

**DISCRIMINATION OF MATCHES USING ATR-
FTIR SPECTROSCOPY AND CHEMOMETRICS**

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**DISCRIMINATION OF MATCHES USING ATR-FTIR SPECTROSCOPY
AND CHEMOMETRICS**

by

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LIST OF ABBREVIATIONS

ANN	Artificial Neural Networks
ATR-FTIR	Attenuated Total Reflection-Fourier Transform Infrared
CA	Cluster Analysis
CV	Canonical Variances
DNA	Deoxyribonucleic acid
EDX	Energy Dispersive X-ray Analysis
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
IR	Infrared
IRMS	Isotope Ratio Mass Spectrometry
ILR	Ignitable liquid residues
KBr	Potassium Bromide
LDA	Linear Discriminant Analysis
PCs	Principal Components
PCA	Principal Component Analysis
PCR	Polymerase Chain Reaction
PLS	Partial Least Squares
R&D	Research and Development
SEM	Scanning Electron Microscopy
SIMCA	Soft Independent Modelling of Class Analogy
SIP	Stable Isotope Profiling
SPSS	Statistical Package for the Social Sciences
USA	United States of America
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

DISKRIMINAN MANCIS MENGGUNAKAN MENGGUNAKAN SPEKTROSKOPI ATR-FTIR DAN KEMOMETRIK

ABSTRAK

Mancis adalah salah satu bahan bukti surih yang boleh dijumpai di lokasi jenayah melibatkan kes pembakaran dengan sengaja. Analisis forensik mancis boleh menjadi bahan bukti penting untuk mengaitkan suspek dengan lokasi jenayah atau mangsa. Walau bagaimanapun, bahan bukti mancis berkemungkinan diabaikan, kerana kehadiran bahan bukti lain yang dianggap penting, selalu tercemar dengan serpihan pasca kebakaran, dan kuantiti yang sedikit. Malah, kajian lepas tentang analisis mancis untuk aplikasi forensik sangat terhad. Dalam kajian ini, satu kaedah analitikal alternatif cepat, tidak merosakkan, sensitif, dan boleh dipercayai iaitu spektroskopi ATR-FTIR telah diguna pakai untuk membezakan 11 jenama sampel mancis. Analisis Komponen Utama-Analisis Diskriminan Linear (PCA-LDA) telah digunakan untuk mendapatkan penafsiran hasil yang lebih objektif. Ketepatan model ramalan PCA-LDA adalah 95.8%, dengan hampir semua sampel batang mancis, kepala mancis belum dibakar, dan kepala mancis telah dibakar, berjaya diklasifikasikan kepada jenama mereka. Ujian buta dilakukan dengan dua sampel yang dianggap tidak diketahui oleh penganalisis dalam dua keadaan berbeza, telah berjaya dihubungkan kepada jenama masing-masing. Kajian semasa ini menunjukkan kaedah analisis yang cepat, menjimatkan kos, kuat, dan tidak merosakkan untuk membezakan sampel mancis dalam penyiasatan forensik.

DISCRIMINATION OF MATCHES USING ATR-FTIR SPECTROSCOPY AND CHEMOMETRICS

ABSTRACT

Matches are one of the trace evidence that could be encountered at the crime scenes of arson cases. Forensic analysis of matches may serve as crucial corroborating evidence to link the suspect to the crime scene or the victim. Nonetheless, matches evidence has been overlooked, due to presence of other prominent evidence, often contaminated with other fire post-debris, and trace in quantity. Furthermore, there has been very limited research in the past on the analysis of matches for forensic applications. In the present study, a rapid, non-destructive, sensitive, and reliable analytical technique namely Attenuated Total Reflectance-Fourier Transform-Infrared (ATR-FTIR) spectroscopy has been utilised to differentiate 11 brands of matches samples. Principal Component Analysis- Linear Discriminant Analysis (PCA-LDA) was employed to generate objective interpretation of the results. The 95.8% accuracy of predictive PCA-LDA model was established with almost all matchstick, unburnt match head, and burnt match head correctly classified to their respective brands. The blind test was conducted with two unknown samples (pretended to be unknown to the analyst) in two different conditions, which were correctly link with their respective source. The current work demonstrated a quick, cost-effective, robust, and non-destructive method for differentiation of matches samples in forensic investigation.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The term ‘arson’ originated from an Anglo-French word that means ‘the act of burning’ (Hinne, 2004). By definition, arson is a criminal act of deliberately setting up fire or causing an explosion to others’ properties such as vehicles, offices, and residential homes (Rahim, 2015). The statistics released by the Fire and Rescue Department of Malaysia (2021) revealed 10,152 recorded fire incidents in 2020 that involved structured fire and vehicles. In 2019 and 2020, residential homes were also the most frequently subjected to deliberate fire requiring investigation measures. Arson could leave the affected victim suffering from emotional distress, financial burden, and potentially lost of life.

The establishment of arson requires effective detection, scientific analysis, and careful consideration by the investigators. In the United Kingdom, only 17% out of 50.5% of arson-related crimes resulted in an arrest (Brown, 2021). Woodman *et al.* (2021) described that there are four elements for the court to reach the guilty verdict of arson which include; a) The property is destructed by means of fire, b) The property belongs to another person, c) The damage of the property by the accused is intentional, and, d) The accused had no lawful excuse for damaging the property. As proving a suspect’s deliberate intent to cause fire is often strenuous, arson is very challenging to prosecute.

The whole forensic investigation of criminal cases begins from the crime scene to court. The process of 3R’s; recognition, recording, and recovery of physical evidence are critical to establish the crime triangle and provide logical explanation on

the events. In the context of fire scenes, the type of evidence encountered by the investigators can be in various forms, although the most frequently found is the ignitable liquid residues (ILR). In suspected arson cases, ignitable liquids such as gasoline, petrol, and diesel are commonly used as accelerants to initiate the fire. They could be easily obtained, inexpensive, and effectively ignite the fire. However, ILR identification solely could not be used to conclude that foul play or arson is involved. Further investigation would be necessary to explain the rationality of the flammable or combustible liquid discovered at the fire scenes (Lentini, 2013). Besides, simple solid fuels such as paper and kindling woods are also practical for initiating arson fires. They are challenging to be detected and identified in post-fire debris. Due to their commonality and may be readily available at the scene, challenges also arise in correctly associating fire with the arsonist (Hennerberg & Morling, 2018).

Matches are another examples of possible trace physical evidence that could be recovered at the fire crime scene. Its production is generally complex and consisted of many chemicals with their defined roles. Matches could be used to firstly lit up the simple solide fuels or even thrown directly into the fire accelerants. At a fire scene, matches may be found in unburnt and burnt forms, depending on the severity of the fire incidents. During the hectic situation, criminals may also accidentally dropped some of the unused matches in the attempt of fleeing from the scene.

Moreover, an incendiary fire that begins with the utilisation of naked flames to a combustible matter often leaves minimal evidence of the action. With the unavailability to determine the ignition source as definitive physical evidence, fire investigators often have to count on other assessments such as the smoke and burn patterns to conclude that the fire is intentional. The damage pattern interpretation is

subjective and considered less reliable evidence in court, as it relies on the investigators' logical inference and interpretation (Hennerberg & Morling, 2018). The execution of Cameron Todd Willingham in Texas, USA, was one of the many controversial wrongful convictions in arson cases due to misinterpretation by the fire investigators. Therefore, fire investigators must systematically and scientifically investigate the fire origin, ignition source, and preservation of the related trace evidence at the fire scenes.

1.2 Problem Statement

Fires are destructive in nature; hence, many other possible trace evidence such as matches, fingerprints, cigarette butts, and glass fragments may be overlooked during the investigation process. The majority of these evidence may sustain fire and are particularly capable of associating a suspect with the crime scene. The evidence preserved at the location could be compared, characterised, and analysed through physical matching and composition of their elements (Tyrrel, 2017).

Matches are one of the familiar ignition sources that could be used in committing arson and found at the fire crime scene. It is reasonably cheap, easy to use, and purchased at any local supermarket. The current common type of match available in the market is safety matches. Safety matches comprised approximately 40 matchsticks in a paper box. Striking the match head to the striker plate produces heat and friction, initiating the potassium chlorate oxidation reaction. Spontaneous sparks from the friction also convert the red phosphorus to white phosphorus and eventually ignite the sulphur in the match head, producing fire (Farmer *et al.*, 2007).

Matches could be used as corroborative evidence to associate the suspect with the crime scene. The physical characteristics and chemical composition of the specific

brand of matches in the suspect's possession could be compared with the trace of burnt matches at the fire scenes. According to the Fire and Rescue Department of Malaysia (2021), ignition sources of matches or lighter were found in 494 fire incidents in 2020. However, there were no information whether the matches were further utilised as one of the case exhibits to help in the criminals' conviction. The statistics of 273 deliberately lit structural fire cases in Victoria, Australia also revealed that only 27% of cases where matches or other incendiary devices were found at the fire scene reached a guilty verdict (Woodman *et al.*, 2021). Due to lack of previous research studies on forensic analysis of matches, its probative value and capability as corroborative trace evidence had not been utilised to the uttermost. This study aims to strengthen the evidential value of matches through the exploration of spectroscopic method as an easy, rapid and non-destructive analytical technique.

1.3 Research Objectives

1.3.1 General Objective

The general objective of this study was to study the significance and evidentiary value of matches in forensic investigation using the ATR-FTIR spectroscopic method.

1.3.2 Specific Objectives

- a) To discriminate various brands of matches using ATR-FTIR spectroscopy and chemometrics analysis.
- b) To establish the potential of unburnt and burnt matches as trace evidence for forensic intelligence and identification purposes.

1.4 Significance of the Study

Physical evidence is vital to establish arson and the associated motives of an incendiary fire. There were also minimal previous studies; thus, the forensic significance of matches as trace evidence had not been fully understood and utilised. Trace evidence such as matches in the context of fire scenes would be substantial corroborative evidence to link the arsonist to the crime scene. The traces of unburnt and burnt matches found as post-fire debris could be compared to the unburnt matches remaining in the suspect's possession.

Apart from that, the gold standard of ILR detection in the fire could establish arson but may not directly point to the perpetrator. Therefore, other trace evidence analysis and massive investigation would be required to associate the suspect with the crime scene and victim. The method is also tedious, destructive, and time-consuming. Hence, ATR-FTIR spectroscopic method coupled with chemometrics would be an alternative method to analyse the traces of matches found at the fire scenes. The method is simple, rapid, non-destructive, and can discriminate the matches brands based on their specific spectral features.

This study will provide new insight into the potential of matches as corroborative evidence and their evidential value in forensic investigation. Besides that, establishing the new analysis technique of matches will aid arson crimes to be more efficiently understood, investigated, and solved. With the responsible perpetrators being put behind bars, the safety level in our country will also be improved eventually.

CHAPTER 2

LITERATURE REVIEW

2.1 History and Evolution of Matches

The earliest match production was believed to originate from China in 577 AD using sulphur-coated pinewood wooden sticks. There was still a lack of knowledge on the phosphorus compound and friction interaction during this period. The matchsticks had to be directed to the smallest amount of flame to light up and expand fast around themselves. In the second half of the 17th century, the first modern self-igniting match was introduced by Jean Chancel, who previously assisted the famous French chemist Louis Jacques Thénard. The match head was produced from potassium chlorate, sulphur, sugar, and rubber. It was ignited by dipping it into a small asbestos bottle filled with sulphuric acid. However, the matches' dangerous mixtures and expensive nature quickly failed (Diezel, 2018).

In 1826, John Walker, an English Chemist, began the evolution of the first friction matches. These friction matches became the foundation of the current matches available in the market today. He combined the mixture of sulphur with gum, sugar, antimony trisulfide, and potassium chlorate to make up the match head, which would ignite when struck between the fold of sandpaper. Around the 1830s, a Frenchman, Charles Sauria, discovered white phosphorus matches that possessed the ability to self-ignite and may cause severe disease, namely phossy jaw. The phossy jaw was a common occupational disease among factory match workers due to inhalation of the toxic fumes. Later in the 1850s, Swedish Gustaf Erik Pasch and Johan Edvard Lundström devised the self-ignition matches and white phosphorus matches into safety matches and utilised only red phosphorus on the ignition surfaces. The new safety matches were economical and safe for health and the environment (History of Matches, 2022). **Figure 2.1** shows

the old basic pattern of the matchbook, patented by Joshua Pusey and sold to the Diamond Match Company in 1894.

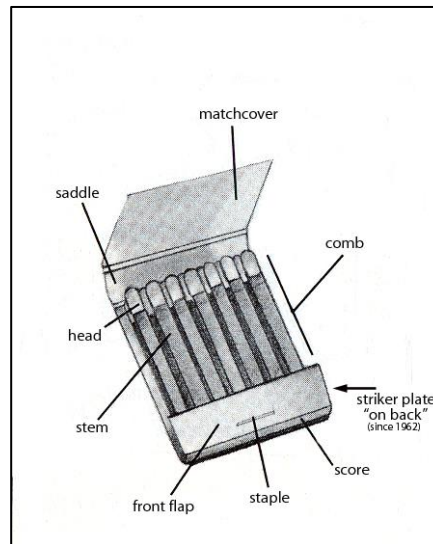


Figure 2.1 The old basic pattern of safety matches.

2.2 The Production and Chemistry of Matches

Matches have been handy to produce fire for many defined purposes. It is convenient on many levels and could be easily obtained at a low price. During the early times, the primarily targeted consumers were cigarette smokers. Nowadays, matches would also be useful for outdoor trips and lighting candles when the electricity is out. As it is generally simple to find in local shops, arsonists could also purchase and use matches to commit crimes. A box of matches typically consists of around 40-50 matchsticks in a cardboard box with a striker plate. White pine and Aspen (*Populus tremula*) are the most preferred light and soft wood for matchstick production as they are rigid enough to be struck without breaking.

Figure 2.2 shows the summary of the production of matches that begins from the soft wood logs transported from the agroforestry plantation to the manufacturing factories. The wood logs first undergo the process called debarking to remove the bark.

Then, the de-barked woods are cut into considerate billets lengths and peeled into well-fitted veneers according to respective manufacturers. The veneers are employed in two ways; for the production of the match boxes, and chopped into splints to serve as matchstick (Ullah *et al.*, 2021). Countries rich with soft wood biodiversities such as India, Pakistan, and Sweden have the facilities and capacities to process the wood logs at their own match factories. However, in a short documentary at the Kelantan Match Factory, it was revealed that the splints for the matchsticks were pre-made and imported from China due to Malaysia’s limited resources (Buletin TV3, 2018).

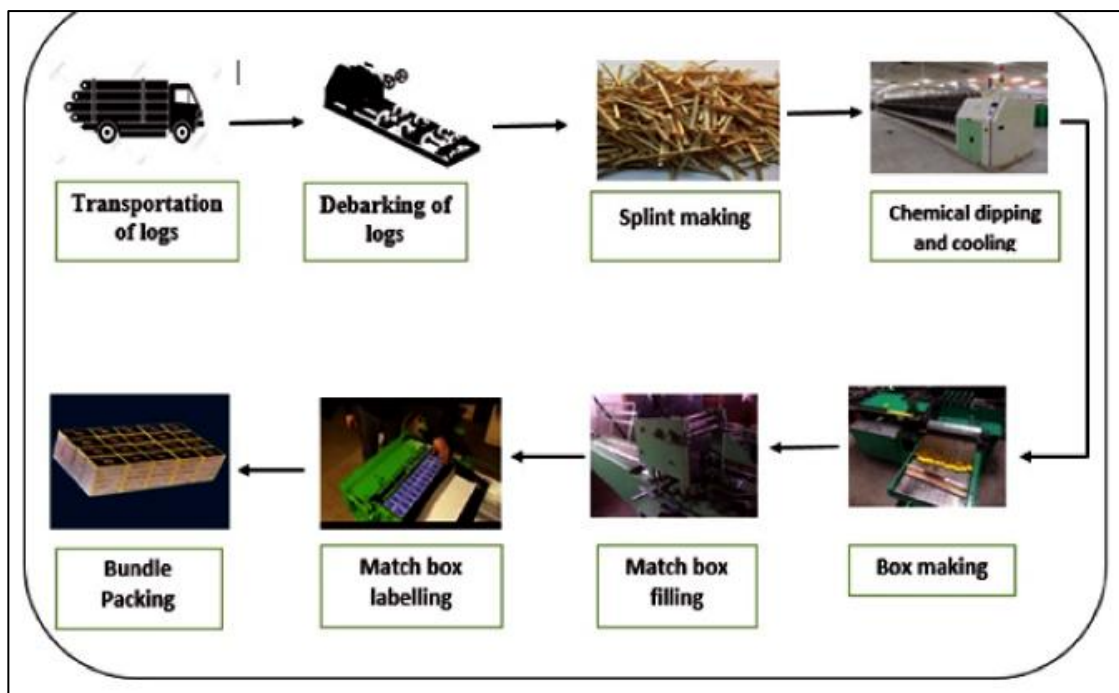


Figure 2.2 Summary of the process in the whole matches production.

Once the woods are cut into splints, they are impregnated into ammonium phosphate, the ‘after-glow’ solution to prevent the smoldering of the matchstick after being extinguished. The match heads are produced by dipping one striking end of the matchsticks into the hot paraffin wax. Various chemicals are used in the match heads,

such as antimony trisulfide, sulfur, powdered glass, potassium chlorate, inert fillers, animal glue, and even water-soluble dye (Farmer *et al.*, 2007). The striking plate at the side of the matchbox also contains other elements such as red phosphorus, powdered glass, and urea-formaldehyde as the adhesive. The role of the chemicals in the production of matches is tabulated in **Table 2.1**.

Table 2.1 Examples of the chemicals utilised in the manufacturing of matches (Wisniak, 2005; Farmer *et al.*, 2007).

No.	Chemicals	Roles
1.	Ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$	<ul style="list-style-type: none"> ▪ Fire retardant, to prevent smoldering of matchstick after extinguished
2.	Parrafin wax, $\text{C}_n\text{H}_{2n+2}$	<ul style="list-style-type: none"> ▪ Provide a small amount of fuel ▪ Extra layers to provide good flammable action
3.	Potassium chlorate, KClO_3	<ul style="list-style-type: none"> ▪ Provide oxygen for ignition and burning
4.	Phosphorus sesquisulfide/ Tetraphorus trisulfide, P_4S_3	<ul style="list-style-type: none"> ▪ Sensitive for ignition on a rough surface
5.	Sulphur, S	<ul style="list-style-type: none"> ▪ Main combustible material
6.	Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$	<ul style="list-style-type: none"> ▪ Powerful oxidising agent ▪ To lower the decomposition temperature of potassium chlorate
7.	Gelatine, $\text{C}_{102}\text{H}_{151}\text{N}_{31}\text{O}_{39}$	<ul style="list-style-type: none"> ▪ Adhesive to bind all the components together and to the matchstick
8.	Zinc oxide, ZnO	<ul style="list-style-type: none"> ▪ Control the flame propagation velocity
9.	Glass powder,	<ul style="list-style-type: none"> ▪ Binder for molten components
10.	Kieselguhr/ Quartz/ Haematite	<ul style="list-style-type: none"> ▪ Fillers to modify the burning rate ▪ Prevent oxidisers and fuel from uncontrol reaction
11.	Red phosphorus, P_4	<ul style="list-style-type: none"> ▪ Produce spontaneous ignition in the air as it reduced into white phosphorus to initiate the decomposition of potassium chlorate

When striking the match head to the plate, an adequate amount of friction converts the trace of red phosphorus into white phosphorus, producing heat. The

immediate reaction of the potassium chlorate in the match head ignites the antimony trisulfide/ sulphur (fuel) and begins the match's combustion process. The burning rate of the oxidiser and fuel reaction is also controlled by fillers (Compound Chem, 2014). The general equation of the matches ignition reaction is shown in **Figure 2.3**.

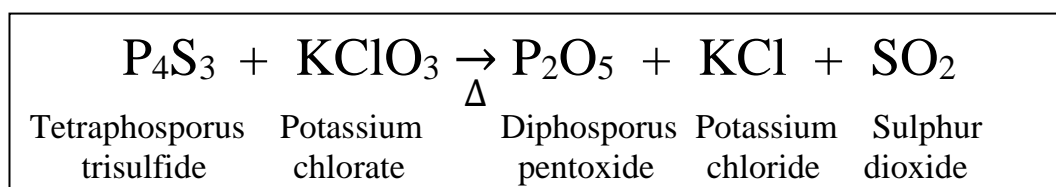


Figure 2.3 The chemistry during the striking of matches onto the striking plate.

2.3 Trace Evidence and Its Evidential Value

‘Every contact leaves a trace’ has become a famous maxim in forensic science investigation since the early 20th century. The Locard’s principle was introduced by Edmond Locard, a medical doctor and lawyer from France. He believed that trace materials that transfer from objects and individuals' interactions are valuable evidence to link suspects, victims, and crime scenes. Trace evidence could also be defined as small and physical evidence found at foreign locations during the crime scene investigation (Trejos *et al.*, 2020). It could include endless possibilities of materials such as paint chips, glass fragments, cigarette butts, fibers, hairs, pollens, soils, and even matches. The evidence is often unintentionally left or removed by the perpetrators during the physical interaction with the victims at the crime scenes.

The main purpose of the trace evidence examination is to compare the questioned sample and determine if it shares a common source with the known sample. Trace evidence is essential in forensic science investigation as associative and corroborative evidence (Cadola *et al.*, 2021). Although the evidence is usually circumstantial, the uniqueness of the trace evidence found at the crime scene could be

crucial for associating and establishing the connection between the receiving item to its original source of materials. It would also enable forensic investigators to better understand the occurrence of crime by corroborating the information on the perpetrator's presence, physical interactions, and eyewitness accounts. Besides that, trace evidence would also be beneficial to identify possible links in serial crimes, eliminate suspects, reconstruct events, and establish charges offenses accordingly (Klaasse *et al.*, 2021).

Trace evidence examinations usually require intensive, detailed microscopic, and instrumental analysis to evaluate its significance and relevance in a particular case. Trace evidence is typically small and may be transient based on its nature, and it could be invisible to the naked eye and often overlooked. The examination will preferably begin with the least destructive to most destructive methods, which have various degrees of discrimination. While comparing the questioned and known samples, the exhibits may share a common source when they could not be distinguished from each other at all stages of the analysis. Contradictingly, forensic scientists could conclude that trace evidence comes from different origins when very distinct features are notable during the examination. However, the conclusion that the exhibit comes from a common source as the known samples do not entirely define that they come from the same origin, as they may also be materials with similar properties (Mejia *et al.*, 2019). Therefore, expert judgment and careful consideration must be made to determine the trace evidence's probative value correctly.

2.4 Challenges and Issues in Trace Evidence Analysis

The case investigation from the crime scene to the court is a complex and lengthy process. It requires presenting probative evidence to meet an allegation's burden

of proof and truth. For the last ten years, forensic science has been subjected to intense global scrutiny (Morgan, 2019).

Trace evidence may exist in many forms at crime scenes, is not readily visible, and may be transitory. For example, light materials such as hair and fibre are less persistent in retaining at a place and may be lost over time. Due to these characteristics, the process of 3R's of evidence; recognition, recording, and recovery are challenging (Robertson & Roux, 2010). The step of trace evidence recognition may also be tricky as they are mixed and contaminated with other items at the location. This complexity may also arise due to the lack of understanding, skills, and knowledge on trace evidence possessed by crime scene investigators.

As trace evidence is usually unable to provide a definitive link between suspects, victims, and crime scenes, it is commonly regarded to have a lesser identifying value (Stoney & Stoney, 2015). The instrumentation for trace evidence analysis, too, requires sensitive and high-technology instruments to imply accurate interpretation. However, the process is undeniably time-consuming and costly. Hence, trace evidence tends to be contemplated as only supporting evidence to provide sufficient information or when DNA or fingerprint evidence is unavailable at times (Suppajariyawat, 2021).

Besides that, the ability of trace evidence to provide a unique and significant lead in a crime scene investigation is complicated due to the minor variation in modern compositions of materials (Caddy, 2001). For instance, quality control and assurance are incredibly desirable in product manufacturing. However, forensic evidence's individualisation and identification setting lead to difficulty due to the items from various brands containing similar constituents and fewer variations of elements.

Moreover, interpreting trace evidence is challenging for forensic scientists to deliver the results' context (Roux *et al.*, 2015). Terms such as 'a match', 'consistent,'

and ‘most likely’ are usually used to explain the result non-ambiguously and understood by the court. It requires deep knowledge and understanding of trace evidence to evaluate the relevancy of its presence at the particular crime scene with all the related circumstances. The interpretation also requires a comparable database for comparing trace evidence materials and its analytical methodology within appropriate reference boundaries (O’Brien *et al.*, 2015). Establishing trace material collections and databases is critical but requires long-term, extended R&D capacity and practical maintenance training.

All in all, trace evidence has come a long way to be accepted as crucial corroborative evidence to support case investigations. Hence, its significance in forensic science should be treasured and recognised fully.

2.5 Forensic Analysis of Matches

Throughout the years, very few publications have explored the capability of matches as forensic evidence. Due to the gap in this specific area of knowledge, matches could often be overlooked when encountered during arson crime scene investigations. As described below, several analytical techniques have been studied in combination for the forensic analysis of matches.

The first study on the forensic analysis of matches was performed by Andrasko *et al.* (1978) in a suspected arson case at the Stockholm police headquarters. During the energy dispersive X-ray analysis (EDX), they found that chlorine, potassium, silicon, aluminum, sulfur, phosphorus, iron, manganese, chromium, zinc, and magnesium elements on the burnt match heads at the fire scene resembles the elemental composition of the most common match brand in Sweden. The burnt matches' wood was in agreement with the matchstick in the suspect's possession. Sixteen other match brands

with different head colors, cross-sections, and lengths were investigated under scanning electron microscopy (SEM) and X-ray analysis. The researchers concluded that SEM analysis allowed the identification of burnt matches within certain limits, and distinct types of matches may be differentiated by X-ray analysis. The elemental composition of unburnt and burnt match heads of the same brands of matches was also the same, except unburnt match heads have a higher concentration of sulphur.

In 1991, Glattstein *et al.* combined optical microscopy, SEM/EDS, and spot tests to detect and identify the match heads in 13 pipe fragments of the post-explosion debris cases. During the preparation of an improvised explosive device, the match heads were often scrapped off from their bases and placed in the device. Eighteen matches from various countries were examined to test the method's general applicability. The results showed that match head residues were detected and identified in 10 out of 13 cases. Besides that, the elemental compositions of the examined match heads were similar, as reported by Andrasko *et al.* (1978). Potassium and chlorine were the major elements found in the match heads, originating from the potassium chlorate (KClO_3), whereas the concentration of silicon and sulphur varies based on the manufacturers.

Kasamatsu *et al.* (2005) suggested that the previous SEM/EDX and X-ray fluorescence (XRF) in examining matches as physical evidence had poor sensitivity and was unsuitable for trace element analysis. To use an analytical tool with a wide dynamic range, high sensitivity, and suitable for simultaneous multi-elemental analysis, the researchers applied inductively coupled plasma-atomic emission spectrometry (ICP-AES) to discriminate 13 match heads by comparing their trace elemental composition and effect of combustion. The match heads were scrapped from the wood or paper base matches before the tedious process of sample preparation. The profiles of all measurable elements were qualitatively analysed using ICP-AES before the quantitative analysis.

Magnesium, aluminium, calcium, iron, zinc, and barium were selected as trace elements for discrimination because a significant variation of emission intensities was previously detected in the match head samples. The study detected magnesium, aluminium, calcium, and iron elements in all match head samples. Zinc was detected in a sample, whereas eight match head samples contained barium. The concentration of calcium, iron, zinc, and barium in burnt match heads was greater than in unburnt match heads due to the weight reduction after combustion.

Additionally, XRD analysis was carried out to investigate the match heads' crystal structure in unburnt and burnt conditions. Hydrous phyllosilicates were considered the major peaks in the spectra, which declined significantly after combustion. The samples were also compared when burnt for 1 second, 2 seconds, and until burnt out completely. The XRD result indicated that the peak intensities of the crystal destruction in the match head were done within 1 second of ignition and were not influenced by the duration of burning time. They recommended ICP-AES analysis for actual casework as it was tested effective for all 13 multi-elemental comparisons of the matches in the study (Kasamatsu *et al.*, 2005).

In the same year, Farmer *et al.* (2005) compared the matches found at the crime scene with the matches seized in the suspect's possession using Isotope ratio mass spectrometry (IRMS) for the first time. In their preliminary study, they concluded that the analysis of ^{13}C and ^2H isotopes of the suspects' matches could be clearly distinguished from the matches found at the crime scene on a two-dimensional fingerprint basis. However, other analytical techniques should be used with the IRMS to enhance the discriminating power. Farmer *et al.* (2007) performed the extension of the previous case study to compare the burnt and unburnt matches found at the crime scene with the matches seized from the suspect's house. The composition of ^{13}C and ^2H

was assessed by Stable Isotope Profiling (SIP) and confirmed with X-ray diffraction (XRD) analysis of the match heads and microscopy of the matchstick. Nine match brands were purchased, and three replicates were analysed from each box. In the SIP analysis, the conclusion that the matches share any commonality was unable to be made, as they are indistinguishable solely through the isotopes signatures. The analysis proceeded with XRD and microscopy.

Many common accessory minerals such as quartz, mica, illite, muscovite, hematite, and gypsum were found in the reference matches and matches found at the scene. However, only the matches seized from the suspect's house contained a distinct mineral identified as bassanite. The authors also described that brand discrimination was difficult due to similar ingredients used in the production and the absence of strict quality control. There were also very distinct appearances between the matches from the matchstick microscopy, such as the color, size of the phloem, and cracked appearance. It was concluded that the matches from the fire scene were not from the exact origin as those in the suspect's possession. Farmer *et al.* (2009) conducted another study using IRMS and SIP to understand IRMS's potential for burnt matchsticks better. The isotopic composition of the ^{13}C and ^2H of the burnt matchsticks samples were examined in mock fire training scenarios, with various types of fire extinguishers and the use of petrol. The study found no statistical difference in the isotope composition between the unburnt and burnt matchsticks tested in the expected condition of actual incidents.

On the other hand, Chen and Chang (2007) combined scanning electron microscopy/energy-dispersive X-ray spectrometry (SEM/EDX) and SPSS Hierarchical Cluster Analysis to study the discrimination effects of burnt matches. The morphological features of 15 boxes of the match heads were categorised into three

groups based on their diameter. The primary element of chlorine and potassium were found in all match heads, whereas sulphur, silicon, and calcium concentration depends on the manufacturers. The findings were consistent as reported in previous publications (Andrasko *et al.*, 1978; Glattstein *et al.*, 1991). Besides that, zinc, titanium, manganese, iron, and chromium elements were also found in diverse concentrations in different match heads samples. The authors asserted that the elemental composition of the burnt match heads was reliable as they were free from all possible contamination, such as newspaper, plywood, and liquid fuels. Only phosphorus, potassium, and calcium were mainly detected in the matchsticks. The application of the multivariate method in the SPSS Hierarchical Cluster Analysis also assisted the match residues' discrimination process. This paper was the last publication that used instrumentation analysis to identify and discriminate matches according to the brands.

In another study, Martin *et al.* (2019) performed DNA profiling from matchsticks. The study incorporated a tape-lifting method to analyse the matchsticks held by seven volunteers in a direct polymerase chain reaction (PCR) amplification and post-extraction PCR. They discovered that direct PCR of the matchsticks provides informative results on the short tandem repeats (STR) profiles. The last recent study is of relevance to the forensic analysis of matches was done by Sharma *et al.* (2020). Twenty-four fresh soft and hardwood samples such as aspen, walnut, maple, alder, and cherry were subjected to ATR-FTIR spectroscopy and chemometrics. The prominent spectral peaks observed in the woods were identified as moisture, cellulose, hemicellulose, lignin, and polysaccharides. The chemometric methods of hierarchical cluster analysis (HCA) and principal component analysis (PCA) successfully discriminated the wood samples, with 81% and 100%, respectively. To date, there has been no published study on matches using ATR-FTIR spectroscopy and chemometrics.

2.6 Attenuated Total Reflectance- Fourier Transform Infrared (ATR-FTIR) Spectroscopy

Attenuated total reflectance-Fourier Transform Infrared (FTIR) spectroscopy is an analytical instrumentation that analyse the functional groups' molecular vibrations that correspond to the infrared absorption frequency. This method can provide specific chemical information about the functional groups that occur because of the energy resonance with chemical bond vibrational motions (Younis *et al.*, 2021). The spectroscopy method could discriminate the source of origin of similar objects from different brands. In forensic science investigation, many trace evidence has been studied using the technique such as ballpoint inks (Lee *et al.*, 2012), firework residues (Martín-Alberca *et al.*, 2016), heroin samples (Yusoff *et al.*, 2018), and cigarette ashes (Sharma & Sharma, 2022).

The optical device being used to measure the interferograms is called an interferometer. The conceptual history of FTIR first emerged in the 19th century when an American physicist, Albert Abraham Michelson, invented the interferometer. The device was later utilised to produce spectra by transforming the interference pattern using Fourier transformation (Shaw & Mantsch, 2017). Traditionally, KBr pellets were used as the FTIR sampling transmission technique. However, it became less regular due to limited sample thickness and impurities that prevent IR radiation from penetrating and providing accurate transmittance value from the detector (Olori *et al.*, 2021). The sampling technique most commonly used for infrared spectroscopy IR is attenuated total reflection (ATR). In ATR-FTIR spectroscopy, reflectance crystal such as zinc selenide, diamond, and germanium provides good contact with the specimen surface.

It also reduces the interference from the substrate by providing excellent surface sensitivity for high-quality in-situ analysis. Besides that, ATR-FTIR spectroscopy is a

non-destructive, time-efficient, affordable, and eco-friendly analytical method that requires minimal sample preparation. Hence, it could be easily implemented in controlled-laboratory settings and fundamental research (Canizo *et al.*, 2019). As shown in **Figure 2.4**, the internal reflectance of the infrared beam in the crystal produces an evanescent wave that is able to penetrate by a couple of microns into the specimen surface. The absorbed radiation beams will reach the detector positioned at the opposite end of the crystal. An IR spectrum is generated as the detector's attenuated IR beam is recorded as an interferogram signal.

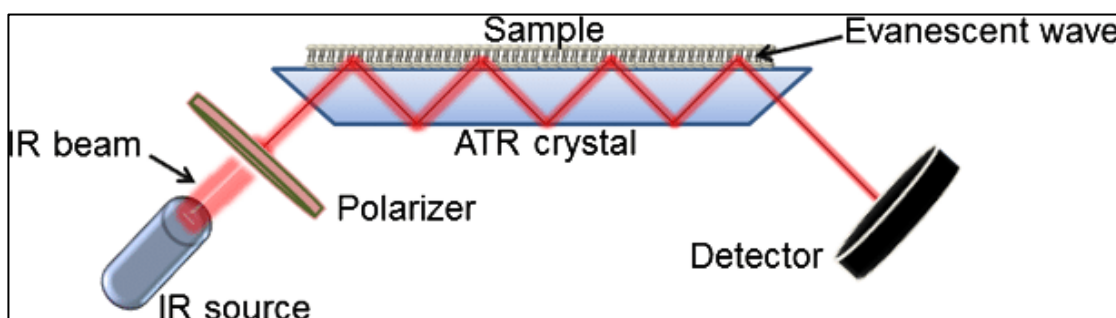


Figure 2.4 Diagrammatic representation of ATR-FTIR spectroscopy.

The electromagnetic spectrum of the infrared region is situated at 12,500 to 500 cm^{-1} . Nevertheless, mid-IR (region 4000 to 400 cm^{-1}) and near-IR (region 12,500 to 4000 cm^{-1}) are the regions most commonly analysed in FTIR spectroscopy. During the sample analysis in the mid-IR region, the molecules will absorb mid-IR energy, enabling the fundamental vibration of specific functional groups to be observed. The mid-IR fingerprint region (1800 to 600 cm^{-1}) also displays well-defined spectra for detecting lipids, polysaccharides, proteins, and carotenoid molecules (Mendes & Duarte, 2021). **Table 2.2** summarises the associated bond stretching with their respective frequency range.

Table 2.2 Frequency Range of the Functional Groups.

Bond	Type of Compound	Frequency Range, cm^{-1}
C—H	Alkanes	2850 – 5970
		1340 – 1470
C—H	Alkenes	3010 – 3095
		675 – 995
C—H	Alkynes	3300
C—H	Aromatic Rings	3010 – 3100
		690 – 900
O—H	Monomeric Alcohols, Phenols	3590 – 3650
		3200 – 3600
		3500– 3650
		2500 – 2700
N—H	Amines, Amides	3300 – 3500
C=C	Alkenes	1610 – 1680
C=C	Aromatic Rings	1500 – 1600
C≡C	Alkynes	2100 – 2260
C—N	Amines, Amides	1180 – 1360
C≡N	Nitriles	2210 – 2280
C—O	Alcohols, Ethers, Carboxylic Acids, Esters	1050 – 1500
C=O	Aldehydes, Ketones, Carboxylic Acids, Esters	1690 – 1760
NO ₂	Nitro Compounds	1500 – 1570
		1300 – 1370

2.7 Chemometrics

Chemometrics is a branch of knowledge that implies statistical methods and mathematics to design and extract as much information from a massive bulk of chemical data and understand its chemical systems (Otto, 2017). Chemometrics had been previously studied to classify and discriminate forensic evidence such as illicit drugs, explosives, perfumes, paints, documents, and gunshot residues (Bovens *et al.*, 2019).

In a standard forensic investigation setting, investigators usually rely on visual comparison for complex spectral and chromatogram analysis to establish that the known and questioned samples originated from the same source. However, visual comparison of the large spectral data is tedious and may lead to subjective and uncertain

interpretation, especially when the samples have identical spectra. The absence of a proper method and lack of statistical knowledge would also jeopardize the evidentiary value of the evidence in question.

There are generally a few basic stages to initiate the chemometrics analysis. The data would be transformed and adapted for exploratory analysis. These preliminary stages are crucial for summarising and visualizing data to further detailed analysis. The available data would give researchers insight into the well-suited chemometrics techniques to be applied (Canizo *et al.*, 2019). The illustrated workflow of chemometrics application in forensic settings to the final incident report, as proposed by Bovens *et al.* (2019), is shown in **Figure 2.5**.

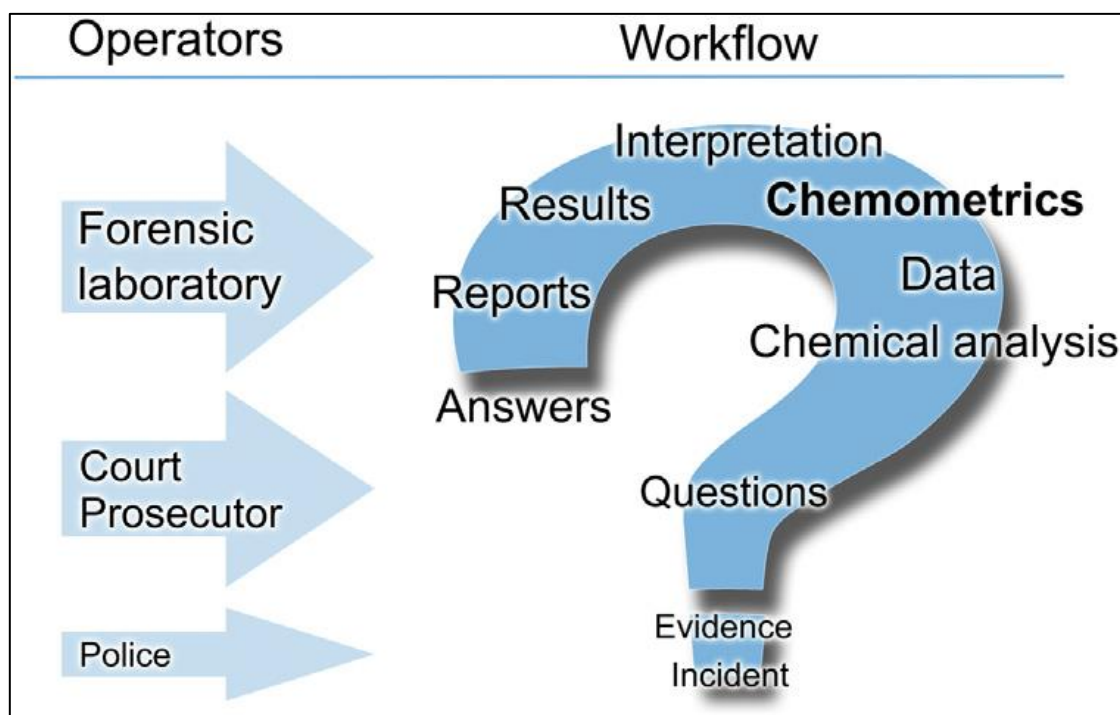


Figure 2.5 The utilization of chemometrics would be useful for interpreting case evidence (Bovens *et al.*, 2019).

Chemometrics would help provide objective inferences and interpretation by simplifying complex data to quantitative, unbiased assessment. Besides that, the pattern recognition in the technique is capable of in-depth and accurate result interpretation by eliminating possible uncertainties of the differences and similarities between the samples. It reduces the possibilities of human error, and the data's reproducibility, reliability, and discrimination would be enhanced through chemometrics (Biancolillo & Marini, 2018). Examples of the techniques include cluster analysis (CA), principal component analysis (PCA), linear discriminant analysis (LDA), soft independent modelling of class analogy (SIMCA), artificial neural network (ANN), and partial least squares (PLS) (Kumar & Sharma, 2018).

In this particular study, spectroscopic data from the matches were interpreted using a combination of PCA and LDA. The method was chosen because it permits quick and relevant discrimination of extensive data while giving precise groups or class predictions.

2.7.1 Principal Component Analysis (PCA)

The structure and patterns generated in the spectroscopic analysis could be difficult to be interpreted due to the massive amount of variables and data. However, PCA works by transforming the variables in the dataset into fewer significant principal components (PCs) but still preserving the maximum variance and information in the original data (Mahmoudi *et al.*, 2021). Karl Pearson introduced this dimensional reduction technique in 1901, which is suitable for any multivariate data analysis such as spectra or chromatograms. PCA is also known as an unsupervised pattern recognition technique and a projection method that requires no prior information on any sample groupings.

PCs, the orthogonal and uncorrelated, significant variables transformed from the raw dataset, permit users to observe the relationship between variables, similarities, and differences among samples. The directions of the data projection in PCA would examine the location where most of the variance is retained (Mishra *et al.*, 2017). Other advantages of PCA include providing better data insight for visualization, dealing with duplication in the data set, lessening the complexity, and enhancing computational efficiency. It is a flexible method that could also tackle datasets that may contain multicollinearity, missing values, and inaccurate measurement (Hasan & Abdulazeez, 2021). The probable number of PCs is less than the number of variables or samples in the particular PCA. The first PC reflects the data set's most significant proportion of variance. It must be determined by locating the axis in which the orthogonal squares of the data points are minimal. The second PC shows the next most outstanding variance value in a conduct perpendicular to the initial PC. Each successive PC expresses the remaining variability in the data set after that. Larger eigenvalues are observed in significant PCs. The total eigenvalues in all the PCs are equivalent to the number of variables in the data set.

In PCA, the information could be visualised and interpreted by various approaches. The conventional form involves plotting the score of one PC against the score of another particular sample, known as the score plots. Samples that cluster closely are correlated, whereas samples plotted distinct apart are different. In the following method for PCA visualization, namely loading plots, the factor loadings representing the cosine of the angle between the PC and each variable will be plotted. Positive cosine indicates that the variables are positively correlated and vice versa. The variables are also interpreted to have no correlation when the cosine is nearly zero. The

last method uses the Kaiser criterion to determine the PC's total. Eigenvalues greater than one are considered significant (Mendlein *et al.*, 2013).

2.7.2 Linear Discriminant Analysis (LDA)

Linear Discriminant Analysis (LDA) is another form of dimensionality reduction technique first developed by Ronald A. Fisher in 1936. Unlike PCA, LDA is a supervised pattern recognition and classification method that require prior input features or defined groups for its multivariate data analysis (Boedeker & Kearns, 2019). For the precise calculation in LDA, the number of variables must be less than the number of samples. Hence, PCA is often performed beforehand to decrease the number of variables. Only a few chosen PCs would be placed in LDA to represent the original data set. A vast number of PCs cause too much-unwanted noise, eventually leading to flawed analysis. Therefore, the selection of the significant PCs for LDA could be made in several ways; (i) Choose a cumulative variance that must be met by the PCs, (ii) Scree plot, or (iii) Kaiser criterion (Mendlein *et al.*, 2013).

In LDA, the linear combination of factors known as canonical variances (CVs) generates a discriminant function that maximizes the ratio of between-to-within class variance, hence permitting most group separation. Patterns between two classes could also be extended to classify multiple patterns. The assumptions are made in LDA that all classes are linearly distinguishable and could be identified according to numerous linear discrimination functions represented by several hyperplanes. The hyperplanes are created to maximize the inter-class distances and minimize the within-class distances (Vaibhaw *et al.*, 2020).

A final result of a successful LDA would allow the classification of the samples according to their respective group. However, a cross-validation step must be performed