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INK DETECTION IN FORGED DOCUMENTS WITH THE USE OF ADVANCEMENT OF MASS SPECTROMETRY

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ABSTRACT

Analysing ink on forged documents is usually used in order to check if the document is genuine or illegal, whether the formula of the ink is the same and the ages of the ink. This chemically has two goals which is to classify the various inks which are available on the market and to determine if there is more than one type of ink available on suspected medical documents. However, the presence of one or more can lead to suspicion. Therefore, ink detection has been an active research topic in the field of medical ethics. Since early years several methods like high-performance liquid chromatography and capillary electrophoresis was introduced where these methods were considered to be slow compared to the other methods. However, among several methods, ambient mass spectrometry was found to be one of the best methods to be used in ink detection. Ambient mass spectrometry rapidly developed in the year 2000 where desorption electrospray ionisation, paper-spray mass spectrometry, direct analysis in real-time mass spectrometry and desorption atmospheric pressure chemical ionisation mass spectrometry were the several methods used in ink detection where desorption atmospheric pressure chemical ionisation mass spectrometry was one of the best methods to be used due to its high sensitivity compared to the other methods. Moreover, researchers found that following DAPCI, Raman Mass Spectrometry and MALDI- mass spectrometry were some of the current methods used in the ink detection. Thereby, this review highlights on the development of mass spectrometry in ink detection in medical ethics. Keywords: Mass Spectrometry, Ink Detection, Ethics, Illegal documents, Real time analysis



INTRODUCTION

Writing ink was first invented in Egypt and China in 2500 BC where soot was used as the main component. After some time, (i.e: in the middle ages) they used Arabic gum, copper sulphate and tannins (Montes *et al.*, 2009). Ink is mainly made of colorants, several resins and a solvent/mixture which contributes to various properties of ink. Furthermore, the inks used in documents can be divided into two groups as ball point and non-ball-point (Ezcurra *et al.*, 2010).

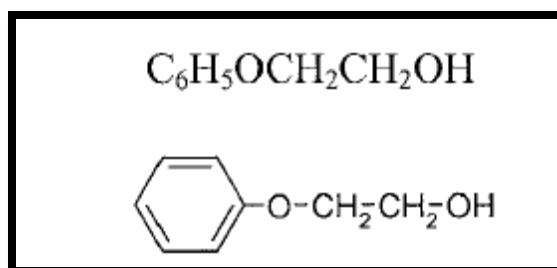
Analysing ink on documents is usually used in order to check if the document is genuine or illegal, whether the formula of the ink is the same and the ages of the ink (Jones, Cody and McClelland, 2006). This chemically has two goals which is to classify the various inks which are available on the market and to determine if there is more than one type of ink available on a suspected document. However, the presence of one or more can lead to suspicion (Weyermann *et al.*, 2007). Moreover, determining the age of ink has two main approaches which are the direct dating and indirect dating. Indirect dating involves on the chemical analysis of ink along with the comparison with known samples in a collection of references where direct dating involves the measurement of components of ink changing with age (Bugler, Buchner and Dallmayer, 2008).

.The first case in ink forgery was reported in 1889 in New York which was related to the chemical examination of ink on a questioned document. After decades, ink forgeries became an active research topic in forensic sciences (Neumann, Ramotowski and Genessay, 2011). Several other methods in order to detect fraudulent documents developed slowly in the year of

1950. However, improvements in this area of study were slow. Before 1950, ink detection was done by observing and examining the particular document by photography where filters were used to enhance various contrasts between different types of inks. Apart from that, documents also were under examination by the observation of colour of inks under different wavelengths of light ranging from ultraviolet to infrared. At times, under chemical tests, metals such as copper and chromium were used to detect fountain pen inks, but none of these methods mentioned above did not provide individualized information in order to characterize the different formulation (Chen, Meng and Cheng, 2001).

Detecting the age of ink on a document can be challenging. As shown in figure 01, the most common compound found in most of the ink is 2-phenoxyethanol (PE) which is a common volatile organic compound.

Figure 1: Structure of the molecule 2-phenoxyethanol (LaPorte et al., 2004).



It is stated that early methods like optical examination, thin layer chromatography had reference ranges limited to few colorants and fluorescent dyes, and methods like capillary electrophoresis and HPLC were found to be slow. However, mass spectrometry turns out to be one of the best method for identification of ink



because it obtains the information on the structure of the analysed molecules. With time, various types of mass spectrometry (MS) has been developed such as electrospray ionisation mass spectroscopy, DART-TOFMS and MALDI-TOFMS (Sun *et al.*, 2016). Among various types of mass spectrometry, ambient mass spectrometry was considered to be the best type to be used in ink detection. Ambient mass spectrometry was first found in the year 1988 by Fenn and is a fast growing and a powerful field providing a highly sensitive

mass spectrometry. There are various applications of ambient mass spectrometry such as detecting the composition of counterfeit pharmaceutical tablets and imaging document verification analysis and identification of fingerprints (Green *et al.*, 2009).

Moreover, as shown in figure 2, ambient mass spectrometry has three diffusion ionisation mechanisms based on their mechanism.

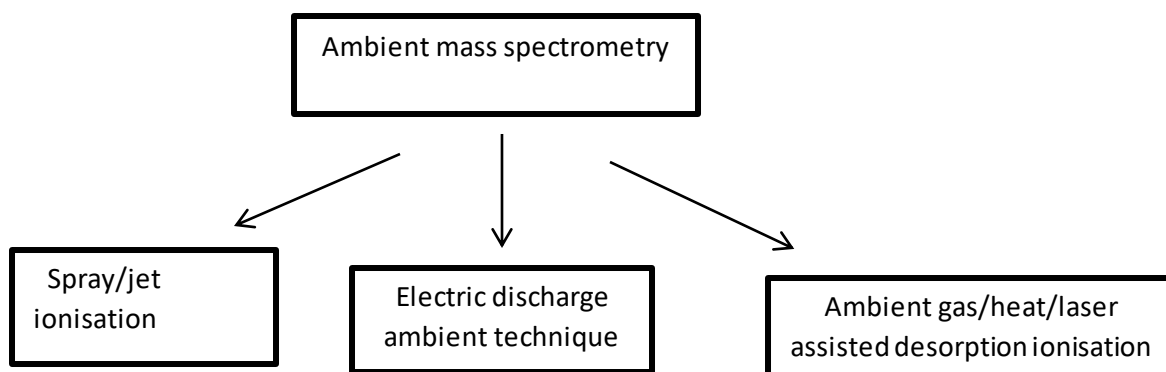


Figure 2: The three types of ambient mass spectrometry based on their mechanism (Black, Chevallier and Eliot, 2016).

This ambient pressure ionisation method can be applied to analyse a range of compounds which includes peptides, proteins, pharmaceuticals, explosives and others. Several ambient methods were developed from year 2000-2010 (Table 1), but only few methods such as paper-spray mass spectrometry (PS-MS), desorption

electrospray ionisation mass spectrometry (DESI-MS), direct analysis in real time mass spectrometry (DART-MS) and desorption atmospheric pressure chemical ionisation mass spectrometry (DAPCI-MS) was used mainly used in ink detection.

Table 1: Development from the year 2000-2010 (Alberici *et al.*, 2010).

Year	Technique introduced
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2000	Secondary electrospray ionisation
2002	Fused droplet electrospray ionisation (FD-ESI)
2004	Desorption electrospray ionisation (DESI)
2005	Direct analysis in real time (DART)
2006	Desorption atmospheric pressure chemical ionisation (DAPCI)

The advantage of ambient mass spectrometry is that direct surface analysis can be done with no pre-treatment or extraction and filtration. One of the main principles of ambient mass spectrometry is that it allows in developing direct ionisation methods which in turn allows desorption and ionisation of analytes. This helps the procedures to be performed rapidly and with less human interference. More than 30 ambient techniques were introduced within few years (Analyst, 2010). Among the various types of techniques of ambient mass spectrometry used, few contribute in ink dating which will be discussed in detailed below, some of the best techniques which can be used for ink detection are; PS-MS, DESI-MS, DART-MS and DAPCI-MS. This review will be mainly focused on the above mentioned four types of ambient

mass spectrometry with its relation to the detection of ink in forged documents.

AMBIENT MASS SPECTROMETRY IN DETECTING INK

Desorption electrospray ionisation MS (DESI-MS)

DESI-MS (Figure 3) was introduced in the year 2004 and was proposed by a scientist named Cooks and his group in University of Purdue (Nielen *et al.*, 2011). However, DESI was performed on ink detection in the year 2009 by Ifa and his co-workers. There are three mechanisms which are involved in this type of mass spectrometry. They are; computer simulations of fluid dynamics, droplet size and velocity measurements and surface charging effects (Morelato *et al.*, 2013). One of the main feature of DESI is



that it is easy for the supply of chemical reagents to the analysis site. By this, the generation of specific reaction products used to confirm the analyte identification is allowed (Takats *et al.*, 2004). Some of the other features in DESI are high speed, formation of positive and negative ions, wide applicability, high throughput, molecular specificity from mass spectrometry and no special surface is

required. The appropriate ionisation mechanism is understood and is believed that it is taken place by a charged-droplet pick up process.

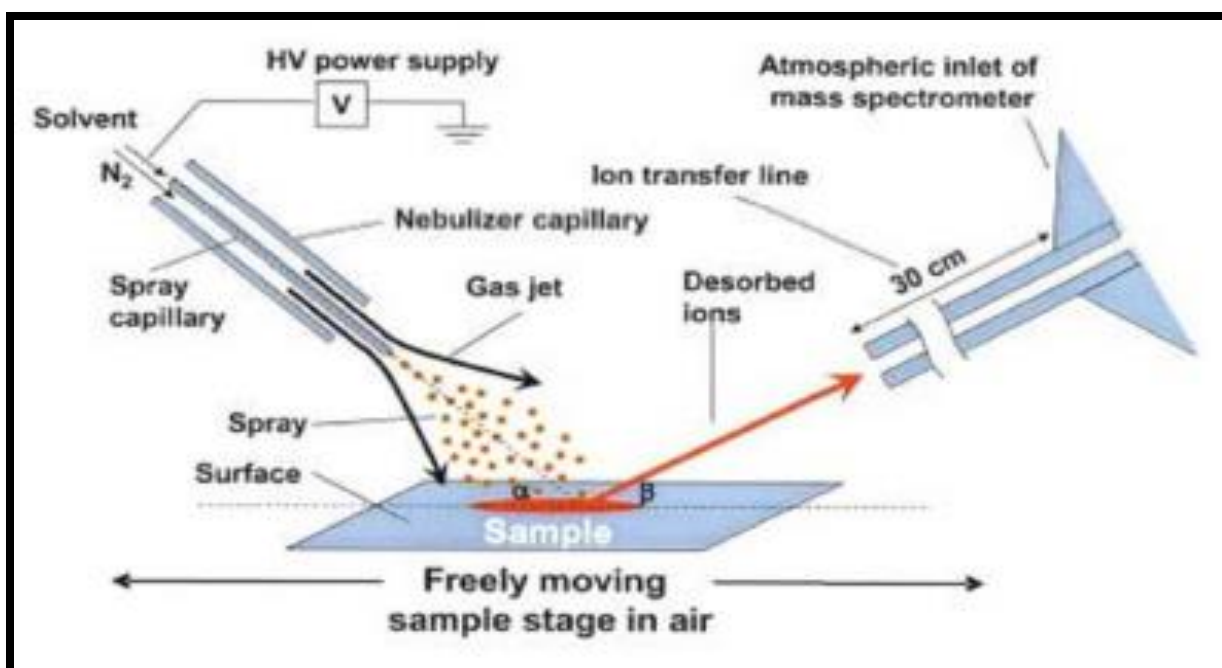


Figure 3: Schematic diagram of DESI (Lin and Chen, 2013).

DESI occurs when charged micro-droplets are directly sprayed from the spray capillary under ambient conditions. The spray will desorb the sample into its ionised form where transports through an atmospheric pressure interface into the MS inlet where the solvent will be removed by heat and vacuum. The mass spectrometer is operated in the positive electrospray ionisation mode along with a specific capillary voltage. The ion source block and the cone voltage are maintained at a particular temperature and voltage

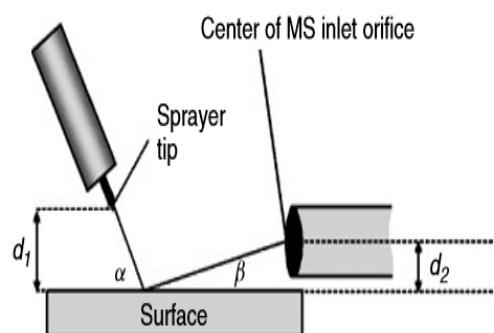
respectively. DESI electrospray needle is usually at a high voltage and spray is aided with nitrogen gas (Ratcliffe *et al.*, 2007). Moreover, methanol or water solution in the ratio 1:1 is electro-sprayed directly on the samples in order to achieve a proper analytical performance (Chen *et al.*, 2007).

However, DESI works best when there is relatively a high pressure sheath gas in the electrospray source, thereby a strong signal can be maintained.

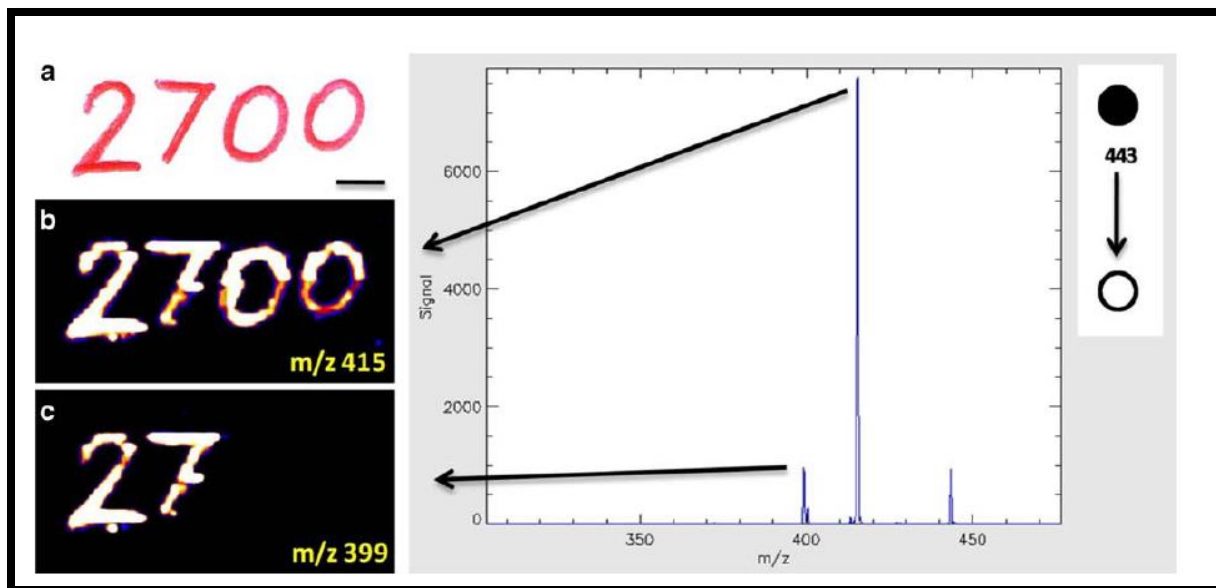


Furthermore, as shown in figure 4, DESI is affected by angles α , β , d_1 and d_2 which has to be taken into consideration, thus the value of the respective angle differs on different types of samples analysed.

Figure 4: Angles taken into consideration in DESI-MS (Takats et al., 2005).



In 2009, Ifa and group of co-workers



performed a study to check how DESI works in ink detection. Number 27 was written in one type of ink which contained pigment rhodamine B and 6G where the two zeros were written in the type of ink containing only rhodamine B. However, even if both the pigments had the same mass to charge ratio which is m/z 443, DESI-MS has the ability to distinguish them by the fragmentation pattern. The graph shows that rhodamine 6G indicated

its main fragment m/z 415 (fig 5b) and rhodamine B indicated its main fragment m/z 339 (fig 5c) which shows a complete difference. Advantages of DESI include of not requiring a sample preparation and also remaining of the sample in its native environment. However, there are number of disadvantages of DESI. Firstly, the solvent has to be impelled which requires an increased speed of gas which results in more power and weight involved than with



low temperature plasma MS (LTP-MS) or DART-MS. Additionally, the ionisation process and the probing process has to take place under vacuum which eventually leads to the change of focal environment which is prior to analysis.

Furthermore, it is also time consuming because the whole surface has to be covered, exploration of large sample area

which eventually results in low analyte spatial resolution and permanent damaging of samples takes place during sampling (Kao *et al.*, 2015). It also requires a number of solvents in order to distinguish inks. The solvent spray and the flow rate has to be selected carefully in order to stop ink from spreading on document which can eventually lead to destruction of the document (Morelato *et al.*, 2013).

Paper-spray mass spectrometry (PS-MS)

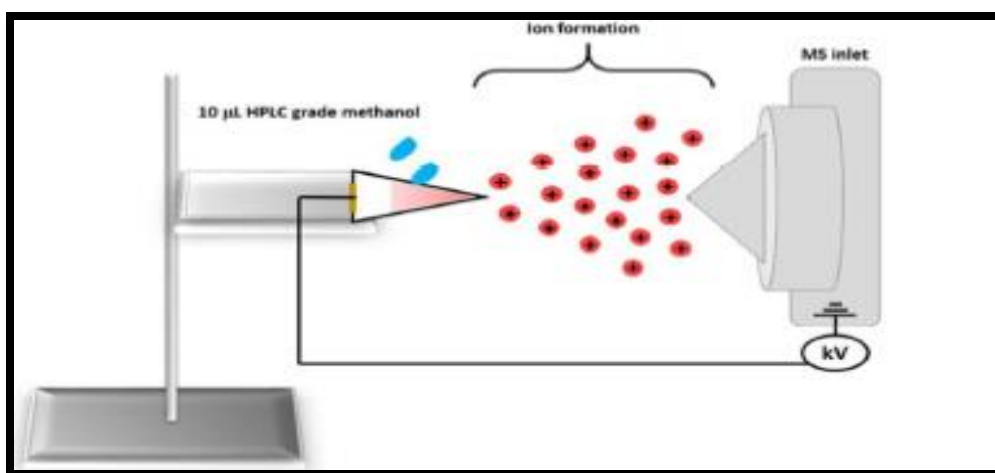


Figure 5: Schematic diagram of PS-MS (Liu *et al.*, 2010).

It was found that one of the major limitations of DESI-MS was that the spray-jet technique had possibilities of damaging the document. However, it seems that PS-MS could be a better method to be used in ink detection. Paper-spray MS is a flexible ambient ionisation method which was first proposed by Cooks and his co-workers in the year 2010. It was considered as one of

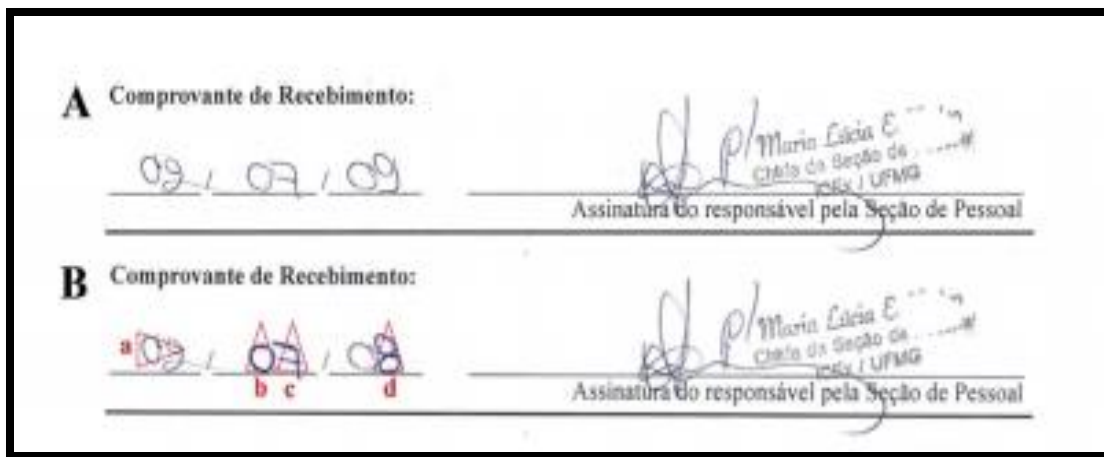
the fastest analysis methods and a well-developed method in the analysis of complex mixtures using mass spectrometry. Moreover, paper spray mass spectrometry (figure 6) can be used to analyse the samples in its original native environment (Epsy *et al.*, 2012).



A paper is cut in the shape of a triangle to have a sharp macroscopic point and placed directly in front of the mass spectrometer inlet. A paper spray mass spectrometer contains a mobile platform which rotates in a 3D movement and paper is fixed with a copper metal clip. Sample to be analysed is placed on the paper where then the paper is wet with a solvent which is usually methanol or a combination of methanol and

deionized water. A high voltage is then applied through the metal clip which will produce ions to be detected by the mass spectrometer. At the same time spray voltage, capillary voltage, tube lens voltage and capillary temperature will remain constant. The mass spectrometer will then produce data which usually remains between the mass to charge ratios of 100-1200 (Jurisch and Augusti, 2016).

Figure 6: (a) Original and (b) counterfeited document. Paper was cut in four different areas in



the triangular shape (a,b,c and d) where the samples were used to detect in the ink forgery done using mass spectrometry (Ferreira et al., 2015).

In 2015, Ferreira and his co-workers decided to analyse the old inks and to detect the superimposition ink lines using PS-MS. They used archived documents in the original form and altered form (Figure 7) using different kinds of pens. Paper spray mass spectrometry was then performed on four different letters in the altered document and mass spectrum was obtained (Figure 8a) where the spectrum clearly indicated the ink components which belonged to original ink with its respective mass/charge ratio

peak (Table 2) and the ink components which belonged to a completely different type of ink (i.e: new pen which was used to change the document) showed different m/z ratio peaks (Table 3) (Figure 5 b,c,d).

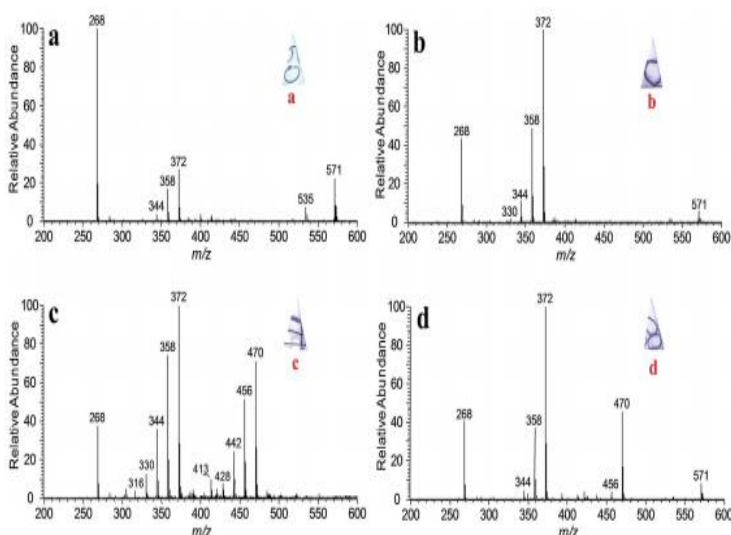




Figure 7: Mass spectrum data obtained by the experiment performed (Ferreira et al., 2015).

Mass spectrum 8b shows an increase in the peak 372 which indicates that there is a high concentration of the ink present, therefore indicating that it has been re-written on the original document. At the same time it is visible m/z 268 has reduced compared to the peak in mass spectrum 8a due to ink degradation. Furthermore, in mass spectrum 8c a complete different m/z value (i.e: m/z 470) is seen which belongs

to a completely different type of ink (Table 3). Mass spectrum 8d again shows one peak which belongs to m/z 470 indicating it contains the basic blue 26 component and its demethylated homologues. Presence of basic blue 26 peaks therefore confirms that a different type of ink was used in this document.

Table 2: Ink components of the original ink used in the document (Ferreira et al., 2015)

Ink component	Mass/charge ratio
1,3 dimethyl-1,3-ditolyl guanidine	268
Basic violet 3	373
Nickel phthalocyanine	571

Table 3: Ink components of the new pen used to alter the document (Ferreira et al., 2015)

Ink component	Mass/charge ratio
Basic blue 26	470
Demethylated homologues of basic blue 26	412 428 442



However, PS-MS had several advantages such as having the ability to ionise complex mixtures with minimum sample pre-treatment (Yang *et al.*, 2012), requires a low sample volume, low cost (Jjunju *et al.*, 2013) and was also cheap and readily available. Direct analysis in real time mass spectrometry (DART-MS)

However, PS-MS also has few limitations where it is not ideal for measuring larger molecules (Lin *et al.*, 2014), it requires a high voltage (Liu *et al.*, 2010) and also is labour intensive.

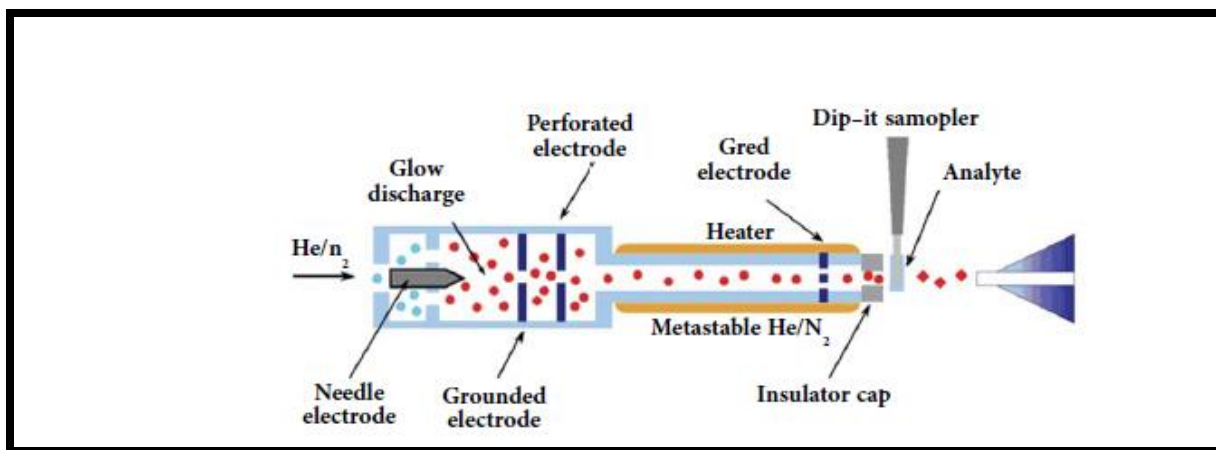


Figure 8: Schematic representation of DART-MS (Shen, Wu and Guo, 2016).

DART-MS (Figure 9) was introduced in 2005 by Cody and his group. Since then it has been attracting interests towards the forensic area of studies. Several applications of DART-MS are ; identification of counterfeit drugs, identification of drugs in urine, identification of arson accelerants and identification of chemical warfare agents (Jones and McClelland, 2013). Moreover, DART-MS is used in ink analysis because the chemical information on the ink is provided in a detailed manner. It can also take the maximum benefit of the power of recent computer databases. DART-MS can also quickly identify intact volatile, semi volatile and non-volatile polar organic compounds in a range of matrices without extractions or chromo-graphic separations (Adams, 2010).

In DART analysis, ionisation is achieved when metastable excited state neutral helium atoms collide to form atmospheric pressure glow discharge along with water of the ionisation source. Helium gas is first sent through a hydrocarbon filter and then sent into the DART discharge chamber where the needle electrode is kept at a specific voltage. This produces helium ions and metastable helium atoms. The gas will then be sent through the grid electrodes and the discharge. After passing through the grid electrode, hot metastable helium atoms enter the open air gap. Sample to be tested will be kept in the middle of the helium stream of the gap and hot gas, metastable helium and protonated water clusters which combines to ionise and evaporate from the sample. Ions produced will move into the mass spectrometer to be analysed. Furthermore, ink on the paper samples will



be wrapped in the end of a metal support and will be held on by a thin aluminium plate. Area of the sample to be analysed is free standing. The sample mount is electrically connected to the spectrometer inlet orifice. Mass spectrometer is operated in the positive ion mode. By this, DART-MS will be dominated by $(M+H)^+$ (i.e; protonated molecules) where M will be considered as the parent molecule (Jones and McClelland, 2013).

In 2006, Jones, Cody and McClelland performed a study on ink detection using DART-MS. They used different types of ink such as blue and black ballpoint, fluid and gel. Pen marks were made between the time period of 7 weeks and 16 prior to analysis (Pavlovich, Musselman and Hall, 2016). However, they were able to distinguish between the types of ink using DART-MS. The results (figure 10) showed various peaks indicating the different types of ink.

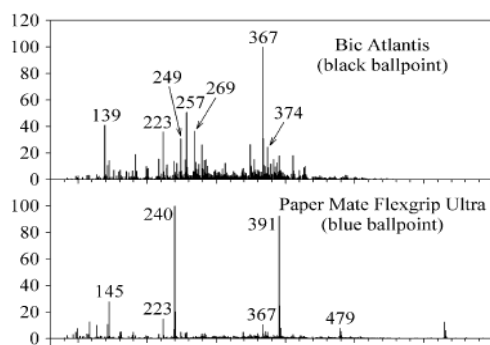


Figure 9: Mass spectra of inks performed using DART-MS. (Jones, Cody and McClelland, 2006)

m/z 367 indicates dioctyl phthalate and m/z 391 indicates Bic Atlantis and paper mate flexgrip. These components of ballpoint ink show strong peaks for the respective components but weak peaks for fluid inks. Similarly, m/z 139 indicates 2-phenoxyethanol which shows a strong/moderate peaks in ballpoint ink and weak peaks in both fluid and gel ink

Several other peaks also was obtained and differentiated which led to the ease of distinguishing the different types of inks used in a document. This eventually led to the idea that DART-MS can be used in ink detection.

DART can analyse chemicals with expansive volatilities by placing a surface closer to the sampling inlet of an API-equipped mass spectrometer (Wells *et al.*, 2008). It also can perform in a low voltage (i.e.; 20V). Moreover, DART also has the absence of interference from the matrix components resulting the absence of ionisation of increased molecular weight non-volatile components in the DART source (Chernetsova *et al.*, 2010). DART is also simple to interpret because regularly they contain signals of ions $[M+H]^+$ and the absence of signals of fragmentation ions (Chernetsova *et al.*, 2010). Few of the



limitations of DART mass spectrometry are; it requires the presence of increased resolution mass / tandem mass as the also not possible to be distinguished.

detector for discerning from their interferents. Additionally, analytes with the same molecular weight is

Desorption atmospheric pressure chemical ionisation MS (DAPCI-MS)

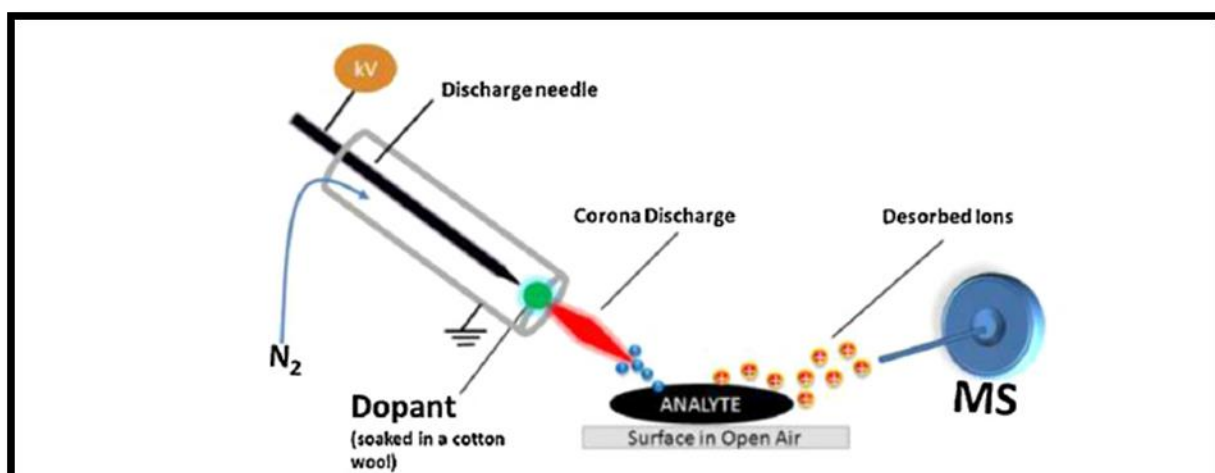


Figure 10: Schematic diagram of DAPCI (Jjunju et al., 2013)

Considering the limitations of DART-MS, DAPCI (figure 11) was shown by Cooks and his co-workers in 2006 (Williams *et al.*, 2006), and was first used to detect trace levels of TNT, PETN and RDX explosives. DAPCI eventually derived from the technique atmospheric pressure chemical ionisation (APCI) (Cooks *et al.*, 2012) and was found to be more sensitive compared to DESI and DART (Zhu *et al.*, 2007). Moreover, DAPCI-MS can also be used for direct analysis of sticky liquids, powdered samples, biological tissue with a noticeable loss of sensitivity (Pi *et al.*, 2011).

A voltage will be applied to the stainless steel needle in order to retain the ambient corona discharge. Gasless DAPCI is

applied to get the images of the letters which are written freshly on surfaces. In order to speed up the DAPCI process nitrogen gas is used to produce pure water vapour (chemical reagent for the DAPCI source). The vapour phase reagent ions will be aimed to collide on the analyte surfaces to produce analyte ions for analysis.

Eventually, the image which appears will rely on the mass spectral data which is gained by the scanning procedure of the document surface.

In 2013, Li and his co-workers performed detection of ink using DAPCI mass spectrometry where they obtained images at different mass/charge ratios. Images were taken using the mass spectral data



(figure 12) which was recorded from 2 signatures which were prepared four hours early. The main dissimilarity between the two signatures is that one letter 'C' was written 10 minutes before the other one. The difference was not clearly visible, but images which were obtained by DAPCI showed distinct differences. For example, peak at m/z 136 (fig 12 [c]) is different

compared to fig 12[d] which was made 10 minutes later. This is indicated by different colours in many places of the letter. Similarly, at m/z 70, m/z 94, m/z 152 images were obtained .However, the chemical component of the ink are homogenously suspended in the mixture. This therefore shows the importance of DAPCI in ink detection.

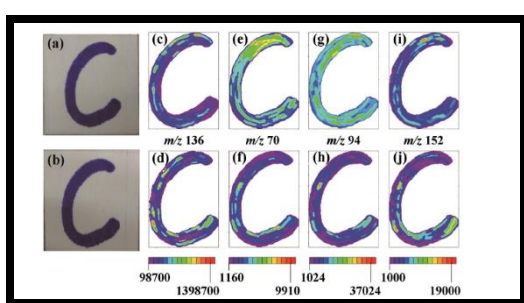


Figure 11: Detection of ink ageing using DAPCI mass spectrometry (Li *et al.*, 2013).

DAPCI has a high sensitivity in order to directly analyse a sample under ambient conditions. It also has a good chemical sensitivity and a fast analysis speed (Zhu *et al.*, 2013). However, one of the main disadvantages of DAPCI is that different angles are required for different ink samples.

SUMMARY AND FUTURE SCOPES

Considering the four best techniques which can be used to detect ink in forged documents it has led to the idea that DAPCI can be considered as one of the best methods out of all the four methods. This is because DAPCI isn't laborious, doesn't involve a multi-step unlike paper spray mass spectrometry. In the meantime, DAPCI doesn't use the spray jet ionisation method like in DESI-MS which will therefore not have chances of altering the document and analytes with the same

molecular weight can be detected unlike DART.

Current methods used in ink analysis are Raman mass spectrometry and MALDI-MS. Raman mass spectroscopy is considered as one of the best methods to be used in ink analysis after DAPCI. Chemical sensitivity is combined easily and has a fast analysis. It also does not require sample pre-treatment like the other methods. However, it has few drawbacks such as low sensitivity, but these problems can be solved by resonance / surface-enhanced Raman spectroscopy (Braz ,Lopez and Garcia-Ruiz, 2013). MALDI-TOFMS is also one of the best methods which can be used in ink detection because large molecules can be identified , where PS-MS (a method mentioned in this review) does not have the ability to identify large molecules (Soltzberg *et al.*, 2007). Therefore, Raman mass spectrometry and



MALDI-MS can be considered as better methods to be used in the analysis of ink in questioned documents.

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REFERENCES

Adams, J. (2011) "Analysis of printing and writing papers by using direct analysis in real time mass spectrometry", *International Journal of Mass Spectrometry*, 301, 109-126.

Alberici, R.M., Simas, R.C., Sanvido, G.B., Romao, W., Lalli, P.M., Benassi, M., Cunha, H.B.S & Eberlin, M.N. (2010) "Ambient mass spectrometry: bringing MS into the "real world", *Anal Bioanal Chem*, 398, 265-294.

Analyst (2010) "Ambient mass spectrometry", *The Royal Society of Chemistry*, 135, 659-660.

Barket, J.D., Patterson, G.E., Justes, D.R., Grossenbacher, J.W., Keil, A.D., Roth, M.J & Wells, J.M. (2008) "Implementation of DART and DESI ionization on a fieldable mass

spectrometer", *American Society for Mass Spectrometry*, 19, 1419-1424.

Black, C., Chevallier, O.P & Elliott, C.T. (2016) "The current and potential applications of Ambient Mass Spectrometry in detecting food fraud", *Trends in Analytical Chemistry*, 82, 268-278.

Bugler, J.H., Buchner, H & Dallmayer, A. (2008) "Age determination of ballpoint pen ink by thermal desorption and gas chromatography – mass spectrometry", *Journal of Forensic Sciences*, 53, 4.

Chen, C & Lin, P. (2012) "Monitoring of Chemical Transformations by Mass Spectrometry", *The Royal Society of Chemistry*, 00, 1-3.

Chen, H., Meng, H & Cheng, K. (2001) "A survey of methods used for the identification and characterization of inks", *Forensic Science Journal*, 1, 1.

Chen, H., Zheng, J., Zhang, X., Luo, M., Wang, Z & Qiao, X. (2007) "Surface desorption atmospheric pressure chemical ionization mass spectrometry for direct ambient sample analysis without toxic chemical contamination", *Journal of Mass Spectrometry*, 42, 1045-1056.



- Chernetsova, E.S., Ovcharov, M.V., Khomyakov, Y.Y., Bochkov, P.O & Varlomov, A.V. (2010) "The use of DART mass spectrometry for express confirmation of empirical formulas of heterolytic compounds", *Russian Chemical Bulletin*, 59, 2014-2015.
- Chernetsova, E.S., Abramovich, R.A & Revel'skii, I.A. (2011) "Structure of chemical compounds, methods of analysis and process control", *Pharmaceutical Chemistry Journal*, 45, 49-51.
- Epsy, R.D., Muliadi, A.R., Ouyang, Z & Cooks, R.G. (2012) "Spray mechanism in paper ionisation", *International Journal of Mass Spectrometry*, 325, 167-171.
- Ferreira, P.S., Silva, D.F.A., Augusti, R & Piccin, E. (2015) "Forensic Analysis of ballpoint pen inks using paper spray mass spectrometry", *The Royal Society of Chemistry*, 140, 811-819.
- Green, F.M., Salter, T.L., Stokes, P., Gilmore, I.S & Connor, G.O. (2009) "Ambient mass spectrometry: advances and applications in forensics", *Surface Interface Analysis*, 42, 347-357.
- Ifa, D.R., Jackson, A.U., Paglia, G & Cooks, R.G. (2009) "Forensic applications of ambient ionization mass spectrometry", *Anal Bioanal Chem*, 394, 1995-2008.
- Jjunju, F.P.M., Tawiah, A.K.B., Li, A., Soparawalla, S., Roqan, I.S & Cooks, R.G. (2013) "Hydrocarbon analysis using desorption atmospheric pressure chemical ionisation", *International Journal of Mass Spectrometry*, 345-347, 80-88.
- Jones, R.W & McClelland, J.F. (2013) "Analysis of writing inks on paper using direct analysis in real time mass spectrometry", *Forensic Science International*, 231, 73-81.
- Jones, W.R., Cody, B.R & McClelland, F.J. (2006) "Differentiating writing inks using Direct Analysis in Real Time Mass Spectrometry", *Journal of Forensic Sciences*, 51, 4.
- Jurisch, M & Augusti, R. (2016) "Detection of signature forgery with erasable pens using paper spray mass spectrometry (PS-MS)", *The Royal Society of Chemistry*, 8, 4543-4546.
- Kao, Y., Cheng, S., Cheng, C & Shiea, J. (2015) "Depth profiling of inks in authentic and counterfeit banknotes by electrospray laser desorption



- ionisation/ mass spectrometry”, *Journal of Mass Spectrometry*, 51, 20-27.
- LaPorte, G.M., Wilson, J.D., Cantu, A.A., Mancke, S.A and Fortunato, S.L. (2004) “The identification of 2-phenoxyethanol in ballpoint inks using gas chromatography / mass spectrometry – relevance to ink dating”, *Journal of Forensic Sciences*, 49,1.
- Li, M., Jia, B., Ding, L., Hong, F., Ouyang, Y., Chen, R., Zhou, S., Chen, H & Fang, X. (2013) “Document authentication at molecular levels using desorption atmospheric pressure chemical ionization mass spectrometry imaging”, *Journal of Mass Spectrometry*, 48, 1042-1049.
- Lin, C., Liao, W.C., Chen, H & Kuo, T. (2014) “Paper spray-MS for bioanalysis”, *Bioanalysis*, 6, 1-10.
- Liu, J., Wang, H., Manicke, N.E., Lin, J., Cooks, R.G & Ouyang, Z. (2010) “Development, Characterization and Application of Paper Spray Ionisation”, *Analytical Chemistry*, 82, 2463-2471.
- Manicke, N.E., Bills, B.J & Zhang, C. (2016) “Analysis of biofluids by paper spray MS: advances and challenges”, *Bioanalysis*, 8, 589-606.
- Morelato, M., Beavis, A., Kirkbride, P & Roux, C. (2013) “Forensic applications of desorption electrospray ionisation mass spectrometry (DESI-MS)”, *Forensic Science International*, 226, 10-21.
- Nielsen, M.W.F., Hooijerink, H., Zomer, P & Mol, J.G.J. (2011) “Desorption Electrospray Ionisation Mass Spectrometry in the analysis of chemical food contaminants in food”, *Trends in Analytical Chemistry*, 30, 2.
- Pavolvich, M., Musselman, B & Hall, A.B. (2016) “Direct Analysis in Real Time – Mass Spectrometry (DART-MS) in forensic and security applications”, *Mass Spectrometry Reviews*, 9999, 1-17.
- Pi, Z., Yue, H., Ma, L., Ding, L., Liu, Z & Liu, S. (2011) “Differentiation of various kinds of *Fructus schisandrae* by surface desorption atmospheric pressure chemical ionisation mass spectrometry combined with principal component analysis”, *Analytica Chimica Acta*, 706, 285-290.
- Ratcliffe, L.V., Rutten, F.J.M., Barrett, D.A., Whitmore, T., Seymour, D.,



- Greenwood, C., Gonzalvo, Y.A., Robinson, S & McCoustra, M. (2007) "Surface analysis under ambient conditions using plasma-assisted desorption / ionisation mass spectrometry", *Analytical Chemistry*, 79, 6094-6101.
- Sanchez, L.M., Curtis, M.E., Bracamonte, B.E., Kurita, K.L., Navarro, G., Sparkman, O.D & Linigton, R.G. (2011) "Versatile method for the detection of covalently bound substrates on solid supports by DART Mass Spectrometry", *American Chemical Society*, 13, 3770-3773.
- Shen, Y., Wu, W & Guo, D (2016) "DART-MS: A new research tool for herbal medicine analysis", *World J Tradit Chin Med*, 2, 2-9.
- Sun, Q., Luo, Y., Yang, X., Xiang, P & Shen, M. (2016) "Detection and Identification of dyes in blue writing inks by LD-DAD-orbitrap MS", *Forensic Science International*, 261, 71-81.
- Takats, Z., Wiseman, J.M., Gologan, B & Cooks, G.R. (2004) "Mass spectrometry sampling under ambient conditions with desorption electrospray ionisation", *Science*, 306, 471.
- Takáts, Z., Cotte-Rodriguez, I., Talay, N., Chen, H. and Cooks, G. (2005) "Direct, trace level detection of explosives on ambient surfaces by desorption electrospray ionization mass spectrometry", *Chemical Communication*, 1950-1952.
- Weyermann, C., Marquis, R., Mazzella, W & Spengler, B. (2007) "Differentiation of blue ballpoint pen inks by laser desorption ionisation mass spectrometry and high-performance thin-layer chromatography", *Journal of Forensic Sciences*, 52, 1.
- Williams, J.P., Patel, V.J., Holland, R & Scrivens, J.H. (2006) "The use of recently described ionisation techniques for the rapid analysis of some common drugs and samples of biological origin", *Rapid Communications in Mass Spectrometry*, 20, 1447-1456.
- Yang, Q., Wang, H., Mass, J.D., Chappell, W.J., Manicke, N.E., Cooks, G.C & Ouyang, Z. (2012) "Paper spray ionization devices for direct , biomedical analysis using mass spectrometry", *International Journal of Mass Spectrometry*, 312, 201-207.
- Zhu, L., Yan, J., Zhu, Z., Ouyang, Y., Zhang, X., Zhang, W., Dai, X., Luo, L & Chen, H. (2013) "Differential Analysis



of Camphor wood products by
Desorption Atmospheric Pressure
Chemical Ionisation Mass

Spectrometry”, *Journal of
Agricultural and Food Chemistry*, 61,
547-552.