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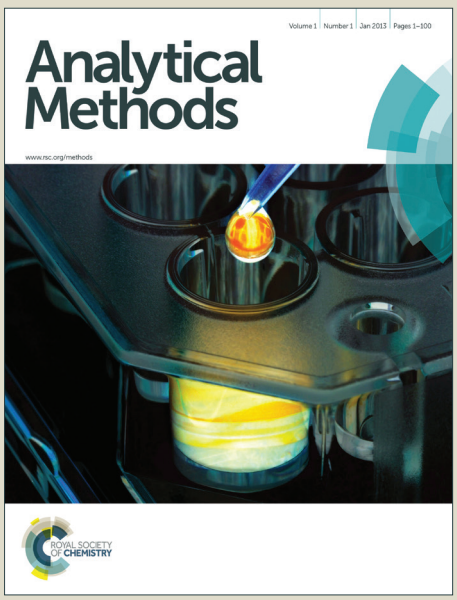

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Drug cross-contamination of latent fingermarks during routine powder dusting detected by SALDI TOF MS

Latha Sundar[a] and Frederick Rowell[a,b]

[a] *Arro Supranano Ltd, INEX Business Support Facility, Newcastle upon Tyne, NE1 7RU, UK*

[b] *School of Pharmacy, Health and Wellbeing, Physical Sciences Building, University of Sunderland, Sunderland SR1 3SD, UK*

Abstract

The process of dusting powders over latent fingermarks was shown to transfer drug contact residues between adjacent marks. This was seen for marks contaminated after contact with two drugs of abuse (cocaine and methadone) and three therapeutic drugs (caffeine, aspirin and paracetamol). The powders used were a commercial black powder, and α-cyano-4-hydroxycinnamic acid both of which also act as ionisation-assisting agents in laser desorption/ionisation time-of-flight mass spectrometry (LDI-TOF-MS). They were applied as the powders using a Zephyr brush, a Squirrel hair brush or a magnetic wand for the magnetisable formulations of the two powders. In each case transfer of drugs from the residue-contaminated mark onto adjacent marks was detected using LDI-MS when the powders were applied using conventional brushes. Such transfer was not detected when magnetisable formulations were used and the powder immediately replaced with fresh magnetisable powder when a developed mark was seen.

Key words; dusting, latent fingermarks, cross-contamination, contact residues, drugs, SALDI-TOF MS, MALDI TOF MS, magnetisable powders, brushing

Introduction

Application of powders to surfaces using brushes at crime scenes is a routine and widely used method for locating the presence of latent fingermarks. The method involves dipping the hairs or fibres of the brush into a pot containing the powder. The loaded brush tip is then lightly brushed over the surface of interest and when contact is made with a latent fingermark the powder selectively adheres to the material of the mark enabling its visualisation. For large surfaces the brush may be re-loaded several times during the dusting process. Examples of commonly used brushes include Zephyr and animal hair types. The former is made of fibres of fibre glass whilst the latter is made of hairs from the tails of animals such as squirrels or camels. An alternative approach uses a magnetic wand to form a wad of powder when the tip of the magnet is inserted into the pot of magnetisable powder. The loaded tip is then brushed over the surface in an identical fashion to that used with classical brushes[1]. The patterns present in the developed latent fingermarks are then generally compared with those stored on an electronic data base to identify the originator of the mark[2]. Often such developed marks are completely or partially smudged when no information on the originator can be obtained.

Recent advances in forensic science have led to methods which obtain additional data from the located latent fingermark on smudged and un-smudged marks. These include extracting DNA from the mark and obtaining the unique DNA profile of the originator[3] and spectroscopic analysis of constituents present in the mark[4,5]. Such analyses require that the powders used in the initial development to locate the mark are not contaminated and recently commercial powders, brushes and lifting tapes have been available that are DNA free[6].

With the advent of highly sensitive spectroscopic methods for latent fingermark analysis such as those based on mass spectrometry[4,5] it is imperative that uncontaminated powders are available to eliminate possible contamination of latent marks during their use and thus

avoiding false positive detection of key analytes. Such analytes include contact residues deposited following earlier contact of fingers with chemicals on surfaces, and with chemicals present within the body and secreted onto the surface of the skin. Examples of the former include drugs[7], nicotine from smokers[8], explosives[9] and lubricants from condoms[10] whilst examples of the latter include drug metabolites[7], lipids[11], amino acids[12] and sex biomarkers[13].

To date there has been few reports that DNA present in the latent fingermark from shed skin cells is transferred from one latent fingermark to another during the process of dusting with a brush[14-16] with no reports on cross-contamination of contact residues of drugs between latent fingermarks during the brushing process. This study examines the effect of applying powders with conventional brushes and the use of a magnet to brush magnetisable powders onto latent fingermarks on the transfer of drugs between latent fingermarks from a drug-contact residue contaminated latent fingermark to adjacent drug-free marks. The powders were chosen to act as dual agents, firstly to develop and hence visually locate the latent fingermarks and secondly to act as ionisation-enhancing agents during subsequent surface-assisted laser desorption/ionisation time-of-flight mass spectrometry (SALDI TOF MS) on the developed fingermark without the need for further treatment of the mark [5,7]. Among the various factors which influences the cross-contamination, the amount of drug originally present in the fingermark contributes a major role. In this study, we have taken 3 concentrations (100 ng,

1 ug and 10 ug) and amount of transfer from the fingermark spiked with these concentrations to the adjacent marks were determined.

Experimental

Materials

The drugs of abuse, cocaine hydrochloride (51621) and methadone hydrochloride (M0267), α- cyano-4-hydroxycinnamic acid, CHCA (70990), and small molecule calibrant compounds

such as papaverine hydrochloride (P3510), caesium iodide (21004) and reserpine (83580) were purchased from Sigma Aldrich, UK. The Iron powder reduced, 99% (A10411) was purchased from Alfa Aesar, UK. Black magnetic powder for mass spectrometry was obtained from Arro Supranano Ltd, UK. For therapeutic drugs, Anadin Extra tablets which contain aspirin (300 mg), paracetamol (200 mg) and caffeine (45 mg) was purchased from a local drug store (Boots, UK). The fingerprinting accessories such as squirrel brush, zephyr brush, and magnetic wand/applicator were purchased from CSI Equipments, UK. MALDI sample target plates (MTP 384 target plate ground steel BC# 28078) were purchased from Bruker Daltonik GmbH, Germany.

Methods

Preparation of magnetisable powders

Commercial black magnetisable powder for mass spectrometry was used as recommended by the supplier. CHCA magnetic powder was prepared using CHCA that had been finely ground using a mortar and pestle, and iron powder (99.9%, 325 mesh). These were thoroughly mixed in the ratio 1:99, CHCA: iron by weight, using a mortar and pestle.

Direct application of drugs to finger tips

An aliquot of a solution of cocaine and methadone in ethanol (10 µl of 10 ug/ml, depositing 100 ng of each drug) was directly applied onto the tip of an un-groomed index finger and the solution allowed to dry. This fingertip then touched the surface of a clean stainless steel MALDI target plate to generate a latent fingermark. Immediately adjacent to this mark, a set of marks was deposited using the index finger from the other hand to generate a row of three un-groomed, uncontaminated latent fingermarks. After 1 hour under ambient conditions, a commercial magnetic wand was inserted into the pot of magnetisable powder and the wad of powder on the tip was used to dust the contaminated mark. In one series of experiments the

same wad was used to dust the adjacent row of three marks applying powder from the mark nearest to the drug-contaminated mark to the furthest. In a second set of experiments, following visual development of the first drug-contaminated mark by the wad of powder, the first wad was discarded into a separate pot and a fresh wad of powder obtained to dust the first adjacent latent mark. This process was repeated for each of the three marks in the row, renewing the powder after each successful development. These procedures were used with both the black and CHCA magnetic powders. In addition the experiments were repeated using deposited drug concentrations of 1 μg and 10 μg per fingertip.

In a third set of experiments, a series of cocaine- and methadone-contaminated latent marks each with three un-contaminated marks were produced as described above using 100 ng, 1 μg and 10 μg of each drug. In this case, only non-magnetisable CHCA powder was used. This was applied using a commercial Squirrel hair brush by dusting the drug-contaminated mark then the three un-contaminated marks using the same powder-loaded brush tip. This was repeated with another set of four latent fingermarks but using a commercial Zephyr brush.

Drug contact residues

The above protocols were now repeated but the un-groomed thumb now made contact with a powder obtained by crushing a single Anadin Extra tablet using a mortar and pestle. The thumb now made contact with the middle and index fingers of that hand to spread the powder evenly and to remove the excess powder and a latent fingermark was produced on the MALDI metal plate by touching the index finger onto the plate. The tablet contained aspirin, paracetamol and caffeine (300, 200 and 45 mg/tablet respectively). The index finger from the other hand was used to deposit three un-groomed latent marks in a row as before, adjacent to the drug-contacted mark. Both magnetisable formulations were again used but were now applied to the surface by direct brushing using a Squirrel hair brush from the contaminated mark to the first and nearest un-contaminated mark, through to the third mark as described

above with the same loaded brush. This was then repeated on a second set of four marks using the Zephyr brush. In an additional experiment the black magnetisable powder was also applied using the magnetic wand but the same wad was used across the row without discarding and renewing the wad between marks.

Surface Assisted Laser Desorption/Ionisation Time Of Flight Mass Spectrometry (SALDI TOF MS)

SALDI TOF MS is a laser desorption/ionisation MS technique that uses particles applied to the sample to aid ionisation of the analytes within the sample on laser irradiation during MS analysis[5,17]. In this case the black silica particles in the commercial black powder and fine CHCA particles were chosen as dusting agents to apply as particles to the latent fingermarks as no further time consuming processing of the dusted marks is required prior to MS.

The MALDI target plate containing the dusted latent fingermarks from the first set of cross-contamination experiments was analysed using an Ultraflex II MALDI TOF MS/MS Spectrometer, Bruker Daltonik GmbH, Germany in positive ion reflectron mode. The instrument is equipped with Smart beam Nd:Yag laser with fixed repetition rate of 50 Hz. Average spectra was acquired for each of the fingermark using a random walk raster randomly covering the area of the fingermark. An average of 1000 shots were collected for each sample at a laser repetition of 50 Hz over a 60 to 1000 mass range. Each fingermark was individually subjected to MS analysis following an established protocol[18] in which areas immediately adjacent to the mark are analysed followed by 6 areas within each mark selected at random. The former produced background spectrums and the latter spectrums from mark constituents. The instrument was calibrated before the start of any analysis and after every six samples analysed using the small mass calibration mixture. This was prepared by mixing 1 mg/ml of papaverine prepared in methanol, 1 mg/ml of reserpine in acetonitrile and 10 mg/ml of caesium iodide in deionised water in the volume ratio of 1:1:2 respectively. 1 µl of

this calibration mix was spotted on the MADLI target plate and allowed to air dry at room temperature. The calibrant solution was spotted at various places surrounding the fingermark. Before analysing the sample, the calibrant closest to the sample was selected and the instrument was calibrated before analysing the sample. In positive ion mode, the peaks for $[Cs]^+$ at *m/z* 132.81, [papaverine + H]$^+$ at *m/z* 340.15 and $[Cs^2I]^+$ at *m/z* 392.72 and [reduced reserpine + H]$^+$ at *m/z* 607.27 were used for calibration. For the analytes, $[M+H]^+$ peak intensities for cocaine at *m/z* 304.16 and those for methadone at 310.22 plus the fragmentation peak at *m/z* 265.21 from these six areas across the mark were averaged for the three ions. Peak intensities of analyte ions were examined as were the intensities of a blank dusted latent mark at the same m/z value. For the blank signals, the mean spectral intensity plus three times its standard deviation was calculated. If the analyte signal intensity was greater than this value it was considered significant and recorded whilst if it was less than this value then it was reported as not undetected (n.d.).

Plates from the second set of experiment were processed in an identical fashion but in this case the intensities of $[M+H]^+$ peaks due to paracetamol (m/z 152.06) and caffeine (m/z 195.07) and $[M+Na]^+$ peaks due to aspirin (m/z 203.04) in the dusted marks were examined.

SALDI TOF MS Imaging (SALDI MSI)

SALDI TOF MS Imaging analyses were carried out on the fingermarks using an Autoflex Speed MALDI TOF MS/MS spectrometer, Bruker Daltonik GmbH, Germany in positive ion reflectron mode. The instrument is fitted with Nd:YAG solid state laser having a wavelength of 355 nm at a raster width of 100 μm and a laser repetition rate of 2000 Hz. 'Fleximaging 3.1' software from Bruker Daltonik GmbH, Germany was used for performing imaging experiments and acquiring Images. Approximately 14 hours was taken to obtain a SALDI MS image of a whole fingermark. The SALDI MS images were reconstructed from the acquired data by selecting appropriate mass filters for the ions.

Results and Discussion

Dusting

Dusting with Squirrel hair, Zephyr or magnetic brushes produced visual images with good definition which appeared best for the black magnetic powders due to the higher contrast and resolution observed. Fig. 1 shows the images of two marks developed following application of magnetisable black powder (a) or CHCA (b) to the Anadin-contacted marks applied using a magnetic wand. The CHCA dusted marks were best visualised under 254 nm UV irradiation as shown in the figure.

SALDI TOF MS of directly spiked fingertips

As expected, characteristic peaks were observed for cocaine and methadone in the directly spiked marks. These peaks are shown in Fig. 2 for marks which had been spiked following deposition of 100 ng, 1 μg and 10 μg of each drug on the fingertip and developed using black magnetic powder. It should be noted that it is likely that quantitative transfer of the drugs from the spiked finger onto the plate will not occur and that in practice the masses transferred will be lower. Similar results were observed following CHCA dusting.

The cross-contamination studies demonstrated that significant transfer of both drugs occurred when brushing from the spiked fingermark to adjacent marks took place. This was seen for both types of non-magnetic powders particularly at the higher spiking concentrations. Table 1 shows the results using the Zephyr brush and Squirrel hair brush with the CHCA powder. With both brushes cross-contamination of both the first and second initially uncontaminated marks was seen but not the third. The degree of cross-contamination in terms of percentage of the directly spiked mark for these drug peak intensities was 9-12% using the Squirrel hair brush and 4-5% using the Zephyr in the second mark for the two higher concentrations although in some cases no drug was observed. No examples of transfer onto the third mark

were observed for these two drugs. In contrast when magnetisable powders were used and fresh powder used when visual marks developed, no significant cross-contamination was observed for both CHCA and black magnetic powders whereas transfer onto the first and second marks was observed when a single wad was used throughout with no renewal between developed marks (data not shown).

Drug contact residues

As noted, developed marks showing good visual mark characteristics were obtained following dusting, particularly with the black magnetic powders as shown in Fig. 1. Also characteristic MS peaks due to paracetamol, caffeine and aspirin were seen in the latent mark resulting from contact with the Anadin powder as shown in Fig. 3 for a mark dusted with black magnetic powder. For all three drugs their sodium and potassium cations were seen but the protonated cations were only observed for paracetamol and caffeine. The corresponding spectrums obtained using CHCA gave the protonated peaks for paracetamol and caffeine but no peaks for aspirin were observed (results not shown). This may reflect the chemical nature of CHCA and aspirin which are both strong acids and their mutual repulsion could have prevented their forming the intimate complexes on the surface of the latent fingermark which would be required to assist adequate ionisation on laser irradiation.

Fig. 4 shows the results for transfer following CHCA dusting with a Squirrel hair brush. No signal due to aspirin was observed but cross-contamination for paracetamol and caffeine was observed in all three initially uncontaminated marks, with very high transfer onto the first adjacent mark (~75% for caffeine and ~28% for paracetamol). The corresponding results for CHCA using a Zephyr brush is shown in Fig.5 where significant transfer was again seen for paracetamol and caffeine but with lower values than those seen with the first transfer with the Squirrel hair brush (below 10%). Similar results were obtained when black magnetic powder was applied using a magnetic wand using the same wad of black magnetic powder throughout

the development process as shown in Fig 6. In this case significant transfer onto all three adjacent marks was observed for all three drugs with about 10% transfer onto the first adjacent mark with aspirin and paracetamol and about 25% for caffeine.

Black magnetic powder was applied in two ways in this experiment. When it was used in a step-wise fashion, renewing powder between marks no cross-contamination was observed as shown in Fig. 7 which shows the presence of the three drugs in the spiked latent fingermark and the absence of drug-derived peaks in the three adjacent marks following selective dusting. As noted above (Fig. 6) use of the same wad produced significant cross-contamination. This demonstrates the need to adopt the protocol where a magnetisable form of powder is used and each time a mark is visually detected on dusting the wad is discarded and a fresh wad of powder is taken up and subsequently used. To further prevent the cross-contamination through the tip of the magnetic applicator, disposable plastic sleeves for the applicator can be used (not used in the present study).

The distribution of the three drugs over the surface of the spiked and adjacent peaks was assessed from the relative intensities of the peaks for each drug analyte obtained from six areas chosen at random and exposed to laser irradiation over the surface for each of the pre-dusted latent fingermarks. These values were averaged and the standard deviation (SD) and % relative standard deviation (RSD) calculated. It was found that for marks dusted with CHCA the RSD values were high (range 77-112) whereas the corresponding values for the carbon black dusted marks were much lower (range 10-26). This may reflect the relative ability of the two agents to form intimate complexes between the powders and the analytes on the surface of the marks rather than the distribution of the powders which appear to have coated the ridges of the marks as shown in Fig. 1. This also shown in the SALDI images obtained for aspirin, paracetamol and caffeine for the black magnetisable powder-developed spiked fingermark (Fig. 8). The visual ridge pattern seen in the black dusted mark (a) is also

seen for each of the three drugs (b,c,d) indicating that the drug contact residues are located on the ridges of the mark. Since no drug-specific MS peaks are seen in the absence of the dusting agents the images probably reflect the deposition of the signal enhancing powder particles upon the ridges. It should be noted that the imaging process is very time consuming taking about 14 hours per scan for the present study and the results appear to merely reflect the distribution of the dusting particles over the ridges of the mark, however the dusting process takes seconds per mark producing excellent visual images which can then be photographed, both steps following well established protocols.

Conclusions

It appears that the use of contaminant-free powders to locate the presence of latent fingermarks on surfaces may not in itself be sufficient to avoid cross-contamination between latent marks. As seen in this study the most commonly used method of developing latent fingermarks of using brushes to dust the surface with powders may transfer residues such as drugs between marks. This appears to occur as a result of uptake of mark material onto the hairs of the brush from one mark which can then be deposited onto adjacent marks on further dusting. It follows that if a contaminated brush is placed back into the pot of powder during the reloading process, the powder in that pot may become contaminated and if both brush and powder are used at other crime scenes cross-contamination between crime scenes could occur. Further studies are needed to confirm this possibility and to monitor possible transfer of other analytes of forensic interest such as endogenous secreted fingermark chemicals including bio-markers and drug metabolites, and additional contact residues such as explosives and condom lubricants.

In order to prevent such cross-contamination it is recommended that a magnetic formulation of developing powder is used and applied in the manner described above. When compared to

the normal powders like fluorescent and aluminium based powders which work well on smooth and non-porous surfaces, magnetisable powders is currently widely used on most of the surfaces especially on textured surfaces as it is more consistent and leaves a clean and smudge free developed fingermark and hence the adoption of the suggested protocol should be easily implemented. Alternative approaches could be the disposal of brushes following visual location of each latent mark or the thorough cleaning of the brush after each successful mark development. The former is likely to be prohibitively expensive and the latter impracticable whereas the recommended method should be relatively cheap and easy to perform.

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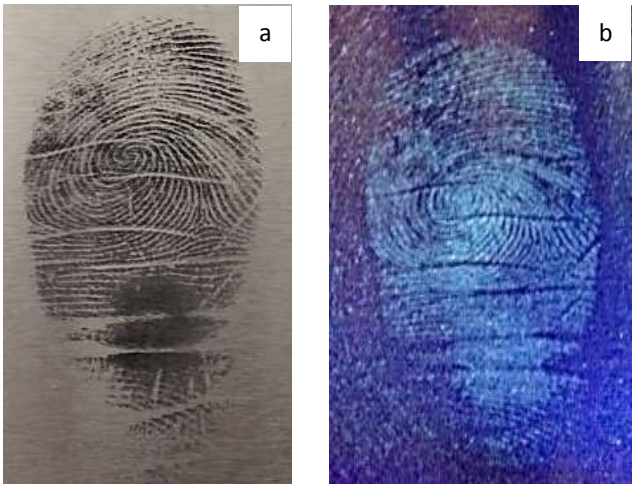

Fig. 1 Images of Anadin Extra spiked fingermarks from the same donor dusted using a magnetic applicator with (a) Black magnetic powder photographed under normal light and with (b) CHCA magnetic powder photographed under UV light, 254 nm

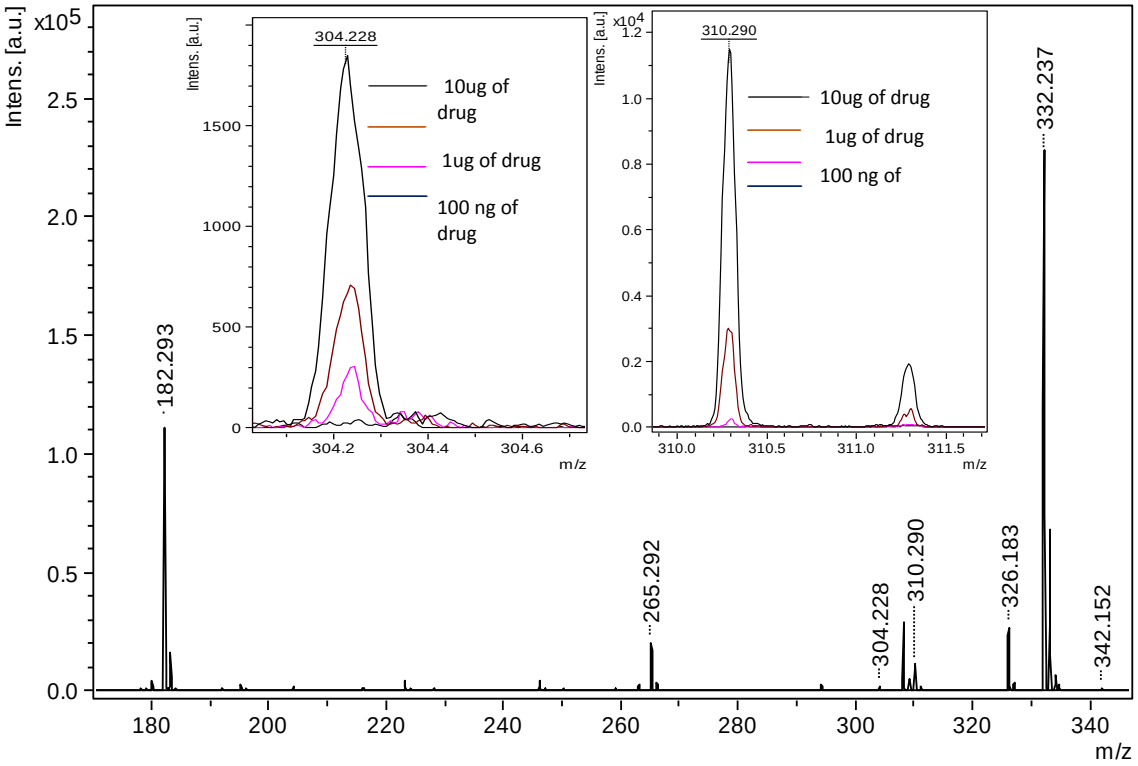

Fig. 2 SALDI MS spectrums of spiked fingermark dusted with black powder showing peaks for cocaine $[M+H]^+$ at *m/z* 304.08 and methadone $[M+H]^+$ at *m/z* 310.15

Table 1 % Cross-contamination of drugs from spiked finger mark to blank finger marks when dusted with CHCA using squirrel and zephyr brushes calculated using the relative *m/z* peak intensities of analyte ions by SALDI TOF MS

Analyte ions	% Cross-contamination compared with spiked mark						
	[a]*m/z* of ions	Mass of drug applied					
		100 ng		1 μg		10 μg	
		Squirrel	Zephyr	Squirrel	Zephyr	Squirrel	Zephyr
Spiked fingermark							
Cocaine $[M+H]^+$	304.16	100	100	100	100	100	100
Methadone $[M+H]^+$	310.22	100	100	100	100	100	100
Methadone fragment	265.21	100	100	100	100	100	100
1st blank fingermark							
Cocaine $[M+H]^+$	304.16	n.d	n.d	n.d	3.6	n.d	3.2
Methadone $[M+H]^+$	310.22	2.0	n.d	8.7	6.6	12.8	5.5
Methadone fragment	265.21	n.d	n.d	n.d	n.d	n.d	3.8
2nd blank fingermark							
Cocaine $[M+H]^+$	304.16	n.d	n.d	n.d	n.d	n.d	n.d
Methadone $[M+H]^+$	310.22	n.d	n.d	1.9	n.d	2.8	n.d
Methadone fragment	265.21	n.d	n.d	n.d	n.d	n.d	n.d
3rd blank fingermark							
Cocaine $[M+H]^+$	304.16	n.d	n.d	n.d	n.d	n.d	n.d
Methadone $[M+H]^+$	310.22	n.d	n.d	n.d	n.d	n.d	n.d
Methadone fragment	265.21	n.d	n.d	n.d	n.d	n.d	n.d

[a]*m/z* are theoretical monoisotopic mass value

n.d – not detected (signal less than mean SD plus 3 x SD for the corresponding blank signal)

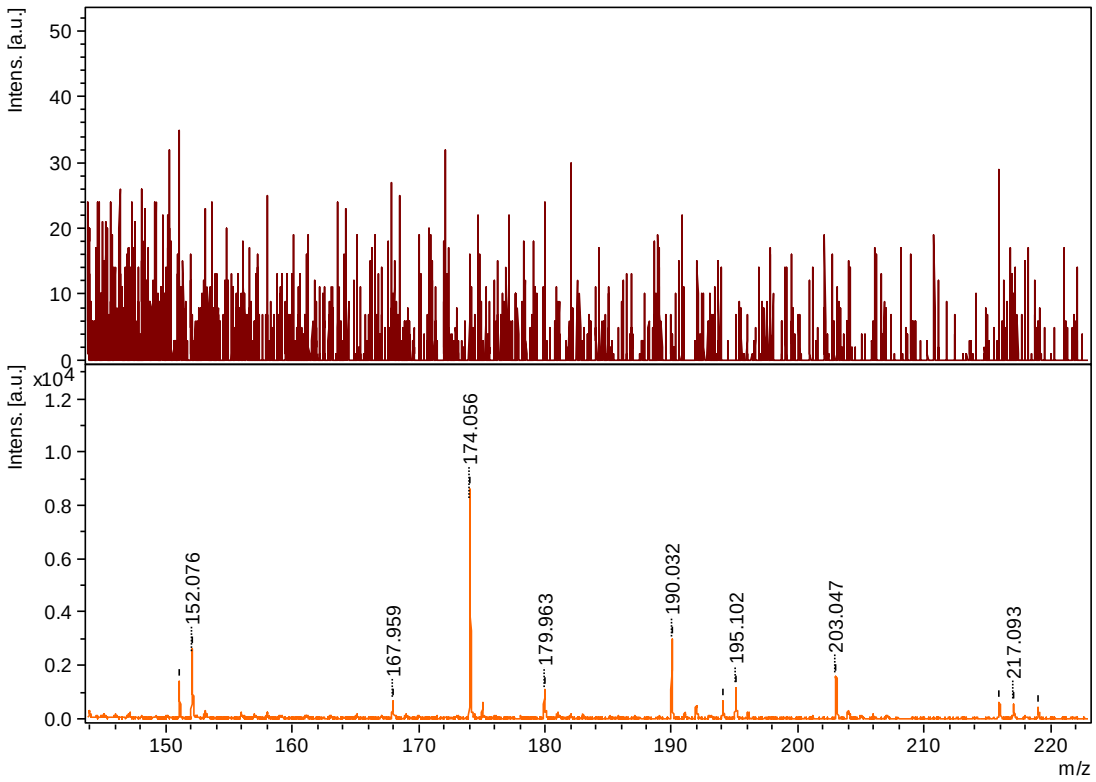

Fig. 3 SALDI MS spectrums of blank (top) and Anadin Extra spiked finger mark (bottom) dusted using black powder showing peaks for paracetamol $[M+H]^+$ at *m/z* 152.07, $[M+Na]^+$ at *m/z* 174.05, $[M+K]^+$ at *m/z* 190.03, aspirin $[M+Na]^+$ at *m/z* 203.03, caffeine $[M+H]^+$ at *m/z* 195.09, $[M+Na]^+$ at *m/z* 217.07

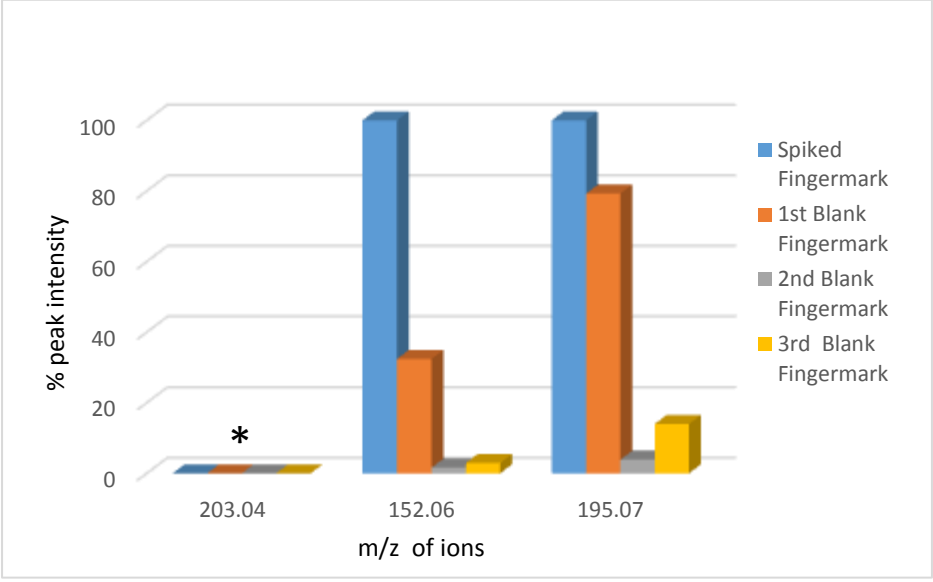

Fig. 4 Relative peak intensities of aspirin $[M+Na]^+$ at *m/z* 203.04, paracetamol $[M+H]^+$ at *m/z* 152.06 and caffeine $[M+H]^+$ at *m/z* 195.07 showing cross-contamination during dusting with CHCA using a squirrel hair brush, expressed as percentage of the corresponding signal from the spiked mark

*not detected (signal less than mean SD plus 3 x SD for the corresponding blank signal)

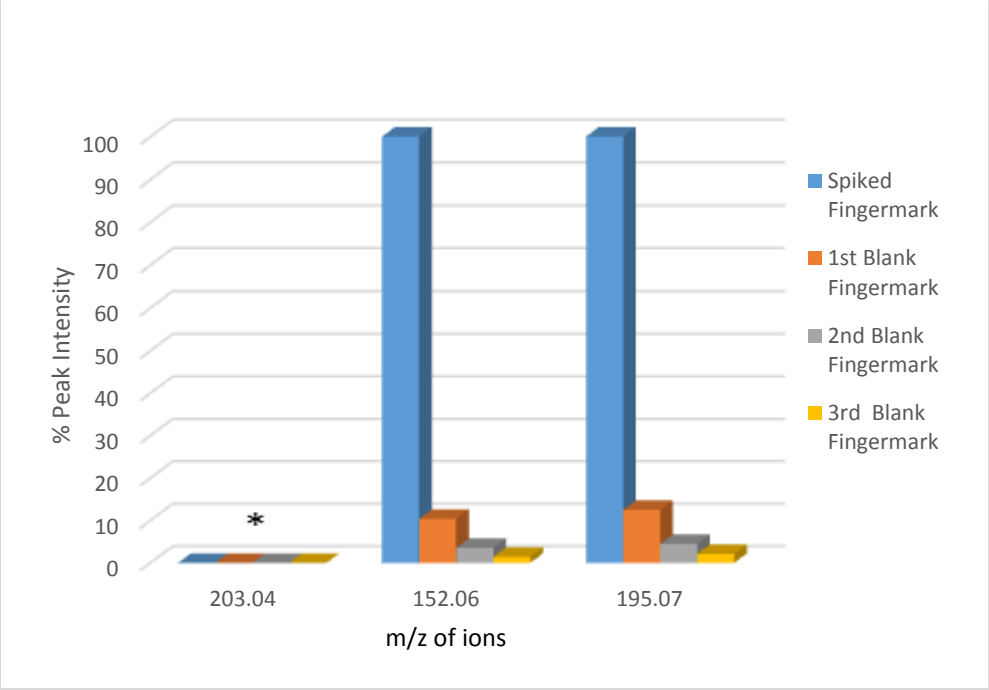

Fig. 5 Relative peak intensities of aspirin $[M+Na]^+$ at *m/z* 203.04, paracetamol $[M+H]^+$ at *m/z* 152.06 and caffeine $[M+H]^+$ at *m/z* 195.07 showing cross-contamination of drugs from spiked finger mark to blank finger marks when dusted with CHCA using zephyr brush expressed as the percentage of the corresponding signal for the spiked mark

*not detected (signal less than mean SD plus 3 x SD for the corresponding blank signal)

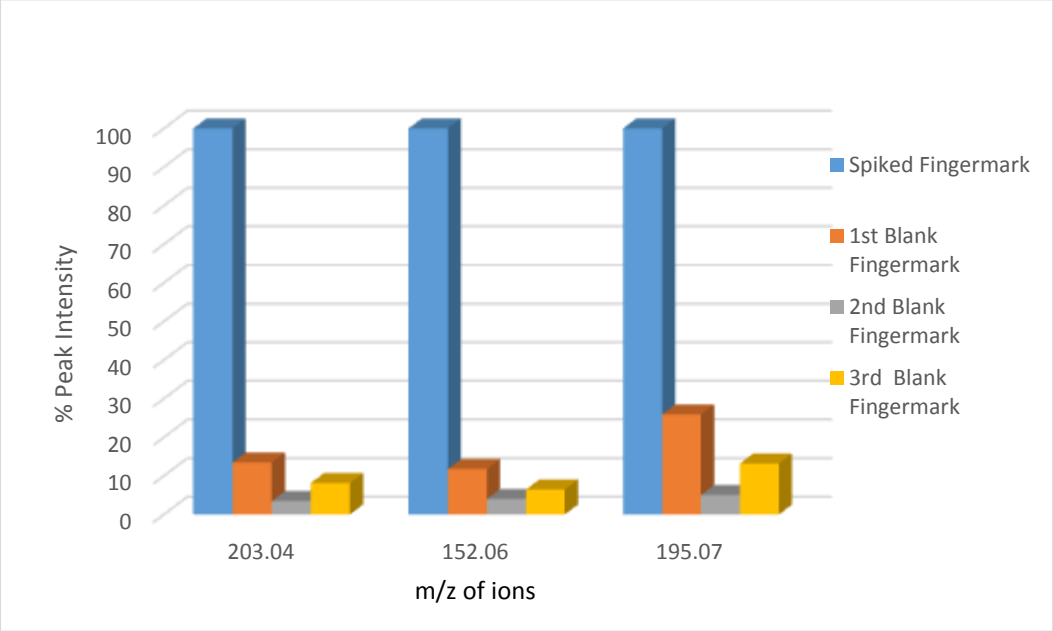

Fig. 6 Relative peak intensities of aspirin $[M+Na]^+$ at *m/z* 203.04, paracetamol $[M+H]^+$ at *m/z* 152.06 and caffeine $[M+H]^+$ at *m/z* 195.07 showing cross-contamination of drugs from spiked finger mark to blank finger marks when dusted with black magnetic powder using a magnetic applicator but without renewing the powder between developed marks

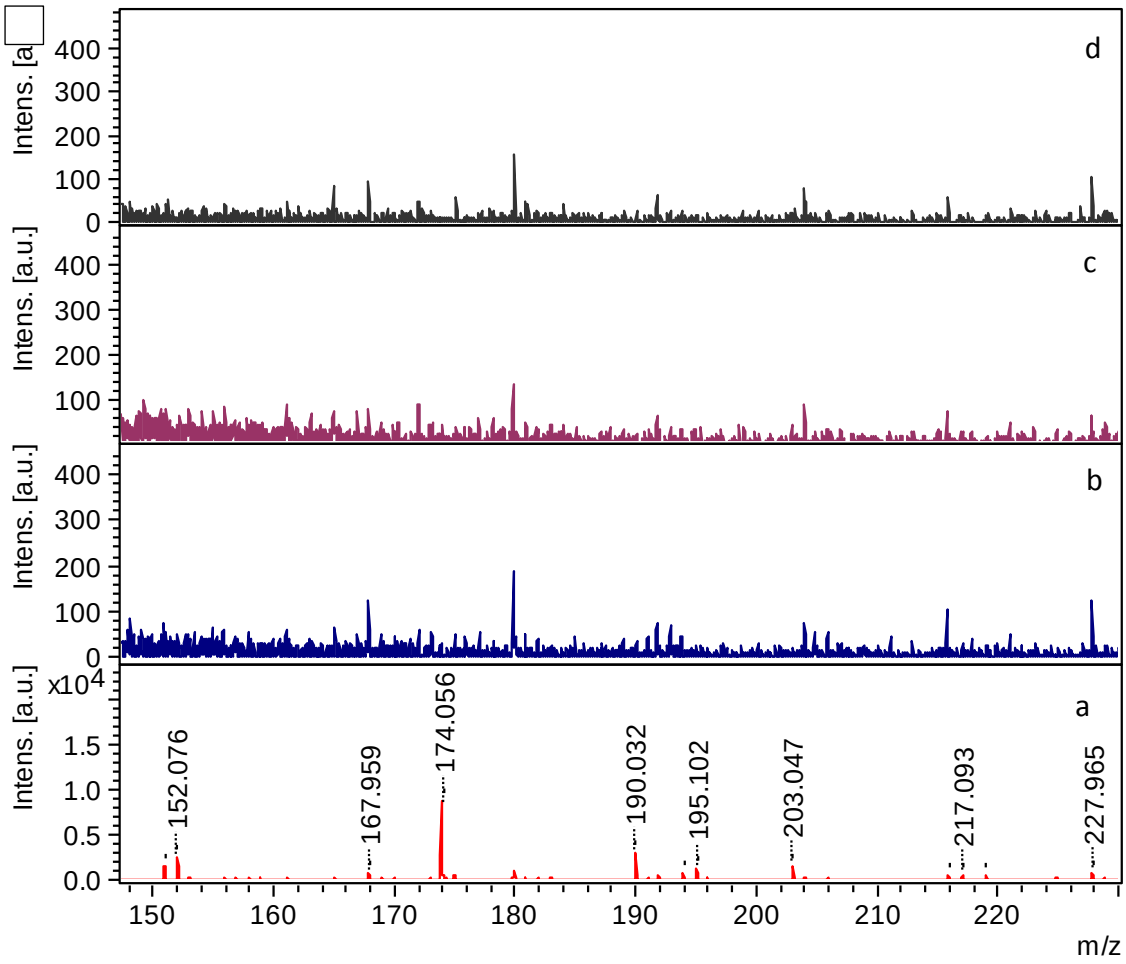

Fig. 7 SALDI MS spectrums of anadin spiked finger mark (a), blank fingermarks in sequence (b,c,d,e) showing peaks for paracetamol $[M+1]^+$ at *m/z* 152.07, $[M+Na]^+$ at *m/z* 174.05, $[M+K]^+$ at *m/z* 190.03, aspirin $[M+Na]^+$ at *m/z* 203.03, caffeine $[M+H]^+$ at *m/z* 195.09, $[M+Na]^+$ at *m/z* 217.07 when dusted sequentially from the spiked fingermark to blank fingermarks (b, c and d) using black magnetic powder after renewing the magnetic wand with fresh powder after each development

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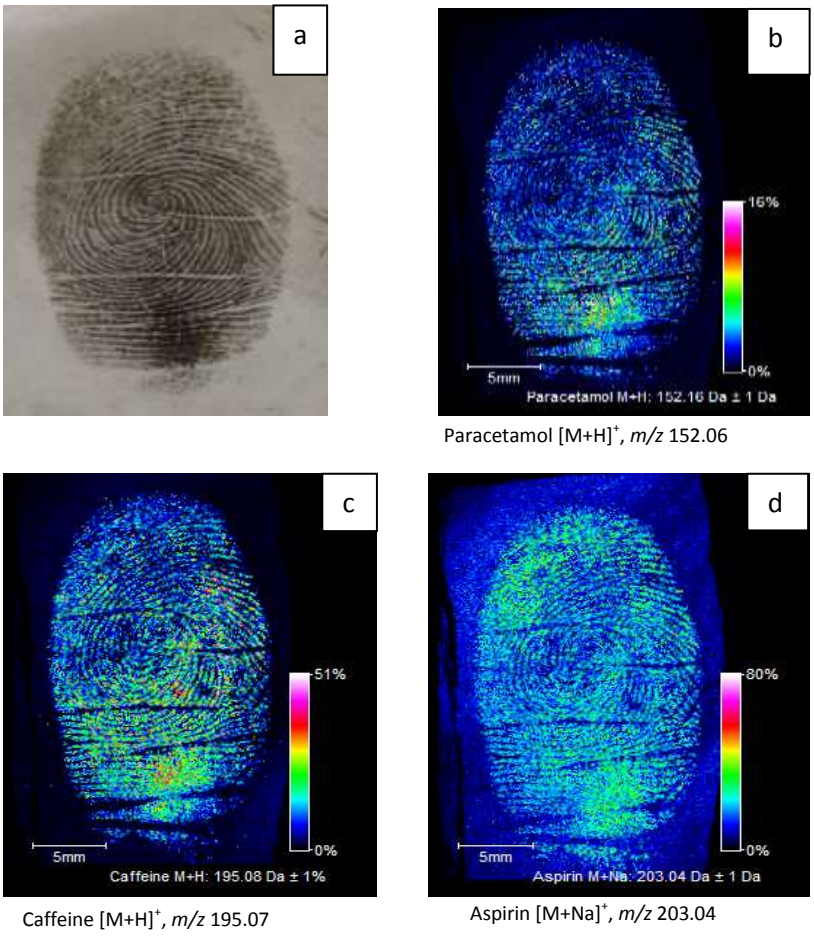

Fig. 8 Images of Anadin Extra spiked fingermarks dusted using a magnetic applicator with (a) Black magnetic powder photographed under normal light and SALDI MS Images of paracetamol $[M+H]^+$ at *m/z* 152.06 (b), caffeine $[M+H]^+$ at *m/z* 195.07 (c) and aspirin $[M+Na]^+$ at *m/z* 203.04 (d).

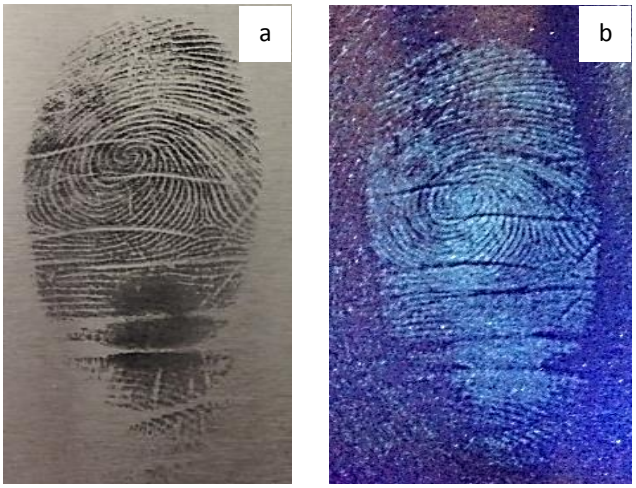

Fig. 1 Images of Anadin Extra spiked fingermarks from the same donor dusted using a magnetic applicator with (a) Black magnetic powder photographed under normal light and with (b) CHCA magnetic powder photographed under UV light, 254 nm

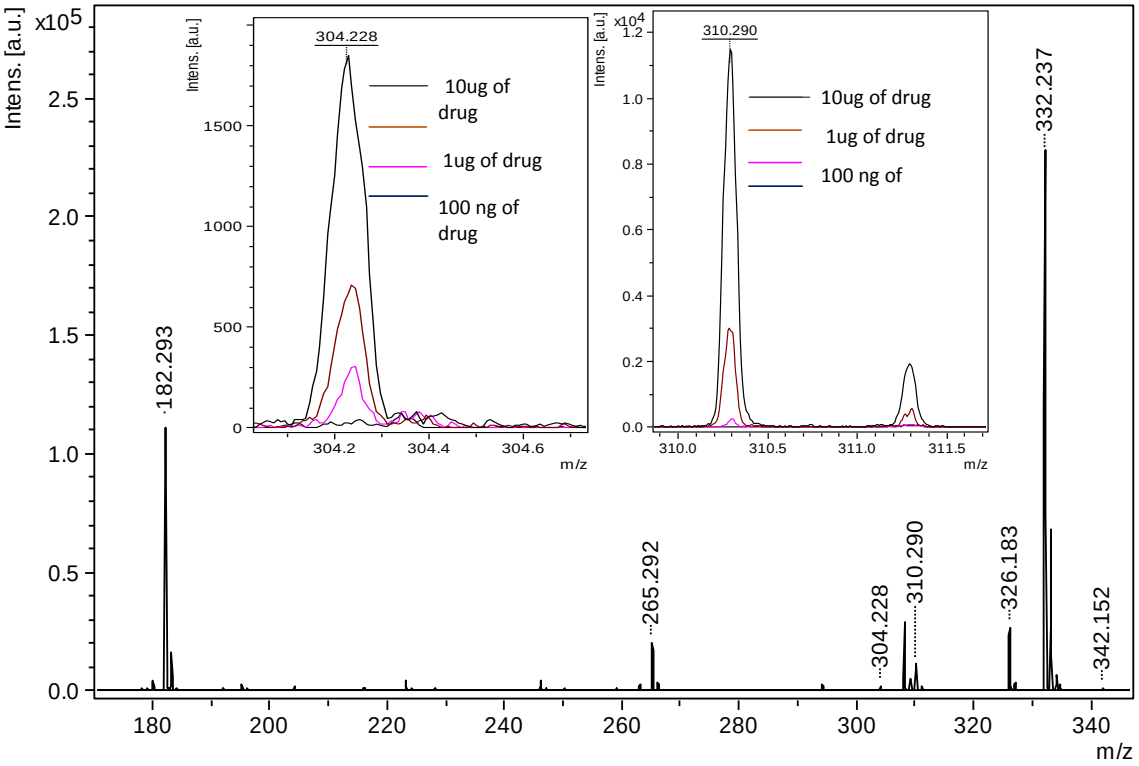

Fig. 2 SALDI MS spectrums of spiked fingermark dusted with black powder showing peaks for cocaine $[M+H]^+$ at *m/z* 304.08 and methadone $[M+H]^+$ at *m/z* 310.15

Table 1 % Cross-contamination of drugs from spiked finger mark to blank finger marks when dusted with CHCA using squirrel and zephyr brushes calculated using the relative *m/z* peak intensities of analyte ions by SALDI TOF MS

Analyte ions	% Cross-contamination compared with spiked mark						
	[a]*m/z* of ions	Mass of drug applied					
		100 ng		1 μg		10 μg	
		Squirrel	Zephyr	Squirrel	Zephyr	Squirrel	Zephyr
Spiked fingermark							
Cocaine $[M+H]^+$	304.16	100	100	100	100	100	100
Methadone $[M+H]^+$	310.22	100	100	100	100	100	100
Methadone fragment	265.21	100	100	100	100	100	100
1st blank fingermark							
Cocaine $[M+H]^+$	304.16	n.d	n.d	n.d	3.6	n.d	3.2
Methadone $[M+H]^+$	310.22	2.0	n.d	8.7	6.6	12.8	5.5
Methadone fragment	265.21	n.d	n.d	n.d	n.d	n.d	3.8
2nd blank fingermark							
Cocaine $[M+H]^+$	304.16	n.d	n.d	n.d	n.d	n.d	n.d
Methadone $[M+H]^+$	310.22	n.d	n.d	1.9	n.d	2.8	n.d
Methadone fragment	265.21	n.d	n.d	n.d	n.d	n.d	n.d
3rd blank fingermark							
Cocaine $[M+H]^+$	304.16	n.d	n.d	n.d	n.d	n.d	n.d
Methadone $[M+H]^+$	310.22	n.d	n.d	n.d	n.d	n.d	n.d
Methadone fragment	265.21	n.d	n.d	n.d	n.d	n.d	n.d

[a]*m/z* are theoretical monoisotopic mass value

n.d – not detected (signal less than mean SD plus 3 x SD for the corresponding blank signal)

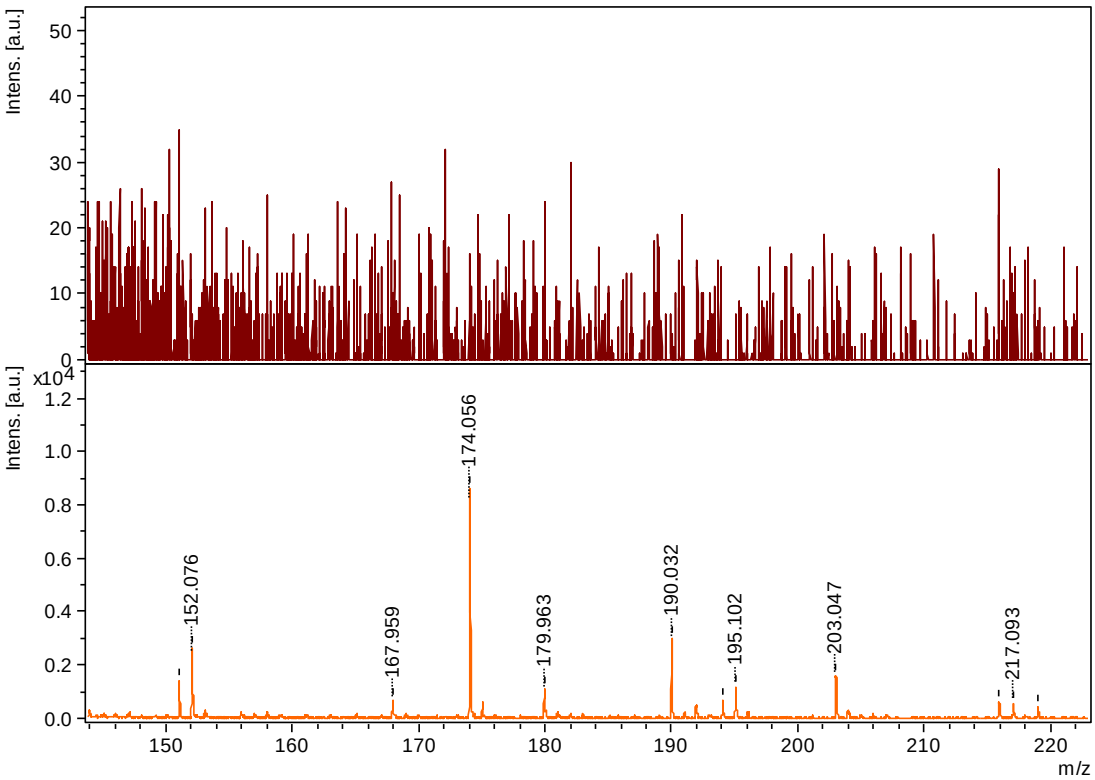

Fig. 3 SALDI MS spectrums of blank (top) and Anadin Extra spiked finger mark (bottom) dusted using black powder showing peaks for paracetamol $[M+H]^+$ at *m/z* 152.07, $[M+Na]^+$ at *m/z* 174.05, $[M+K]^+$ at *m/z* 190.03, aspirin $[M+Na]^+$ at *m/z* 203.03, caffeine $[M+H]^+$ at *m/z* 195.09, $[M+Na]^+$ at *m/z* 217.07

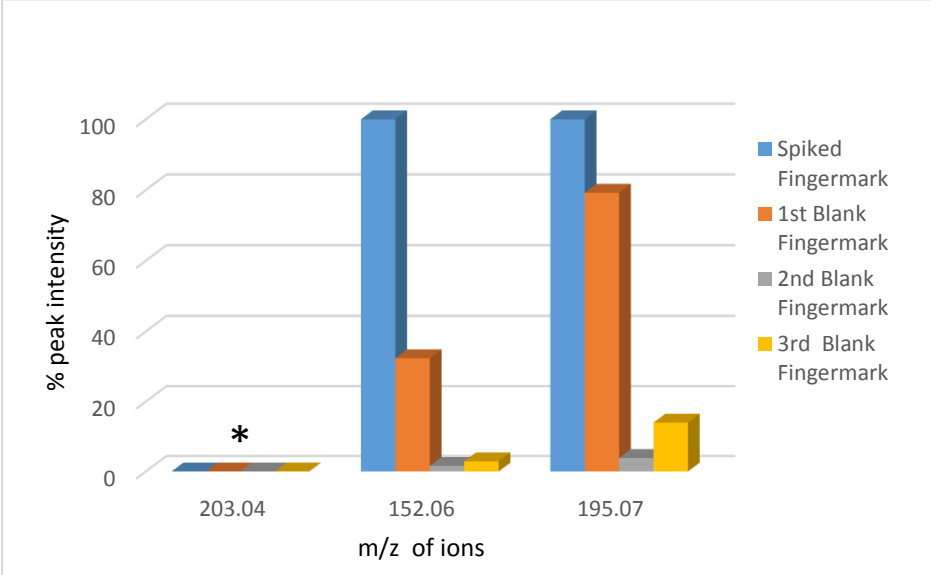

Fig. 4 Relative peak intensities of aspirin $[M+Na]^+$ at *m/z* 203.04, paracetamol $[M+H]^+$ at *m/z* 152.06 and caffeine $[M+H]^+$ at *m/z* 195.07 showing cross-contamination during dusting with CHCA using a squirrel hair brush, expressed as percentage of the corresponding signal from the spiked mark

*not detected (signal less than mean SD plus 3 x SD for the corresponding blank signal)

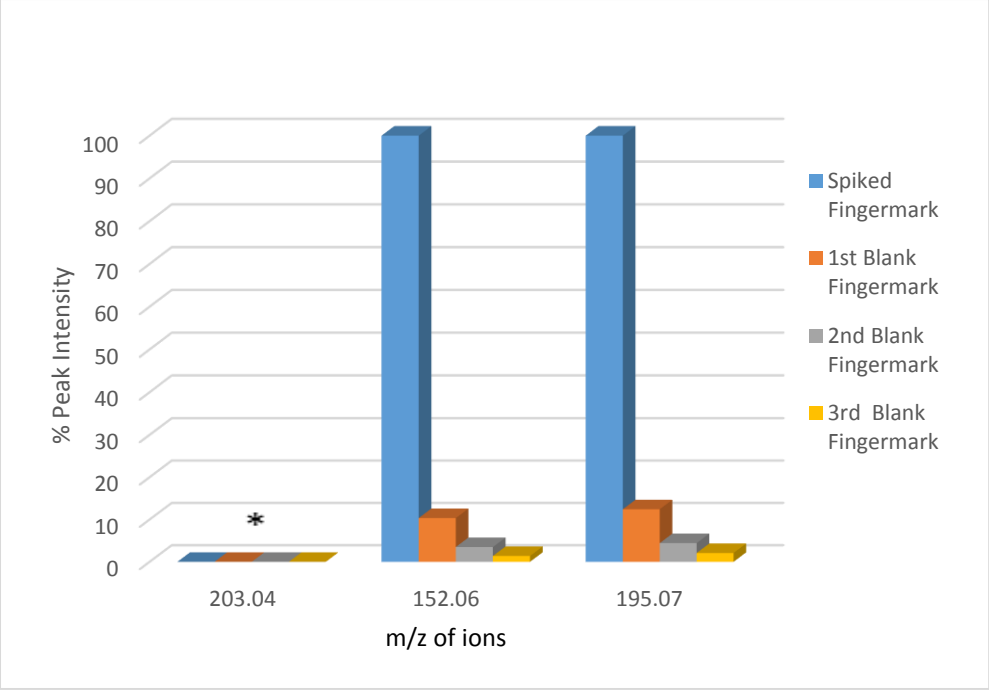

Fig. 5 Relative peak intensities of aspirin $[M+Na]^+$ at *m/z* 203.04, paracetamol $[M+H]^+$ at *m/z* 152.06 and caffeine $[M+H]^+$ at *m/z* 195.07 showing cross-contamination of drugs from spiked finger mark to blank finger marks when dusted with CHCA using zephyr brush expressed as the percentage of the corresponding signal for the spiked mark

*not detected (signal less than mean SD plus 3 x SD for the corresponding blank signal)

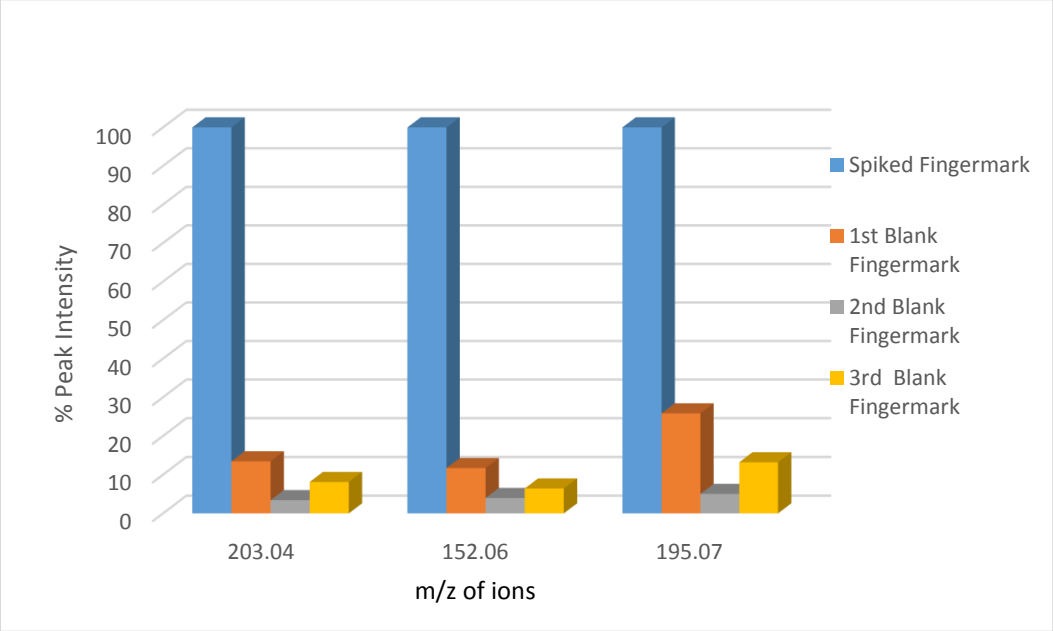

Fig. 6 Relative peak intensities of aspirin $[M+Na]^+$ at *m/z* 203.04, paracetamol $[M+H]^+$ at *m/z* 152.06 and caffeine $[M+H]^+$ at *m/z* 195.07 showing cross-contamination of drugs from spiked finger mark to blank finger marks when dusted with black magnetic powder using a magnetic applicator but without renewing the powder between developed marks

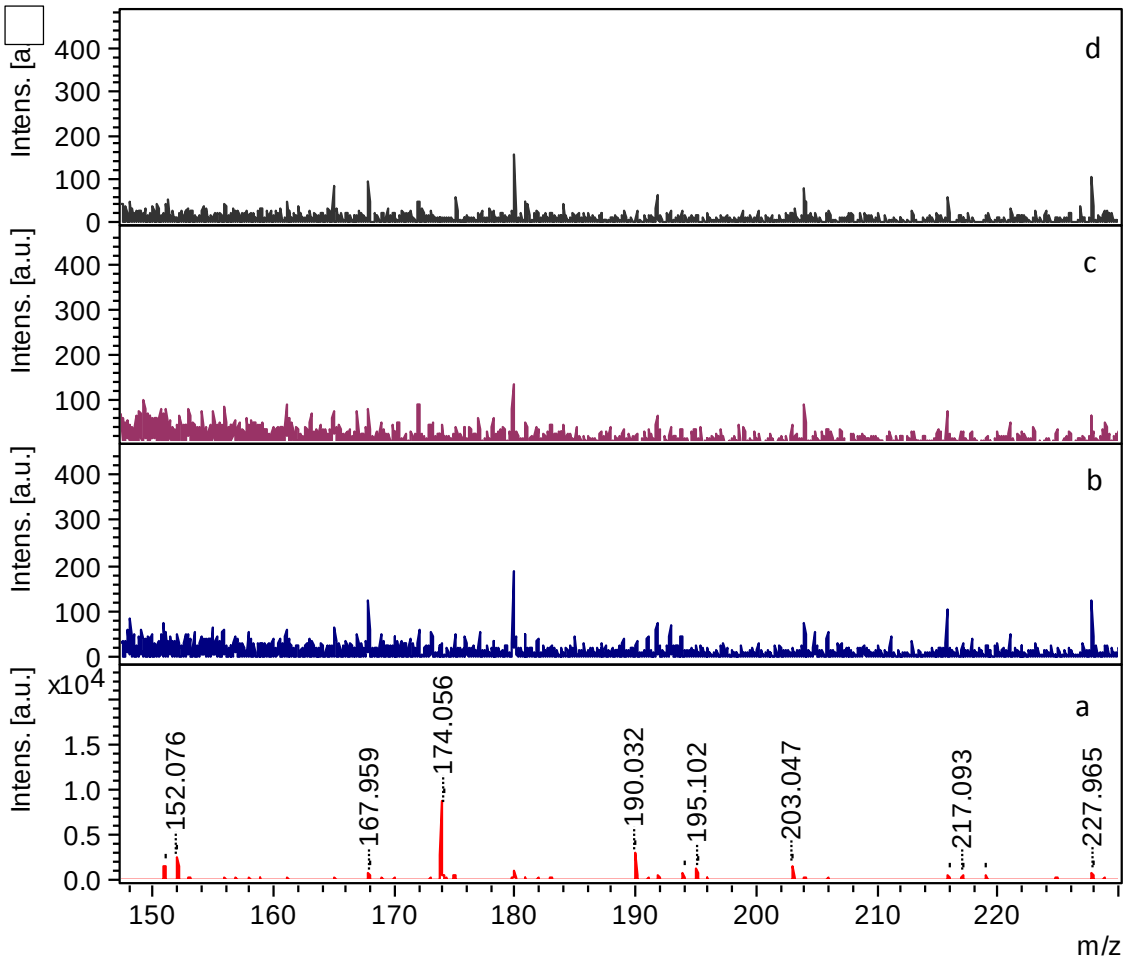

Fig. 7 SALDI MS spectrums of anadin spiked finger mark (a), blank fingermarks in sequence (b,c,d,e) showing peaks for paracetamol $[M+1]^+$ at *m/z* 152.07, $[M+Na]^+$ at *m/z* 174.05, $[M+K]^+$ at *m/z* 190.03, aspirin $[M+Na]^+$ at *m/z* 203.03, caffeine $[M+H]^+$ at *m/z* 195.09, $[M+Na]^+$ at *m/z* 217.07 when dusted sequentially from the spiked fingermark to blank fingermarks (b, c and d) using black magnetic powder after renewing the magnetic wand with fresh powder after each development

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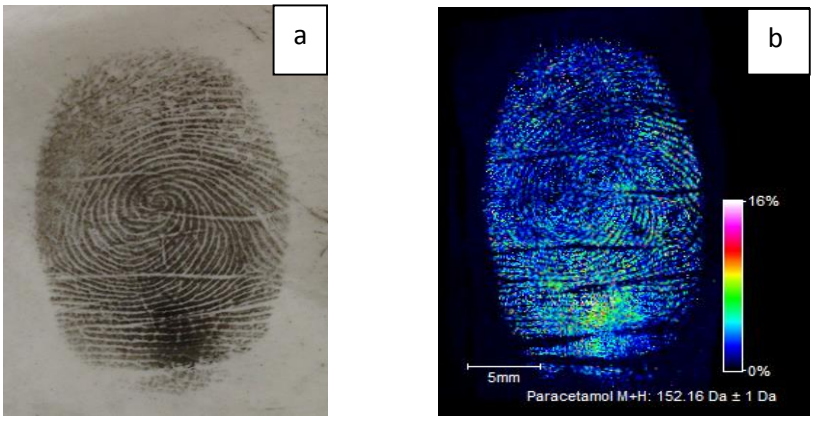
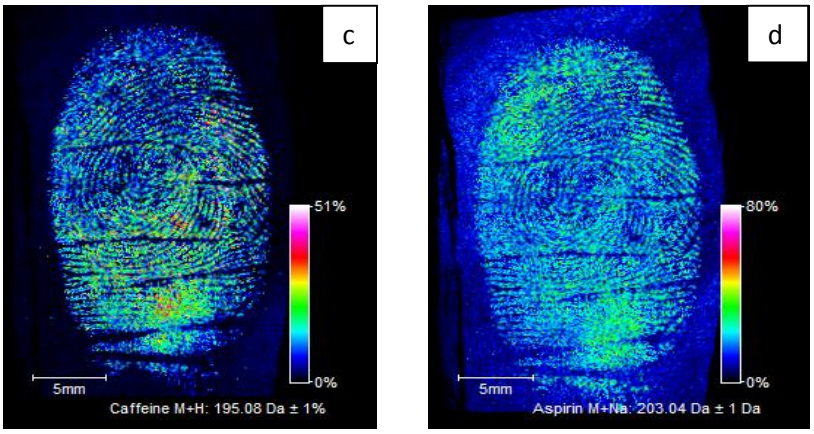


Paracetamol $[M+H]^+$, *m/z* 152.06



Caffeine $[M+H]^+$, *m/z* 195.07

Aspirin $[M+Na]^+$, *m/z* 203.04

Fig. 8 Images of Anadin Extra spiked fingermarks dusted using a magnetic applicator with (a) Black magnetic powder photographed under normal light and SALDI MS Images of paracetamol $[M+H]^+$ at *m/z* 152.06 (b), caffeine $[M+H]^+$ at *m/z* 195.07 (c) and aspirin $[M+Na]^+$ at *m/z* 203.04 (d).