality control test strip (right) made from the undiluted artificial solution from Sisco.

(histidine) and free fatty acids (oleic acid). For triglycerides (triolein), the overall intensity was much lower for paper (60,000–120,000) than for glass (700,000– 80,000,000). The same observations could be made for the other compounds from the free fatty acids and triglyceride chemical classes present in the artificial solutions (data not shown).

In addition, intensity variations were smaller for the paper substrate than for the glass for triglycerides, which meant that cellulose allowed for a better repartition of these compounds on its surface. Regarding triglycerides, a hypothesis is that a migration phenomenon occurs for this class of compounds. Because of the porosity of paper, the molecules seem to be absorbed, resulting in a smaller quantity remaining on the surface of the paper compared with the glass, which is non-porous.

Overall, the surface properties have some influence on the repartition of the compounds on its surface. It appears that porous materials require a more concentrated artificial sebum solution than non-porous substrates. These results also emphasise why a higher concentration had to be used for the sebum solution for the printing of the quality control test strip.

3.4. Pattern homogeneity

To assess the pattern homogeneity, multiple test strips composed of one layer of artificial sweat followed by one layer of artificial sebum were printed and cut in three lengthwise. The left and right sections were processed with ninhydrin and Oil Red O, respectively, while the middle section was left unprocessed (Fig. 5).

Regarding the unprocessed test strip (visible due to the red food colouring), the pattern appeared homogenous. The shape of the squares, the borders, as well as the rectangular lines were clearly defined and visible on the paper.

The same observations could be made after processing with ninhydrin and Oil Red O. Overall, these results emphasised that the printer had a satisfactory resolution and allowed for homogenous distribution of the printed chemicals. Moreover, the superimposing of two layers (sweat and sebum) during the printing process did not seem to affect the homogeneity of the pattern or the reactivity of the underlying amino acids.

Some minor printing issues were encountered, most likely due to the cartridge batches that were used. Indeed, some ninhydrin-processed full squares tended to be less defined at the edges (Fig. 6). The issue could be visually identified due to the use of a diluted dye in the printed solutions. In such cases, the cartridge used for the artificial sweat layer had to be changed. This phenomenon did not occur for the artificial sebum layer.

When it came to MALDI-MS imaging analyses, further conclusions could be drawn regarding the homogeneity of the compound distribution. As an example, the distribution of eight compounds on the lined square of the printed test strip is illustrated in Fig. 7. A limit of tolerance of ± 10 ppm has been set. The scale was automatically adjusted by MSiReader software [41] to display the best contrast between the compound of interest selected and the background.

In all cases, the five lines of the pattern were visible, which meant that the resolution of the printing was precise enough to print thin lines.

If most compounds were imaged with an excellent spatial distribution, inhomogeneities were observed for some compounds. For triglycerides (tricaprylin, tricaprin, trilaurin, trimyristin, tripalmitin and triolein), the spreading was homogenous within each line, and the edges were well defined. But for tricaprylin, a blur could be noticed around the border of the stripes. This phenomenon could be due to the diffusion of this compound in the paper during or after the printing process. Indeed, the edges of the lines were in lighter blue, which meant that tricaprylin was more present at these points. The paper signal could be excluded as a source, as the analysis of the blank square did not emit any signal at this *m/z*. This diffusion effect of triglycerides is not new and has already been observed by O'Neill and Lee with MALDI-MSI on steel and glass surfaces [43]. Overall, these results seem to extend this phenomenon on porous substrates like paper. For histidine (an amino acid), this diffusion effect was even more pronounced. The insides of the lines were almost empty, and all of the molecules were gathered at the edges. It is well known that amino acids tend to migrate from several microns down in the paper [44]. However, here it appeared that histidine was repelled at the borders of the lines. Such a phenomenon could be due to the printing process, which deposed more liquid at the edges of the pattern, as seen with the inhomogeneity of the square borders in Fig. 6. The lipid layer is not a cause, as it occurred also when only the artificial amino acid layer was printed. This phenomenon could also be observed in Fig. 5 after the application of ninhydrin reagent. The purple colouration was more intense at the edges of the patterns.

Finally, for cholesterol, the five stripes were distinguishable but not homogenous at all (Fig. 7). One hypothesis is that the compound

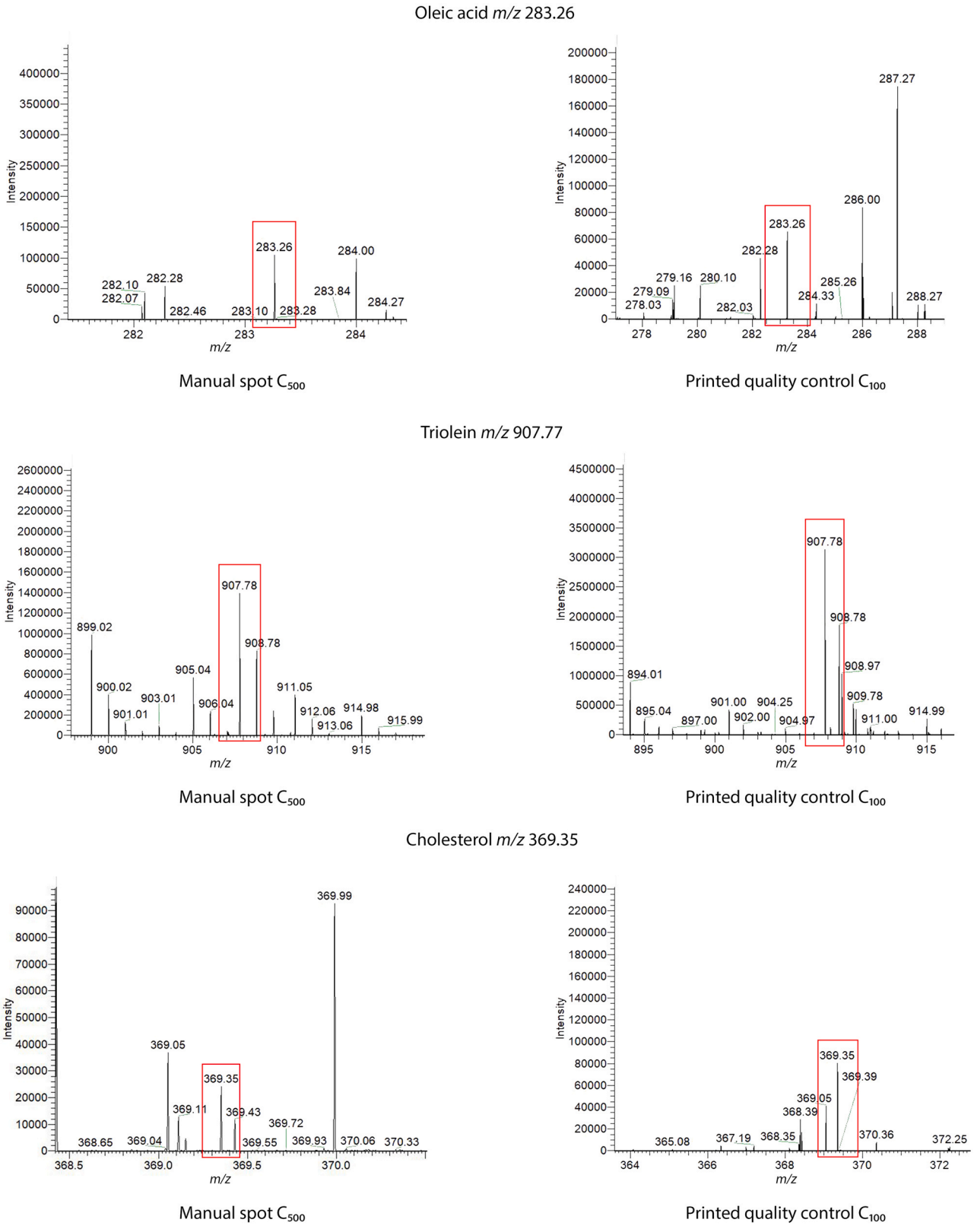

Fig. 3. *m/z* spectra obtained for manual spots (left) and printed quality control test strip (right) for oleic acid, triolein and cholesterol at the indicated concentrations.

itself is blocked by the jetting nozzles because the printing parameters need to be further optimised for this category of molecule. Since the detection of cholesterol was performed on manual spots, a detection failure may be ruled out.

3.5. Stability over time of the quality control test strips

Regarding the evolution of the pattern over one month, a diffusion in the paper of the sebum can be observed after 7 days, whereas

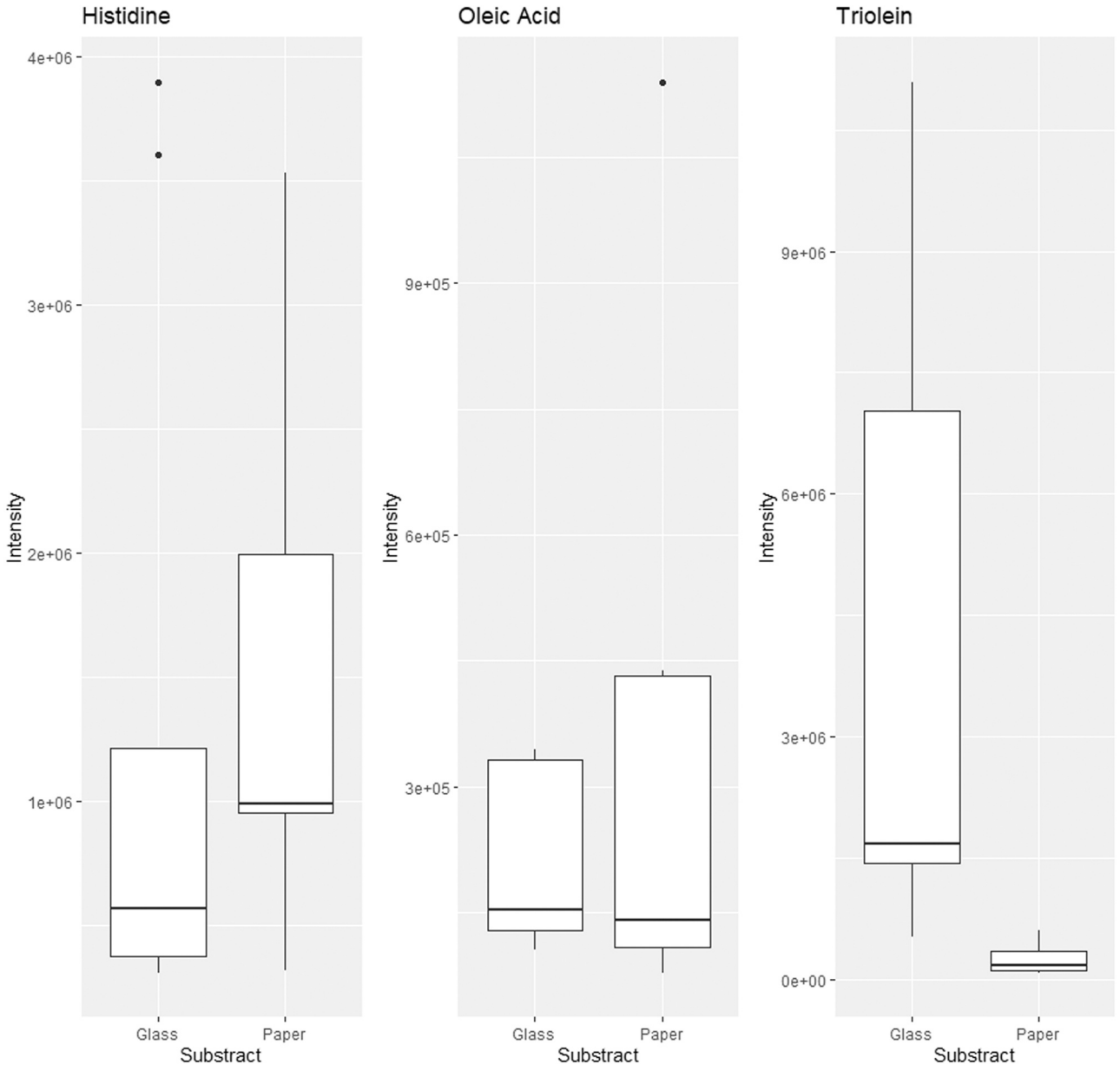

Fig. 4. Comparisons of intensities between glass and paper substrates for histidine (C_0 artificial sweat), oleic acid and triolein (C_{500} artificial sebum) after MALDI-MSI analysis.

the eccrine part remained consistent/homogenous (Fig. 8). Therefore, the printed tests had to be sprayed with the matrix within 7 days after printing with chemical solutions.

Note that the simplified solution was always lighter than that of the formulation from Sisco et al. [33] after ninhydrin treatment because it contained one single amino acid instead of 10, as did the eccrine artificial solution from Sisco et al.

According to Janssen-Bouwmeester et al. [34], printed fingermarks using the formulation from Sisco et al. [33] can be stored and conserved in a freezer, sealed in zipper storage bags, for almost one year without losing quality. More than 30 printed quality control test strips are currently stored in the freezer to corroborate this result. At this point, the results have been successfully verified for five-month-old quality control test strips stored at −25 °C in zipper storage bags. The intensities measured for the compounds of interest presented in Table 4 perfectly fit in the variability observed with 24-hour-aged printed quality control test strip.

3.6. Artificial solution storage

No information regarding the lifetime of the artificial solutions was provided by Sisco et al. [33] Therefore, a comparison between a 12-month-old solution (sweat and sebum) and a one-week-old solution was made to determine how long the solutions could be stored. Furthermore, for each solution, the test strips were analysed on different days to determine their maximum storage time.

The results after ninhydrin and Oil Red O treatments showed that there were no significant differences between the 11-month-old and the freshly made solutions (Fig. 8). These observations indicate that the artificial solutions, either eccrine or sebum, can be stored in the fridge for at least over a year.

When it comes to MALDI-MS(I) analysis, the same trend was observed regarding the age of the solutions. The intensity of the different compounds tended to vary a little between the solutions (old, new, simplified), but we could not assess if the differences

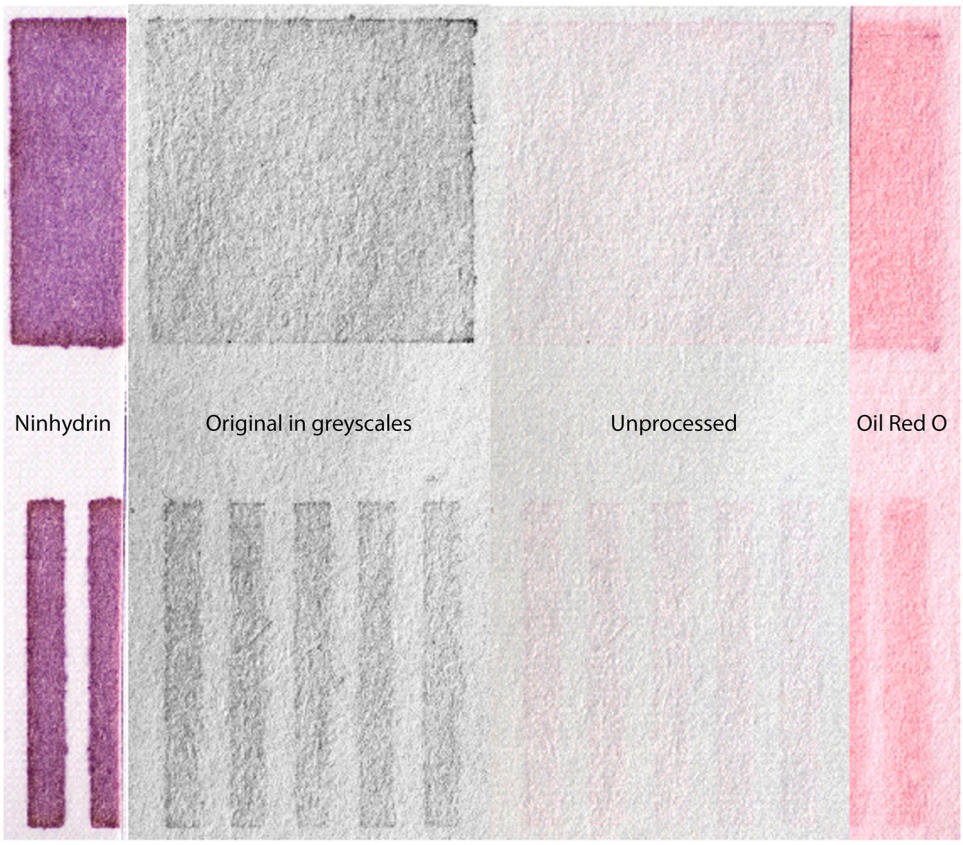

Fig. 5. Illustration of the printed quality control test strip using the sweat and sebum solutions from Sisco, printed successively, before and after ninhydrin (left) and Oil Red O (right) processing.

observed were due to either the printing process or the matrix deposition rather than the age of the solution itself. Indeed, the intensity variations reported entered the normal variation that can be encountered between two printing processes within the same day for the same solution.

Regarding the conservation of the printed quality control test strip itself, an excellent signal of the compounds, with no or non-significant intensity variations, could still be achieved after 10 days if the matrix was sprayed within one day after the printing. It appeared that the matrix tended to prevent the diffusion and the

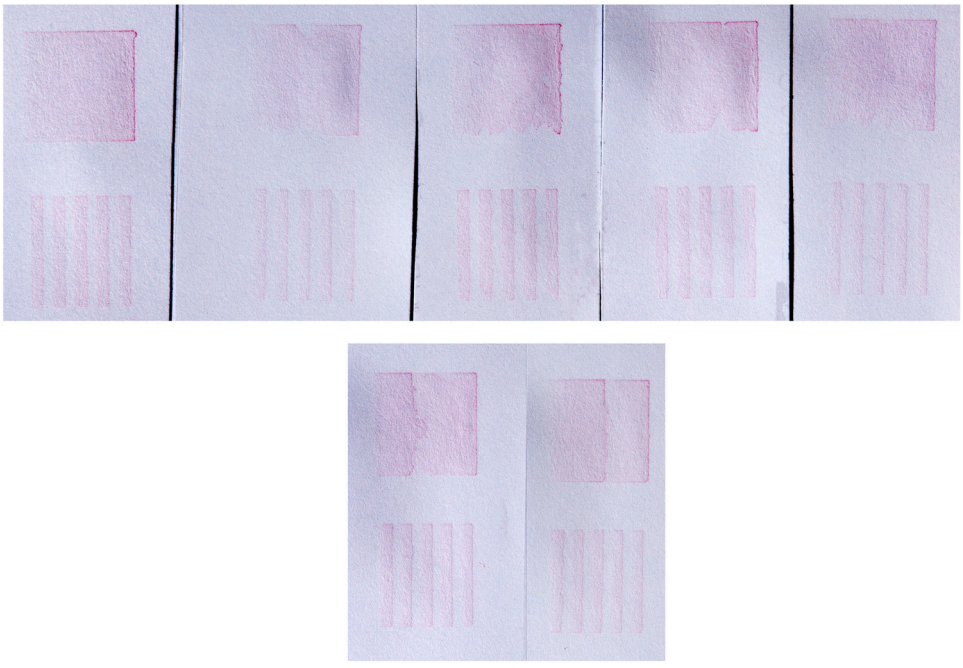

Fig. 6. Illustration of the different printing problems encountered on unprocessed quality controls.

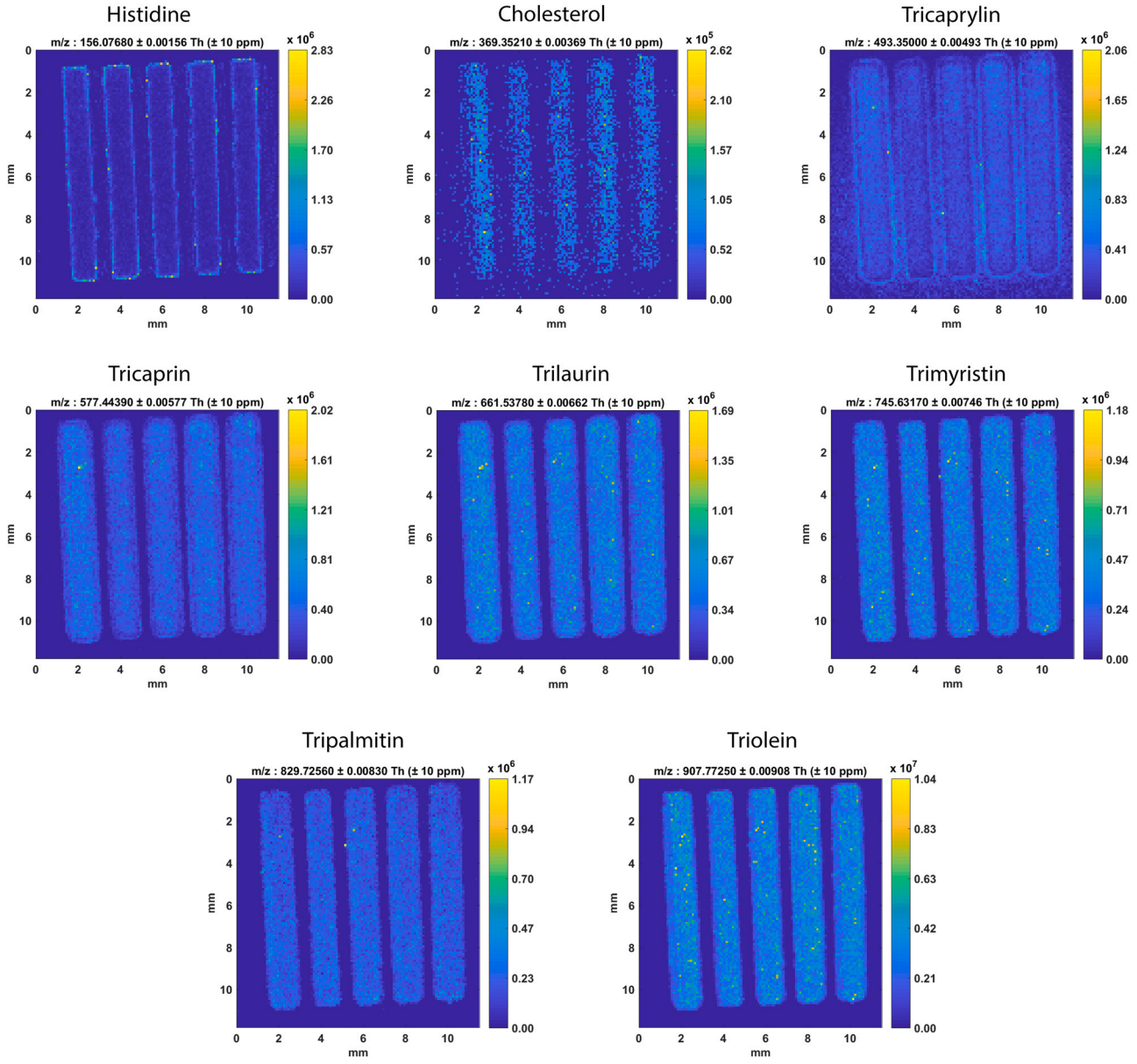

Fig. 7. Illustration of the distribution of eight compounds within the lined pattern of the printed quality control test strip (with simplified solutions) after MALDI-MSI analysis. The scale represents the maximum and minimum abundance of the selected compound within the pixels of the image.

degradation of the chemical compounds. This was probably due to the binding of the matrix molecules with those of the artificial solutions.

4. Discussion

4.1. Artificial sweat and sebum solutions

The formulations from Sisco et al. [33] were first selected for their claimed ability to mimic natural secretions, qualitatively and quantitatively [31]. One drawback is certainly the preparation time, as 42 compounds need to be weighed in specified quantities and dissolved. Once the eccrine and the sebum solutions are made, they need to be mixed together. With regards to costs, the prepared artificial sweat is relatively cheap (less than two euros per litre); however, this is not the case for the sebum (hundreds of euros) portion.

In the context of a quality control test strip for fingermark analysis with MALDI-MSI, such complexity may not be relevant. The main goal here was to rapidly check if the instrument was able to detect each class of molecules present in fingermarks. For this reason, only 13 compounds were retained for the simplified solution recipes. This offered the best compromise between keeping a certain complexity for the artificial formulations and having a fast and efficient analysis for quality control test strips. This statement is corroborated by the fact that the results presented in this article are valid for both complete and simplified formulations. The only modification made to the formulation from Sisco et al. [33] was the solvent used to liquefy the sebum. A mix of 1:1 2-propanol and hexane was employed in this study. Indeed, the eccrine and sebum solutions could not be mixed homogenously using the Steareth-20 emulsifying agent as prescribed by Sisco et al. Moreover, the cosmetic cream obtained in their article could not be liquefied, which constitutes a major issue for printing the final emulsion. Even if the cartridges could be heated by the printer system, one problem remained with using the emulsion from Sisco et al., the transfer from the storage bottle to the cartridge. Indeed, a syringe had to be used to fill the cartridge. Even if the sebum solution was heated

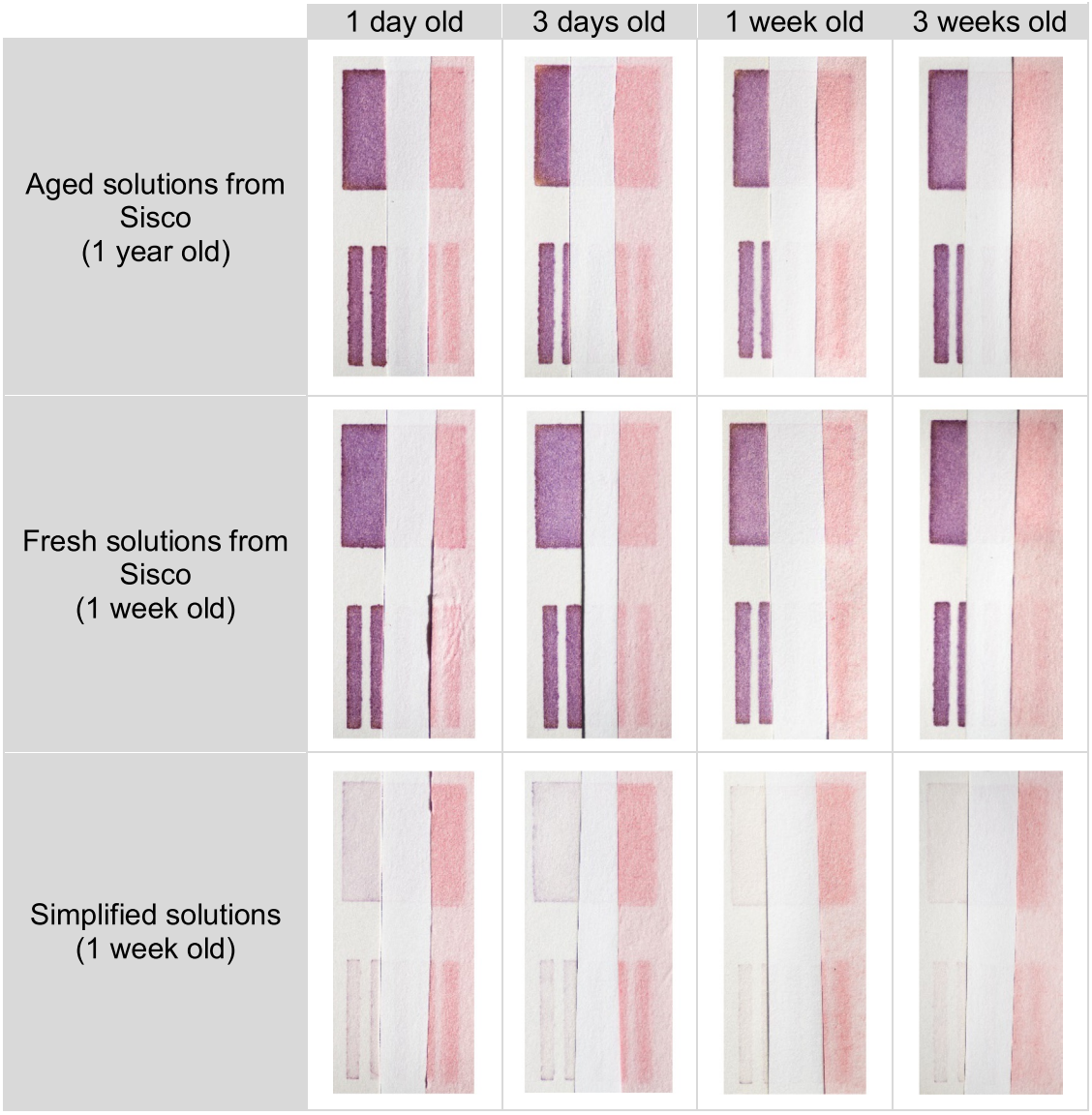

Fig. 8. Evolution of the printed quality controls over the time. Left side of the quality control was processed with ninhydrin, the center part was left unprocessed and the right side was processed with Oil Red O. Three different solutions were used to print the quality controls: a one year old one and a fresh one from Sisco's formulation and fresh one prepared with the simplified solutions.

continuously, once the syringe was filled, the sebum would return to a solid state almost immediately. Therefore, the sebum could not be transferred into the cartridge in time. Mixing artificial sebum with 1:1 2-propanol and hexane was the best solution found to overcome this difficulty.

The dilution tests demonstrated that it was possible to use diluted sebum (C_{100} for the printing, up to C_{500} for manual spots), therefore decreasing the costs for the concentrated sebum solution.

It appeared that the eccrine solution could not be diluted, but that was not the case for the sebum. If a manual deposition were desired, it could be diluted 500 times, whereas for printing with the Dimatix Material Printer 2850 from Fujifilm, a dilution of 100 times was needed. Keeping the ratios of the original formulation between sweat and sebum was not a priority here. However, this could be an issue for those willing to work with proportions closer to reality.

Since the printer induced variations while printing the two layers, C_{100} was chosen for the printing method to overcome this problem. This concentration allows the use of a high chemical profile that can be detected even if the quantity deposited on the substrate by the printer is lower than usual.

4.2. Chemical printer

In this paper, the choice was made to use a dedicated chemical printer instead of fingertip pads or a modified inkjet printer to create the quality control test strips for MALDI-MSI. A pattern was designed using the printer software. Since the sweat and sebum solutions were non-miscible, the quality control test strip was made by printing two layers of the designed pattern on paper, starting with the artificial sweat. Using a dedicated chemical printer offers many advantages, such as the versatility of the printable shapes and types of substrates supported (e.g., paper, glass, adhesives, etc.) or the possibility of printing several layers without moving the substrate, therefore ensuring a perfect superposition of the impressions. Moreover, the printable area allows using substrates up to 25 mm in thickness, which would not be possible with a modified inkjet printer.

However, from this study, it appears that many experiments must be conducted before the device can be properly optimised. Because of the wide variety of possibilities that this printer offers, many parameters must be optimised: the jetting waveform

(piezoelectric mechanism), the temperature of the plate and the cartridge, the cleaning cycles, the jetting voltage of the nozzles, the angle of the cartridge and the number of printing cycles considering the volume of the cartridge (1.5 mL). If several chemicals with different viscosity degrees are used, the optimisation process must be performed for each chemical.

In this study, the parameters selected were efficient for both sweat and sebum, even though the solutions did not have the same chemical properties. Although the sebum formulation with 1:1 hexane: 2-propanol was more volatile and less viscous than water, the DI Water waveform allowed the achievement of an excellent resolution and relatively satisfactory printing quality. No leakage was observed from the jetting nozzles, and no evaporation from the cartridges occurred during the printing sessions. More problems were encountered with the artificial sweat cartridges. The nozzles clogged regularly during printing despite the fact that the dedicated DI Water waveform for water from the printer was used. Further optimisation study is therefore required to solve this problem, as well as the printing problems observed in Fig. 6, which were not due to nozzle clogging.

In the case of the Fujifilm DMP-280 printer, cartridges are limited to 1.5 mL and supposed to be only used once, as it is not possible to reopen them once the lid has been clipped on. Given their cost (i.e., up to 80 euros per cartridge in our case), this could be a major limitation to large-scale use. This could explain why most of the publications consider modified inkjet printers.

Further investigation should be conducted to determine the origin of these problems (cartridge defaults, batch defaults, printer parameters, etc.). In their study, Janssen-Bouwmeester et al. [34] used a similar printer (Dimatix Materials Printer DMP-2831 from Fujifilm) with almost the same characteristics as ours. They focused more on the optimisation of the waveform and developed a jetting waveform specific to sweat that slightly differs from the DI Water we used in this study. This could be a starting point for the resolution of the problems encountered in this study. However, it also must be noticed that some printing problems can be seen in the figures they present in their article (e.g., offsets within the pattern).

Regarding the costs of the Fujifilm Dimatix (printer and cartridges), more comparative studies should be conducted to determine if a modified inkjet printer is able to print artificial sweat as well as artificial sebum, considering the different chemical proprieties of these solutions. This could be an alternative for anyone willing to print artificial solutions on paper substrates. For all other substrates, a dedicated printer will be required. For each substrate, an entirely new optimisation process is highly recommended.

4.3. Application of the quality control test strip in practice

In this study, we emphasise the creation and use of a printed test strip as a quality control test strip for MALDI-MSI in the context of fingermark analysis. Despite the variations induced by the printing process, each category of molecule could be successfully detected by the instrument over a period of several months. Practically, such a control test strip could be used at the beginning of each day of analysis. During the last decade, MALDI-MSI has been an emerging technology widely used in fingermark research with several publications on it each year [1,4]. However, contrary to many analytical methods such as liquid chromatography or gas-chromatography mass-spectrometry-based techniques, no calibration curve or internal standard can be used for MALDI-MSI analysis to ensure the analytical capacities of the instrument. The preliminary quality control test strip presented in this study was designed to try to overcome this limitation. With simplified formulations, the developed quality control test strip is affordable and can easily be implemented in many laboratories. Furthermore, the quality control test strips can be stored in a freezer with zipper storage bags and be preserved for several months according to Janssen-Bouwmeester et al. [34] and to our results. This is a step towards the development of a quality control test strip for MALDI-MSI in the context of fingermark research. In the long term, this could lead to the possibility of monitoring mass spectrometry instruments such as MALDI-MSI over time with the implementation of control cards. Using this standard would provide more reliability to the published results in this domain, as no analytical standard has been yet developed.

Overall, the methodology explored is easy to set up and is a first step towards the creation of standardised quality control test strips that could provide a guarantee of quality for all analysis conducted on MALDI-MSI instruments.

4.4. Exportation to other fields

The test strip creation process presented in this article was done with two artificial solutions representative of some fingermark compounds. However, the methodology can be adapted to multiple fields of research. The artificial solutions can be designed for specific compounds targeted in other domains, such as drug detection, metabolomics or ink components. Of course, some optimisation of the printing parameters will be required, but the creation process of the quality control test strips remains the same.

Such quality control is not necessarily limited to MALDI-MSI LTQ Orbitrap instruments. It may be used for many other mass-spectrometry-based techniques, as demonstrated by Sisco et al. [33], or (fingermark) detection techniques to ensure the validity of chemical solutions. The main adjustments that should be done for each mass spectrometry instrument are the determination of the *m/z* of interest regarding the targeted mass range and their optimal concentrations for printing. The chemical composition of the test strip presented in this study, constitutes a good starting point as it covers the most common mass range used in mass spectrometry applied to fingermarks. However, depending on the techniques that is used and the desired goal, the chemical composition and concentration of the solution could be modified to optimize the response signal or to adapt to a specific mass spectrometry technique or configuration, as long as the prepared solution remains printable. Overall, the proposed methodology is a step forward to the creation of a standardised and reproducible quality control test strip that could be used for inter-laboratory comparisons as well as long-term quality monitoring. Further research is still required, though.

Regarding fingermark detection techniques, such test strip may be used as a versatile efficiency indicator in a sequence of processes applied to porous substrates. Provided that further developments and testing are carried out, such a quality control may replace the use of multiple test strips specific to only one detection reagent class as for amino acids [31].

5. Conclusion

This study describes the first steps of development of a quality control test strip for MALDI-MSI analysis in the context of fingermark detection as well as for fingermark detection solutions. Such control allows for the assessment of both chemical analysis performance and imaging capabilities of the mass spectrometry instrument and the validity of fingermark reagents due to a printed pattern made of artificial sweat and sebum. The use of a dedicated chemical printer (Fujifilm DMP-280) enables the printing of a specific pattern. Some improvements still need to be made, but this technology is quite promising and offers many development possibilities, such as printing on complex substrates such as adhesives, steel or glass. Once printed, the quality control test strips can be

stored for 7 days at ambient temperature or for several months in zipper storage bags stored at −25 °C.

Compounds representative of each class of molecules present in the artificial solutions as well as the overall mass range analysed by MALDI-MSI were successfully detected. Consequently, the inspection of the chemical detection capabilities of the instrument took less than one hour per day, including the matrix preparation and deposition steps. Regarding the imaging capabilities, a longer analysis time is required.

Due to the control possible of the composition in these dedicated printed quality control test strip this is a first step towards the establishment of an accurate long-term quality monitoring process for many mass-spectrometry-based instruments as well as towards encouraging inter-laboratory comparisons.

CRediT authorship contribution statement

Marie Gorka: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Aurélien Thomas:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Andy Bécue:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

There are no conflicts to declare.

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References

[1] A. Bécue, H. Eldridge C. Champod, Fingermarks and Other Body Impressions - A review (August 2016-June 2019), 2019.
[2] S. Chadwick, S. Moret, N. Jayashanka, C. Lennard, X. Spindler, C. Roux, Investigation of some of the factors influencing fingermark detection, Forensic Sci. Int. 289 (2018) 381–389, https://doi.org/10.1016/j.forsciint.2018.06.014
[3] A. Bécue, Emerging fields in fingermarks (meta)detection - a critical review, Anal. Methods 8 (45) (2016) 7983–8003, https://doi.org/10.1039/C6AY02496C10.1039/c6ay02496c
[4] S. Francese, R. Bradshaw, N. Denison, An update on MALDI mass spectrometry based technology for the analysis of fingermarks – stepping into operational deployment, Analyst 142 (2017) 2518–2546, https://doi.org/10.1039/c7an00569e
[5] M. Gorka, M. Augsburger, A. Thomas, A. Bécue, Molecular composition of fingermarks: assessment of the intra- and inter-variability in a small group of donors using MALDI-MSI, Forensic Chem. 12 (2019) 99–106, https://doi.org/10.1016/j.forc.2018.12.002
[6] A. Thomas, P. Chaurand, Advances in tissue section preparation for MALDI imaging MS, Bioanalysis 6 (7) (2014) 967–982, https://doi.org/10.4155/bio.14.63
[7] R.M. Caprioli, T.B. Farmer, J. Gile, Molecular imaging of biological samples: localization of peptides and proteins using MALDI-TOF MS, Anal. Chem. 69 (23) (1997) 4751–4760, https://doi.org/10.1021/ac970888i
[8] Home Office, Fingermark visualisation manual, 2014.
[9] K. Kaplan-Sandquist, M.A. LeBeau, M.L. Miller, Chemical analysis of pharmaceuticals and explosives in fingermarks using matrix-assisted laser desorption ionization/time-of-flight mass spectrometry, Forensic Sci. Int. 235 (2014) 68–77, https://doi.org/10.1016/j.forsciint.2013.11.016
[10] K.A. Kaplan-Sandquist, M.A. LeBeau, M.L. Miller, Evaluation of four fingerprint development methods for touch chemistry using matrix-assisted laser desorption ionization/time-of-flight mass spectrometry, J. Forensic Sci. 60 (3) (2015) 611–618, https://doi.org/10.1111/1556-4029.12718
[11] M.J. Bailey, R. Bradshaw, S. Francese, T.L. Salter, C. Costa, M. Ismail, P.W. R, I. Bosman, K. Wolff, M. de Puit, Rapid detection of cocaine, benzoylecgonine and methylecgonine in fingerprints using surface mass spectrometry, Analyst 140 (18) (2015) 6254–6259, https://doi.org/10.1039/c5an00112a
[12] G. Groeneveld, M. de Puit, S. Bleay, R. Bradshaw, S. Francese, Detection and mapping of illicit drugs and their metabolites in fingermarks by MALDI MS and compatibility with forensic techniques, Sci. Rep. 5 (2015) 1–13, https://doi.org/10.1038/srep11716
[13] S. Francese, R. Bradshaw, B. Flinders, C. Mitchell, S. Bleay, L. Cicero, M.R. Clench, Curcumin: a multipurpose matrix for MALDI mass spectrometry imaging applications, Anal. Chem. 85 (10) (2013) 5240–5248, https://doi.org/10.1021/ac4007396
[14] L. Ferguson, F. Wulfert, R. Wolstenholme, J.M. Fonville, M.R. Clench, V.A. Carolan, S. Francese, Direct detection of peptides and small proteins in fingermarks and determination of sex by MALDI mass spectrometry profiling, Analyst 137 (20) (2012) 4686–4692, https://doi.org/10.1039/c2an36074h
[15] N. Lauzon, M. Dufresne, V. Chauhan, P. Chaurand, Development of laser desorption imaging mass spectrometry methods to investigate the molecular composition of latent fingermarks, J. Am. Soc. Mass Spectrom. 26 (6) (2015) 878–886, https://doi.org/10.1007/s13361-015-1123-0
[16] R. Wolstenholme, R. Bradshaw, M.R. Clench, S. Francese, Study of latent fingermarks by matrix-assisted laser desorption/ionisation mass spectrometry imaging of endogenous lipids, Rapid Commun. Mass Spectrom. 23 (19) (2009) 3031–3039, https://doi.org/10.1002/rcm.4218
[17] M.J. Bailey, N.J. Bright, R.S. Croxton, S. Francese, L.S. Ferguson, S. Hinder, S. Jickells, B.J. Jones, B.N. Jones, S.G. Kazarian, J.J. Ojeda, R.P. Webb, R. Wolstenholme, S. Bleay, Chemical characterization of latent fingerprints by matrix-assisted laser desorption ionization, time-of-flight secondary ion mass spectrometry, mega electron volt secondary mass spectrometry, gas chromatography/mass spectrometry, X-ray photoelectron spectroscopy, and attenuated total reflection Fourier transform infrared spectroscopic imaging: an intercomparison, Anal. Chem. 84 (20) (2012) 8514–8523, https://doi.org/10.1021/ac302441y
[18] R. Bradshaw, A. Cressein, S. Francese, Technical note: a rapid methodology for the analysis of latent fingermarks by MALDI MS imaging, HTX Imaging 32 (062013) (2013).
[19] G.B. Yagnik, A.R. Korte, Y.J. Lee, Multiplex mass spectrometry imaging for latent fingerprints, J. Mass Spectrom. 48 (1) (2013) 100–104, https://doi.org/10.1002/jms.3134
[20] B.L. Walton, G.F. Verbeck, Soft-landing ion mobility of silver clusters for small-molecule matrix-assisted laser desorption ionization mass spectrometry and imaging of latent fingerprints, Anal. Chem. 86 (16) (2014) 8114–8120, https://doi.org/10.1021/ac5010822
[21] T. Guinan, D.C. Vedova, H. Kobus, H.N. Voelcker, Mass spectrometry imaging of fingerprint sweat on nanostructured silicon, Chem. Commun. 51 (2015) 6088–6091, https://doi.org/10.1039/C4CC08762C10.1039/c4cc08762c
[22] H.-W. Tang, W. Lu, C.-M. Che, K.-M. Ng, Gold nanoparticles and imaging mass spectrometry: double imaging of latent fingerprints, Anal. Chem. 82 (5) (2010) 1589–1593.
[23] L. Ferguson, R. Bradshaw, R. Wolstenholme, M. Clench, S. Francese, Two-step matrix application for the enhancement and imaging of latent fingermarks, Anal. Methods 83 (14) (2011) 5585–5591, https://doi.org/10.1021/ac200619f
[24] R. Bradshaw, S. Bleay, R. Wolstenholme, M.R. Clench, S. Francese, Towards the integration of matrix assisted laser desorption ionisation mass spectrometry imaging into the current fingermark examination workflow, Forensic Sci. Int. 232 (1–3) (2013) 111–124, https://doi.org/10.1016/j.forsciint.2013.07.013
[25] L. Ferguson, S. Creasey, R. Wolstenholme, M.R. Clench, S. Francese, Efficiency of the dry-wet method for the MALDI-MSI analysis of latent fingermarks, J. Mass Spectrom. 48 (6) (2013) 677–684, https://doi.org/10.1002/jms.3216
[26] R. Bradshaw, N. Denison, S. Francese, Implementation of MALDI MS profiling and imaging methods for the analysis of real crime scene fingermarks, Analyst 142 (9) (2017) 1581–1590, https://doi.org/10.1039/c7an00218a
[27] T. Kent, Standardizing protocols for fingerprint reagent, J. Forensic Identif. 60 (3) (2010) 371–379.
[28] V.G. Sears, S.M. Bleay, H.L. Bandey, V.J. Bowman, A methodology for finger mark research, Sci. Justice 52 (3) (2012) 145–160, https://doi.org/10.1016/j.scijus.2011.10.006
[29] International Fingerprint Research Group (IFRG), Guidelines for the assessment of fingermark detection techniques, J. Forensic Identif. 64 (2) (2014) 174–200.
[30] L. Schwarz, An amino acid model for latent fingerprints on porous surfaces, J. Forensic Sci. 54 (6) (2009) 1323–1326, https://doi.org/10.1111/j.1556-4029.2009.01168.x
[31] R. Steiner, C. Roux, S. Moret, Erratum: Borderud SP, Li Y, Burkhalter JE, Sheffer CE and Ostroff JS. Electronic cigarette use among patients with cancer: Characteristics of electronic cigarette users and their smoking cessation outcomes. Cancer. doi: 10.1002/ cncr.28811, Controlling fingermark variability for research purposes: A review, Wiley Interdisciplinary Reviews, Forensic Sci. 121 (2019) 800, https://doi.org/10.1002/wfs2.1338
[32] W. Zadnik, W. Van Bronswijk, A.A. Frick, P. Fritz, S.W. Lewis, Fingermark simulants and their inherent problems: a comparison with latent fingermark deposits, J. Forensic Identif. 63 (2013) 593–608.
[33] E. Sisco, J. Staymates, K. Schilling, A chemically relevant artificial fingerprint material for the cross-comparison of mass spectrometry techniques, Can. Soc. Forensic Sci. J. 48 (4) (2015) 200–214, https://doi.org/10.1080/00085030.2015.1083167
[34] R. Janssen-Bouwmeester, C. Bremmer, L. Koomen, S. Siem-Gorre, M. de Puit, Positive control tests for fingermark development reagents, Forensic Sci. Int. 310 (2020) 110–259, https://doi.org/10.1016/j.forsciint.2020.110259
[35] A. Jeanneret, A. Anthonioz, A. Bécue, Printed artificial sweat as replacement for natural fingermarks: qualitative and quantitative approach considering an amino acid reagent, Sci. Justice 61 (2021) 249–259, https://doi.org/10.1016/j.scijus.2021.01.004
[36] N. a. listed, FUJIFILM Dimatix Materials Printer DMP-2850 User Manual, 2017.

[37] N. a. listed, LTQ Orbitrap XL Hardware Manual, Thermo Fisher Scientific, 2008.
[38] C. Champod, C. Lennard, P. Margot, M. Stoilovic, Fingerprints and Other Ridge Skin Impressions, Second edn., CRC Press,, 2004, p. 427.
[39] A. Beaudoin, New technique for revealing latent fignerprints on wet porous surfaces: Oil Red O, J. Forensic Identif. 54 (4) (2004).
[40] M. Honig, J. Yoak, Oil Red O: a comparative study, J. Forensic Identif. 66 (2) (2016) 118–133.
[41] G. Robichaud, K.P. Garrard, J.A. Barry, D.C. Muddiman, MSiReader: an open-source interface to view and analyze high resolving power MS imaging files on Matlab platform, J. Am. Soc. Mass Spectrom. 24 (5) (2013) 718–721, https://doi.org/10.1007/s13361-013-0607-z
[42] C. Smith, G. O'Maille, E.J. Want, C. Qin, S.A. Trauger, T.R. Brandon, D.E. Custodio, R. Abagyan, G. Siuzdak, METLIN: a metabolite mass spectral database, Ther. Drug Monit. 27 (6) (2005) 747–751.
[43] K.C. O'Neill, Y.J. Lee, Effect of aging and surface interactions on the diffusion of endogenous compounds in latent fingerprints studied by mass spectrometry imaging, J. Forensic Sci. 63 (3) (2018) 708–713, https://doi.org/10.1111/1556-4029.13591
[44] J. Almog, M. Azoury, Y. Elmaliah, L. Berenstein, A. Zaban, Fingerprint's third dimension: the depth and shape of fingerprints penetration to paper - cross section examination by fluorescence miscroscopy, J. Forensic Sci. 49 (5) (2004) 981–985.