Abstract

Objective: It has been greatly attempted to learn more about chemical information on fingerprints using new techniques and also nano particles bound to specific antibodies for the detection of a variety of substances, including narcotic drugs and medicines. Over the last few years, the sensitive techniques of gas chromatography and mass spectrometry have been found for the detection of residues in the samples with very low values. **Method:** In this study, sampling was taken from fingerprints through optimized methods with chemical solvents and gas chromatography/mass spectrometry (GC/MS) techniques. Samples included a group of volunteers aged 30 to 40 years. Sampling was done by means of glass slides and extraction with solvents of sodium hydroxide, ethanol, and chloroform solutions. Analysis and detection of debris, including nicotine, Tramadol, Methamphetamine, and Cocaine was fulfilled using derivatization and gas chromatography/mass spectrometry. **Results:** The results showed that the use of derivatization as a sensitive method along with gas chromatography/mass spectrometry can detect very small amounts of nicotine in existing samples. **Conclusion:** The results of this research can be used as a way to detect drug residues in fingerprints and ultimately they can be important in providing a standard method for the analysis of these residues.

Keywords: Fingerprint, Drug Residues, Gas Chromatography/Mass Spectrometry

The Recognition of Chemicals in Fingerprints by Gas Chromatography / Mass Spectrometry

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Introduction

For more than one century, the police have been using fingerprint for identifying criminals at the scene of crime. The common methodology for this purpose has been using a white powder which visualizes the latent fingerprint of a criminal if his/her hand has been greasy, since the powder is absorbed by the fingerprint's deposits. With the help of new technologies and approaches, it is possible to recognize the least latent remnants on the surfaces, including Amino acids and glucose (Caldwell, Henderson &Kim, 2001). In a general observation, it can be claimed that the science of fingerprint is completely related to the chemistry based on chemical reaction of a variety of pigments with existing molecules in fingerprint including fats or sugars. In this way, according to the type of target molecule existing in the chemical environment of fingerprint, different methods can be developed and optimized for detecting fingerprint. In recent years, there has been a trend towards gaining more information from fingerprint, in addition to its traditional use for identification. Given the latent remnant of a layer of skin cells on the surface touched by someone, it is possible to extract genetic information from DNA and proteins of the related person and investigate his/her identity via other biological studies. Fingerprint contains a large amount of tissue's sweat (%90) and also Mesophyll cells of skin. The cellular part of sweat on palm includes information of Amino acids and profiles of fatty acids of cells. Given the limited amount of sample existing in the fingerprint, gaining any piece of information on this ground needs precise techniques of detective systems alongside the efficient methods for sample collection for these systems. Studies on the ground of using fingerprint as a useful source for criminal and detective information in recent years have been significantly developed and the first detective kit for drug diagnosis from fingerprint by nanotechnology is expected to be introduced to the market very soon. In recent years, studies on using nano-ingredients containing drug specified antibodies have increased. Therefore, it is possible to develop a nano-detective kit for each type of drug by using specific antibodies for each one (Hazarika, Jickells, Wolff & Russell, 2008, 2010). From among other techniques of interest to researchers on the ground of analyzing fingerprint, is the mechanical technique of mass spectrometry (Song et al, 2012, Briget et al, 2012). Since this technique is so sensitive, it has the capability of detecting the type of many different chemical materials and confirming the presence or absence of them, changes in quality and quantity of them, and effects of the factors such as time on them. So, it is possible to detect everyone's identity by investigating profiles of Amino acids and fatty acids in their fingerprints and determine their age and the time passing from its development (Croxtona, Barona, Butler, Kent & Sears, 2010). One of the modern applications of this technique is to determine the remnants of drugs and addictive substances from the latent fingerprint. This is possible by using mass spectrometry systems

which are connected to separating technique of high performance liquid chromatography (HPLC). In this procedure, the desired compound is separated from other existent substances in the fingerprint by HPLC and, then, it is identified by mass spectrometer. The application of this technique was reported as a successful experience for identifying remnants of methadone addictive substance in fingerprint of the addicts under treatment and also identifying tranquilizing drug of Lorazepam in patients' fingerprints (Goucher, Kicman, Smith & Jickells, 2009; Jacob, Jickells, Wolff & smith, 2008). This study tries to develop an appropriate and effective sampling method according to the maximum efficiency of sample collection for instrumental phase. It is also attempted to propose a concentration method, appropriate sampling method, and, finally, a sensitive systemic technique which enables the detection of qualitatively chemical molecule existing in the fingerprint. In the first phase of this study, an appropriate systemic way for identifying molecule is developed and optimized. Then, the method of providing sample and appropriate sampling for desired systemic technique is optimized and experimented. The aim of this study is to investigate appropriate methods of collecting sample from fingerprints, extraction methods, and appropriate technique of instrumental analysis and, at the end, to achieve feasibility for observing chemical molecule in fingerprint. The results of this study can be used as an addiction test or a method for the chemical analysis of the fingerprints left at the scene of crime.

Method

In this study, compounds of nicotine, Tramadol, methamphetamine, cocaine and methadone were used for investigating potentials for detective methods. Given accessibility of smokers, some of the stages of the study were carried out by standard substance of nicotine for determining the methods of extracting and systemic optimizing and the second stage of study was carried out on the narcotic samples consumed by the participants.

For providing samples, some male volunteers from 30 to 40 years were chosen and some of them had a history of addiction for at least 3 months and one person was chosen as the control group who had no history of addiction. These people at the outset washed their hands with alcohol and ethanol and, then, gently dried them. For taking samples their pointer fingers were used with which they touched the sampling surface for a few times. Sampling was carried out on a glass slide of microscope which had already been carefully cleaned. When the participants touched the slides, the slides were put in a closed container and they were kept at a temperature of -80° C for the next stage of study. This method was selected for the sake of a report stating Lorazepam drug is identified in fingerprints (Jacob, Jackals, Wolff andSmith 200).

For extracting compounds from the fingerprint, 1000 microliters of De-chloromethane and Methanol solvents with an equal proportion were used (Kintz, Kieffer, Messer, & Mangin, 1993; Lee et al, 2007). Extracted methanol contained C-sorbitol (40µg/mL) as an internal standard. De-Chloromethane was used duo to its semi-polar state and its ability of solving fatty acids in fingerprint. Container of slides was put into the Ultrasonic system and it was trembled for 10 minutes. The first layer solution was extracted and its solvent was evaporated by Rotary system. Then, 500 micro liters of hydro oxide sodium (%5) were added to the extracted residuum and the last extraction was done by 500 micro liters of Chloroform. Extracted Chloroform solution was centrifuged for 10 minutes and it was passed from a 0.45-micron filter and its solvent was evaporated. For carrying out the GC study, derivatization processes were done on the remnant of residuum. Related studies and measurements were carried out by means of GC/MS 4000 Varian model with trap ion detector and temperature programming. A pole with 30 meters in length and 0.25 µm in diameter and the proportion of 10.1 split was used. The injector's temperature was 250° C. The temperature of the pole at the outset of experiment was 80° C and was reached 300° C with the speed of 10 degrees per minute and it was held in this temperature for 10 minutes.

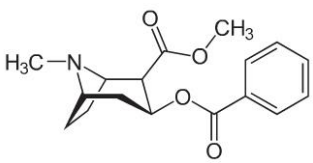
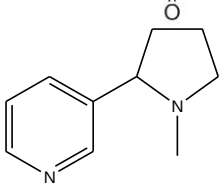
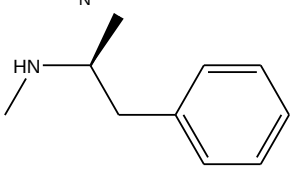
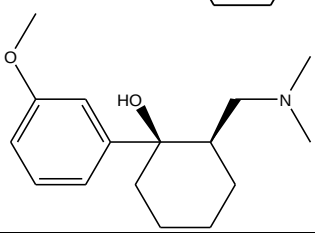
For derivatization of the dried sample, 20 mg Monoxide Amin Hydro Chloride were used in dried Pyridine, which 40 micro liters were added to each sample and they were put under 37° C for 2 hours. Then 70 micro liters compound of MSTFA were added to each sample and they were placed under 37° C for 45 minutes (Roessner et al, 20066). Nicotine recognition was done based on differentiation recognition with MSTFA after nearly 7 minutes. The derived compounds were injected into the system and they were identified. This was done according to the method developed by Roessner for derivatization in compounds for GC analysis (Roessner et al, 2006). Nicotine diagnosis was done based on the recognition of its derivatization with MSTFA in 7 minutes.

Results

Nicotine's standard analyses with ESI/Q-TOF system: having this molecule fabrics, it is possible to carry out selected ion Monitoring (SIM) for observing all fabrics; therefore, the last chemical molecule is confirmed. For the analysis and conformation of carried out differentiations and determining the exact mass of provided differentiation of each compound, a solvent with the density of 10 micro molar was provided from each compound in methanol solution and was injected into the system. Then, the analysis of diagnosis or non-diagnosis of substance was done on all experimental samples through an optimized method of GC method.

The analyzed structure of compounds and their molecule mass are presented in the following table.

Table1: The analyzed structure of compounds and their molecule mass

Compound's noun	Compound's structure	Mass molecule of compound	Molecule mass of differentiated compound
Cocaine		303	376
Nicotine		162	235
Methamphetamine		149	222
Tramadol		263	336

The analysis of fingerprints with GC/MS technique: in the next step, GC/MS system's ability for determining nicotine in existing samples was investigated. For this purpose, derivatization and volatilization of compounds in fingerprints were used along with their reaction with MSTFA. For identifying the compounds, the library of the system was used. (Figure 1)

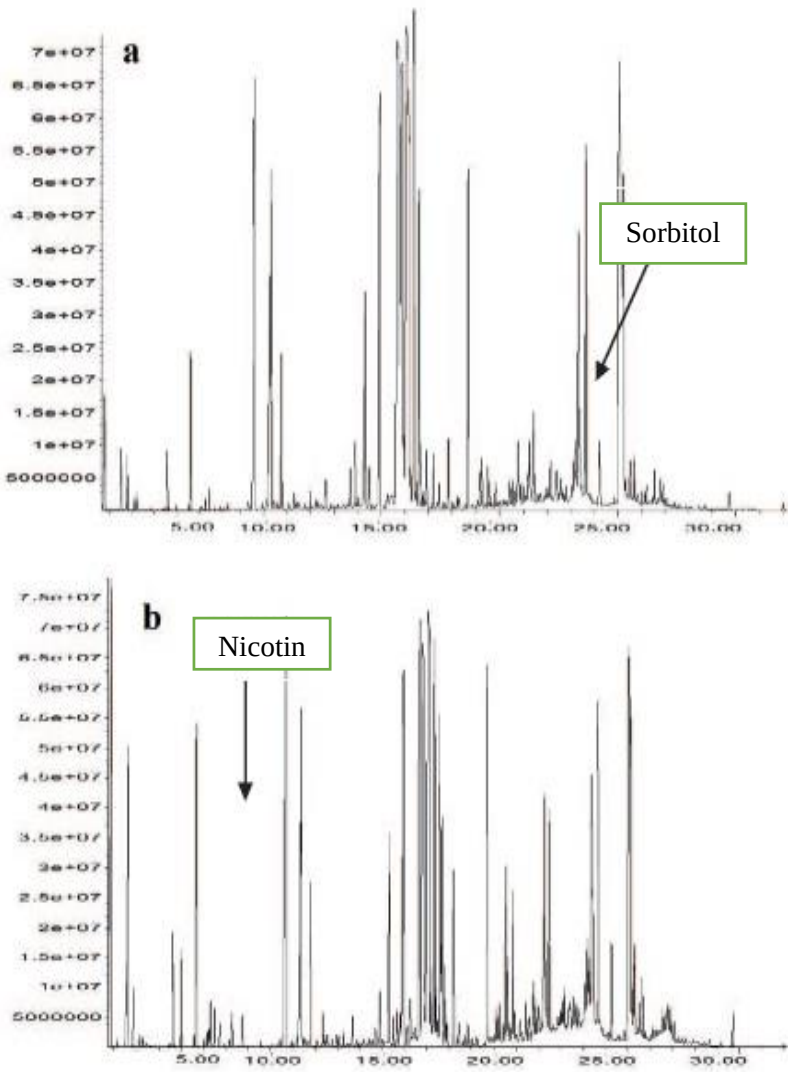


Figure 1: Differences in amount of Tramadol in two samples

In this way, GC/MS technique showed that it is well able to analyze small amounts of nicotine. This technique alongside derivatization method has the potential to distinguish other groups of metabolites such as Amino Acids and fatty acids (figure 2)

Figure 2: The list of identified compounds in the fingerprint with GC/MS system

Identifying tramadol in fingerprints: after the optimization of extracting methods and determining optimized method of analyzing with GC/MS technique, tramadol diagnosis was carried out. Given the fingerprints gained from a volunteer individual who had consumed tramadol, the sampling was carried out in two intervals of 15 and 30 days. Then, the optimized method for determining surviving time of tramadol after consumption was performed. As it is seen in figure 3, a very small amount of tramadol in the fingerprint was found on the 15th day. For the same reason, the composition of tramadol continued for more than 15 days again and sampling was done on the 30th day. As it is seen, the existence of this compound was identified in 12.2 minutes in chromatogram and its changes in fingerprint were well recognized by this technique.

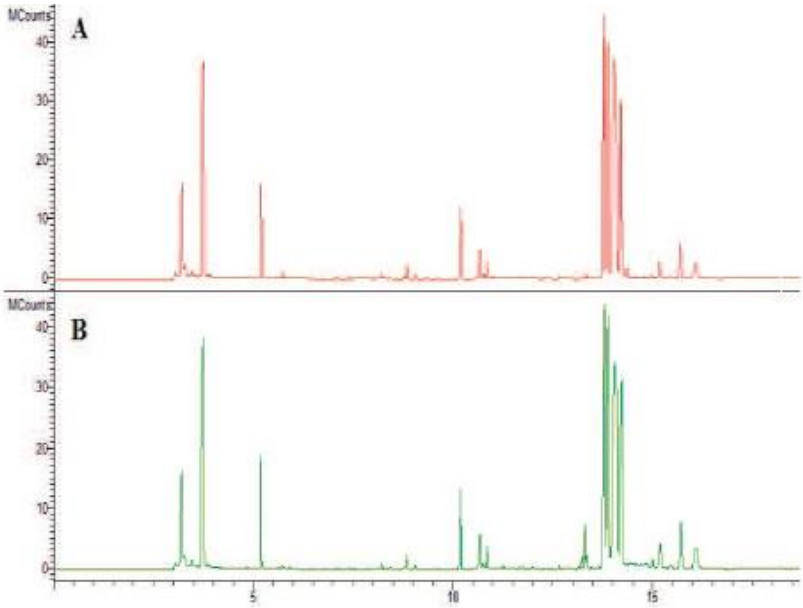


Figure 3: Identifying Tramadol in taken samples

Identifying methamphetamine in fingerprint: After optimization of extracting methods and determining optimized method of analyzing with GC/MS technique, identifying methamphetamine in addition of tramadol in fingerprint of an individual who had used crystal was carried out.

As it is shown in figure 4, profile of crystal consumer's fingerprint is so different from other samples.

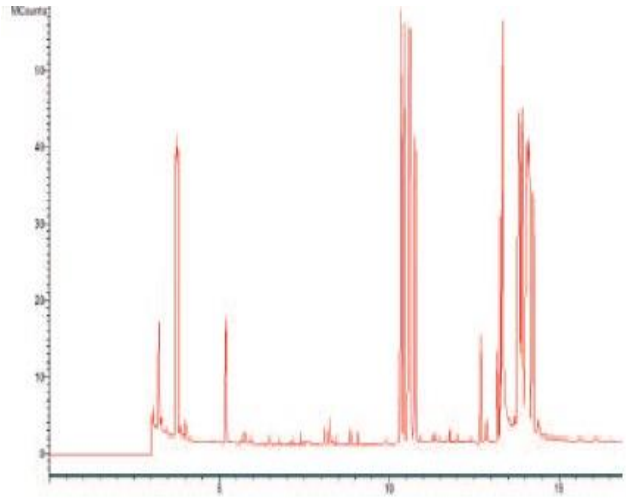


Figure 4: Identifying Methamphetamine in one of the taken samples

Identifying cocaine in fingerprint: in many different samples, there are grass and cocaine which is known as a powerful stimulus. This compound was also extracted and identified in the fingerprint taken from a consumer.

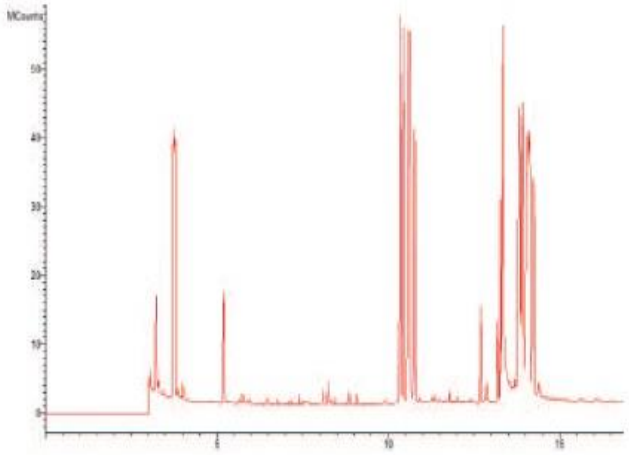


Figure 5: Identifying Cocaine in one of the taken samples

Discussion and Conclusion

Given the results of this study, it can be said that the proposed methods have the potential to detect nicotine and other similar addictive compounds. The use of this method including dichloromethane/methanol mixture as an extractive solvent and more extracting by alkaline solvent of hydroxide sodium had appropriate responses for the extraction of the compounds. It was confirmed that this method could identify existing substances in the samples, even though the GC/MS method was time consuming. Using such a method had already been employed for identifying methadone in fingerprints (Goucher et al, 2009). Such an analysis for Lorazepam with LC/MS-MS method has already been reported and it has been shown that methanol/dichloromethane solvent was effective for extracting (Jacob et al, 2008). This report has shown that if the quantity of drug is determined, pharmacodynamics' studies on fingerprints with these techniques will be possible due to the specification of dose of consumption and consumption intervals. GC/MS technique provides the potential for using library in identifying all observed compounds in Chromatogram. Given these results, a vast group of these compounds including Amino Acids, sugars, fatty acids and Carbonic Acids were identified in fingerprints. These results provide the potential to investigate metabolism of body cells according to the type of consumed drugs, age differences or any kind of illness. This method is more dependent on extracting and higher sensitivity of gas chromatography for small amounts of substances than diagnosis methods. Given the use of very

narrow and tall poles (between 30 to 60 meters) in gas chromatography, extracting efficiency for compounds is higher in this method. According to Fihen et al (2000), this method was able to identify more than 100 types of compounds just in 50 milligrams of a tree. Using derivatization in compounds with MSTFA compound leads to their flux and evaporation which creates an analysis of potential for them with GC. This method is advantageous to liquid chromatography as follows: Gas chromatography and required identifiers for differentiation are less expensive than solvents and maintenance of liquid chromatography systems. There is the possibility of applying derivatization and gas chromatography with existing domestic facilities; however, providing LC-Q/TOF systems is so expensive. GC/MS system is able to identify a vast group of substances and existing metabolites including Amino Acid, carbonic acids, and sugars that are so valuable for metabolic studies. In GC/MS technique, it is possible to use popular compound of Sorbitol as a domestic standard.

Generally speaking, the result of this study has shown that there is a possibility to recognize remnants of consumed substances in fingerprints. With comparing applied techniques, it is possible to say gas chromatograph/mass spectrometry (GC/MS) technique which is accessible inside the country alongside the optimized derivatization method in this study can be used as an appropriate method for developing this science inside the country and taking the next steps.

References

Bright, N.J., Webb, R.P., Bleay, S., Hinder, S., Ward, N.I., Watts, J. F., Kirkby, K. J. , Bailey, M. J. (2012). Determination of the Deposition Order of Overlapping Latent Fingerprints and Inks Using Secondary Ion Mass Spectrometry. *Analytical Chemistry*, *84*, 4083–4087

Caldwell, J. P., Henderson, W., Kim, N. D. (2001). Luminescent visualization of latent fingerprints by direct reaction with a lanthanide shift reagent. *Journal of Forensic Sciences*, *46*, 1332–1341

Croxtona, R. S., Barona, M. G., Butler, D., Kent, T., Sears, V. G. (2010). Variation in amino acid and lipid composition of latent fingerprints. *Forensic Science International, 199*, 93-102

Fiehn, O., Kopka, J., Dörmann, P., Altmann, T., Trethewey, R. N., Willmitzer, L. (2000). Metabolite profiling for plant functional genomics. *Nature Biotechnology, 18*, 1157-61

Goucher, E., Kicman, A., Smith, N., Jickells, S. (2009). the detection and quantification of lorazepam and its 3-O-glucuronide in fingerprint deposits by LC-MS/MS. *Journal of separation science, 32*, 2266- 2272

Hazarika, P., Jickells, S., Wolff. K., Russell, D. (2008). Imaging of latent fingerprints through the detection of drugs and metabolites. *Angewandte Chemie International Edition*, *47*, 10167–10170

Hazarika, P., Jickells, S., Wolff. K., Russell, D. (2010). Multiplexed detection of metabolites of narcotic Drugs from a single latent fingermark. *Analytical Chemistry, 82*, 9150–9154

Jacob, S., Jickells, S., Wolff, K., Smith, N. (2008). Drug Testing by Chemical Analysis of Fingerprint Deposits from Methadone-Maintained Opioid Dependent Patients Using UPLC-MS/MS. *Drug Metabolism Letters*, *2*, 245-247

Kintz, P., Kieffer, I., Messer, J., Mangin, P. (1993). Nicotine analysis in neonates' hair for measuring gestational exposure to tobacco. *Journal of Forensic Sciences, 38*, 119-23

Lee, J. G., Lee, C. G., Kwag, J. J., Rhee, M. S., Buglass, A. J, Lee, G. H. (2007). Fast analysis of nicotine in tobacco using double-shot pyrolysis--gas chromatography--mass spectrometry. *Journal of agricultural and food chemistry, 55*, 1097-102.

Roessner, U., Patterson, J. H,, Forbes, M. G, Fincher, G. B, Langridge, P., Bacic, A. (2006) An investigation of boron toxicity in barley using metabolomics. *Plant Physiology, 142*, 1087–1101

Song, W., Mao, Z., Liu, X., Lu, Y., Li, Z., Zhao, B., Lu, L. (2012). Detection of protein deposition within latent fingerprints by surface-enhanced Raman spectroscopy imaging. *Nanoscale, 9*, 213-221.