DETERMINATION OF LEAD, CADMIUM AND NICKEL FROM PAINT CHIPS USING ATOMIC ABSORPTION SPECTROPHOTOMETRY WITH CHEMOMETRICS FOR FORENSIC INVESTIGATION

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UNIVERSITI SAINS MALAYSIA

2022

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by

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Thesis submitted in partial fulfilment of the requirements
for the degree of Master of Science (Forensic Science)

September 2022

CERTIFICATE

This is to certify that the dissertation entitled 'determination of lead, cadmium and nickel from paint chips using Atomic Absorption Spectrophotometry with chemometrics for forensic investigation' is the bona fide record of research work done by Mazuin Bt Che Mahmood during the period from February 2022 to September 2022 under my supervision. I have read this dissertation and in my point of view it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation to be submitted in partial fulfilment for the degree of Master of Science (Forensic Science).

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DECLARATION

I hereby declare that this dissertation is the result of my own investigations, except where otherwise stated and duly acknowledged. I also declare that it has not been previously concurrently submitted as a whole for any other degrees at Universiti Sains Malaysia or other institutions. I grant Universiti Sains Malaysia the right to use the dissertation for teaching, research and promotional purposes.

……………………………..

(MAZUIN BT CHE MAHMOOD)

Date: 7/9/2022

ACKNOWLEDGEMENT

Alhamdulillah, I would like to thank my supervisor, Dr. Chang Kah Haw for the guidance and great advice in completing this thesis and also for all my coursemates who give their opinion and update all the work and important date during completing this thesis. I would like to express my gratitude to L/Kpl Hafiz from Balai Peringat and Sjn Norolhuda Bt Mustapha from IPK Kelantan for the support and endless help. I truly appreciate the School of Health Sciences and thank all the people whose had assisted in the completion of this project. Thank you for my husband, Saiful Idham Bin Mohd Hazizi and family for great love and support during handling my work. Last but not least, I would like to express my gratitude to Allah SWT for giving the opportunity and helps me in finishing this thesis.

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LIST OF ABBREVIATIONS & SYMBOLS

AAS	Atomic Absorption Spectrometry
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
Cd	Cadmium
Cr	Chromium
Cu	Copper
FAAS	Flame Atomic Absorption Spectrometry
FTIR	Fourier Transform Infrared
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
HF	Hydrofluoric Acid
HNO3	Nitric Acid
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
Mg/L	Milligram/Litre
Ni	Nickel
OSHA	The Occupational Safety and Health Administration
Pb	Lead
PCA	Principal component analysis
PLM	Polarised light microscopy
PyGC-MS	Pyrolysis gas chromatography - mass spectrometry
R^2	Regression Coefficient
RSD	Relative Standard Deviation

SEM-EDS	Scanning electron microscopy - energy dispersive X-ray spectroscopy
Ti	Titanium
UV-VIS	Ultraviolet-Visible
XRD	X-ray powder diffraction
PC	Principal Compound
WHO	World Health Organization
%	Percent

PENENTUAN PLUMBUM, KADMIUM DAN NICKEL DARIPADA SERPIHAN CAT MENGGUNAKAN SPEKTROFOTOMETRI PENYERAPAN ATOM DENGAN KIMOMETRIK BAGI PENYIASATAN FORENSIK

ABSTRAK

Cat merupakan bahan bukti forensik yang boleh dijumpai di tempat kejadian jenayah, terutamanya dalam kejadian berkaitan kenderaan. Bahan bukti sedemikian, melalui pemeriksaan secara terperinci, boleh membantu mengaitkan orang, tempat dan objek asalnya sampel cat tersebut. Secara rutin, perbandingan forensik dilakukan untuk memerhati kesamaan dan perbezaan dari segi penampilan, susunan lapis, saiz, bentuk, ketebalan, ataupun sebahagian ciri-ciri fizikal dan kimia daripada dua sampel cat yang tidak diketahui dan rujukan. Namun, sampel rujukan berkemungkinan tidak tersedia dalam kesemua kejadian. Justeru, usaha perlu dimulakan untuk mendapatkan lebih banyak maklumat tentang profil sampel cat untuk memberi petunjuk penyiasatan forensik. Kajian ini bertujuan untuk menentukan kandungan plumbum (Pb), kadmium (Cd) dan nikel (Ni) dalam sampel serpihan cat menggunakan spektrofotometri penyerapan atom nyalaan (FAAS) diikuti dengan pengkelompokan dan/atau pembezaan melalui kemometrik. Dalam kajian ini, sejumlah 65 sampel cat telah dikumpul daripada pelbagai sumber. Sampel tersebut telah ditimbang dengan tepat dan dikenakan kepada prosedur pencernaan asid menggunakan kombinasi asid nitrik dan hidrogen peroksida. Kesemua sampel yang dicernakan kemudiannya dianalisis dengan menggunakan FAAS. Adalah didapati kebanyakan sampel cat yang diuji dalam kajian ini telah dikesan dengan kehadiran tiga elemen yang disasarkan, kecuali 14 sampel bagi Pb, 8 sampel bagi Cd and hanya dua sampel bagi Ni. Penghuraian profil elemen dengan analisis komponen utama (PCA) telah membolehkan pembezaan sebahagian sampel cat daripada kelompok utama dan mencadangkan perbezaan mereka dari segi kandungan Pb, Cd dan Ni. Kesimpulannya, aplikasi FAAS telah membenarkan penentuan Pb, Cd dan Ni dalam sampel cat dan PCA telah membolehkan pembezaan. Bahan bukti sedemikian patut dianalisis untuk profil element mereka bagi membantu penyiasatan forensik.

DETERMINATION OF LEAD, CADMIUM AND NICKEL FROM PAINT CHIPS USING ATOMIC ABSORPTION SPECTROPHOTOMETRY WITH CHEMOMETRICS FOR FORENSIC INVESTIGATION

ABSTRACT

Paint is an important forensic evidence found at crime scene, especially in vehicular related incidents. Through detailed examination, such evidence could aid in linking people, places, and an object where the paint sample originated from. Routinely, the forensic comparison is conducted to observe the similarities and differences in appearance, layer sequence, size, shape, thickness, or some physical or chemical characteristics of the two paint samples in question and reference. However, reference samples might not be available on all occasions; therefore, efforts shall be initiated to generate more information on the profiles of paint samples to provide forensic investigative clues. This study aimed to determine the contents of lead (Pb), cadmium (Cd) and nickel (Ni) in the paint chip samples using Flame Atomic Absorption Spectrophotometry (FAAS) followed by clustering and/or discrimination through chemometrics. In this study, a total of 65 paint samples were collected from various sources. These samples were accurately weighed and subjected to an acid digestion procedure using a combination of nitric acid and hydrogen peroxide. All the digested samples were then analysed using FAAS. It was found that most paint samples tested in this study were detected with the presence of the three target elements, except 14 samples for Pb, 8 samples for Cd, and only two samples of Ni. Decomposition of the elemental profiles by principal component analysis (PCA) allowed for discrimination of certain paint samples from the main cluster, suggesting their

differences in the contents of Pb, Cd, and Ni. To conclude, the application of FAAS enabled the determination of the Pb, Cd and Ni in the paint samples and PCA allowed for discrimination, where such evidence shall be analysed for their elemental profiles to assist the forensic investigation.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Paint is a coloured substance that is applied to the surface of any substrate, including wood, metal, plastic, and many other composites. Paint systems are always multi-layered because adhesion to substrates, anti-corrosion properties, barrier effects, obtaining the desired appearance and resistance to atmospheric degradation are difficult to achieve with a single layer (Caddy, 2001). Generally, paint can be found on the surface of many things to protect the materials or for decorative purposes. The protective role of paint is to shield the substrate from environmental agents such as UV radiation, moisture, and oxygen while for decoration, paint may disguise the inferior construction materials or even prevent the recognition of an object's usual appearance (Bently, 2001). There are a variety of paints that can be used for different purposes, such as automotive paints, architectural paints, tool paints, bike paints, cosmetic paint (fingernail polish), and boat paints (Bently, 2001).

Paints are composed of three main ingredients - a binder, a pigment, and a solvent. Apart from that, certain paints can have modifiers such as desiccants, corrosion inhibitors, catalysts, UV absorbers and plasticizers (Rayland, 2012). Among the three main components, binder provides adhesion and cohesion to hold the pigment and ensures that the paints remain attached to the substrate. Paint binders are usually polymers dissolved in the paint or suspended in it by emulsifiers (Ravikumar et al., 2012). The pigment is used to provide color, opacity, and gloss to optical materials. Paint can sometimes serve as a protective layer on the surface beneath it and the adhesive used to hold the paint together.

This is important because ultraviolet light can destroy both of these things. Occasionally, pigment also prevents corrosion and serves as a reinforcing function for the paint itself, aiding the binder to stick (Ravikumar et al., 2012). Lastly, the solvent is a medium where the paint components are mixed to make them easy to apply. Paint also contains small droplets that can attach to the desired surface. The solvents used during manufacturing help create a coating, but they are lost when the coating is applied. During the post-curing period, applying heat often helps the loss (Bentley, 2001).

Paint from criminal activity can provide useful and important evidence in most incidents because the colour, coating sequence and resin composition of vehicle paint vary widely between brands. Forensic evidence was the investigation of incidents such as car crashes, car crashes or deaths, robberies, wrongful deaths in significant cases involving car paint (Caddy, 2001). The colours, textures, and finishes of paint used on cars are specific to the make and model of car, as well as the year of manufacture. However, some paint characteristics are common to many brands of cars. Therefore, compositional analysis of paint chips from vehicles involved in hit-and-runs or vehicular-related incidents can be crucial for determining their credibility (Malek et al., 2019). Forensic examination of paint chips continues to be important in the forensic investigation.

Heavy metals are typically defined as those with high densities, atomic weights, or atomic numbers. Heavy metal is defined as metallic elements that have a relatively high density compared to water. In physics, heavy metals are usually characterized by determining their atomic number, but chemists and biologists are probably more interested in their chemical behaviour. There were many arguments about the definition and the classification of heavy metals from the periodic table. Heavy metals are generally accepted as those naturally occurring metals with atomic numbers greater than 20 and elemental densities greater than 5 gcm-3. Screening the periodic table reveals a total of 51 elements classified as heavy metals.

Heavy metals such as lead (Pb), chromium (Cr), and cadmium (Cd) are often found in automobile paints and can be toxic if ingested or inhaled (Vattanasit et.al, 2021). Auto parts such as switches, batteries, headlight bulbs, brake lights, data tapes, floppy disks, power boxes and car radios can also contain Cd, Cr and Nickel (Ni). As these vehicles age, they can pose a threat to the environment and public health (Nduka et.al, 2019).

1.2 Problem Statement

Automobile paints play an important role to assist the forensic investigation of vehicular related incidents. There is a possibility that paint chips can be transferred from one place to another whenever there is contact. Therefore, paint related evidence can aid in linking the people, objects and/or places through forensic comparison between the questioned paints chip recovered from a crime scene and reference samples taken from the known source. However, limited information could be retrieved when only questioned sample is available to the forensic investigators. The examination of such forensic evidence might only tell the physical characteristic such as the colour of the vehicle, given that the topcoat colour is still intact.

Information on the chemical profiles of paint samples might contribute to forensic investigative clues and leads through the application of instrumental techniques. The organic profiles of the paint samples, particularly through the application of Fourier transform infrared spectroscopy, had been extensively established where comparison of paint samples could be initiated for grouping and discrimination (Chen & Feng, 2015). However, there was a lack of studies which compare the elemental profiles of the paint chip samples collected from vehicles, and whether such profiles could allow for the determination of the common source or discrimination from other sources. Previous studies on the examination of paint compositions had reported the variations among paints, depending on the intended uses as well as the preference of the manufacturers (Beveridge et al., 2001). This study was conducted to investigate the presence of heavy metals, namely Pb, Cd and Ni, in the paint samples collected from vehicles. This three element was chosen due to the use of these metals in car manufacturing and will these three metals affect the metal content in car paint. If they were detected, these heavy metals were also further quantified to determine their respective contents in the paint samples. Based on the elemental profiles, whether a paint sample could be discriminated from other sources were also studied.

1.3 Aim and Objectives

The general aim of this study was to determine and compare the composition of Pb, Cd, and Ni in paint chip samples by flame atomic absorption spectrophotometer (FAAS) in couple with chemometrics for forensic investigation. To achieve the aim, the specific objectives are set as follows:

i. To validate the FAAS method for the detection of Pb, Cd, and Ni.

ii. To cluster and discriminate the paint chip samples using the chemometric method based on their elemental profiles.

1.4 Significance of Study

The outcome of this study could determine if the target heavy metals were existed in the paint samples tested. If yes, the contents of such heavy metals were further quantified and compared to the allowable levels. Reference paint samples might not always be available to the forensic investigator whenever there is vehicular related incident. In such scenarios, only the questioned sample is available for analysis. Therefore, in additional to physical examination such as the observation of colour and sequence layer, such forensic evidence shall be tested with an instrumental technique for their organic and inorganic profiles. With information on the profiles, the probable source of the paint samples could be generated, providing investigative clues to track the possible vehicle which could have contributed to such evidence.

CHAPTER 2

LITERATURE REVIEW

2.1 Paint

Paints are coatings or films with decorative and protective functions (Ryland & Suzuki, 2012). A colored substance that, when spread on a surface and dried, forms a thin decorative or protective layer. Paint can be made in many colours and have different types, with the most common type of paint is the automotive finish paint, architectural coating for structural paint, as well as house paint and maintenance painting. Paint composition can be varied in terms of their performance characteristics, economic issues, and environmental and safety concerns (Rayland & Suzuki, 2012).

Paints are used to protect, decorate and extend the life of natural and synthetic materials, acting as a barrier against environmental influences. It protects the material for long-lasting from weathering oxidation process, damage by insects, and various substances from corrosion. Ultraviolet, moisture, and oxygen are environmental influences, and substrates must be coated to protect them from these agents as a protective role (Bently, 2001). Paint also gives a high-class finish, attractive colours and pleasing surface design and appearances, improving the beauty of materials (Bently, 2001). Table 2.1 shows the major composition of paint with their respective functions (Lambourne, 1999).

Table 2.1: The major composition of paint

	Components	Typical function
Vehicle (Continuous phase)	Polymer or resin (Binder)	Provides a basis of continuous film, sealing or otherwise protecting the surface to which the paint is applied. Varies in the chemical composition according to the end use.
	Solvent or diluent	The means by which the paint may be applied. Avoided in a small number of compositions such as powder coating and 100% polymerisable systems.
Pigment (Discontinuous phase)	Additives	Minor components, wide in variety and effect including catalyst, driers, and flow agents.
	Primary pigments (Fine particle organic or inorganic)	Provide opacity, colour and other optical or visual effects. Frequently used for aesthetic reasons. In primers, the pigment may be included for anti-corrosive properties
	Extender (Coarse particle inorganic matter)	Used for a wide range of purposes including opacity/ obliteration (as an adjunct to primary pigment); to facilitate sanding, e.g. in primary surfaces.

2.2 Paint System

Coating systems are multi-layered because barrier performance, adhesion to substrates, corrosion resistance, resistance to atmospheric aging, and the desired appearance are difficult to achieve in a single coat (Bently, 2001). There are decorative and automotive paints are the two types of paint systems. A decorative paint system has three different types of paint which are gloss coat, undercoat, and primer to be applied on a substrate e.g. wood. Decorative paint is usually used to provide a colourful, pleasing, and decorative appearance to the surface whatever the size or object and to enhance the strength and durability of the coating. An automotive paint system should be painted in multiple layers depending on the desired effect (Bentley, 2001). Table 2.2 shows decorative and automotive paint layer systems.

Table 2.2: Decorative and automotive paint system (Bently, 2001)

<table>
<tr><th colspan="2" rowspan="2">Decorative paint system</th><th colspan="2">Automotive paint system</th></tr>
<tr><th>Solid colour</th><th>Metallic colour</th></tr>
<tr><td rowspan="2">Gloss coat</td><td rowspan="2">50µm</td><td rowspan="2">Topcoat 40µm</td><td>Clearcoat 40µm</td></tr>
<tr><td>Metallic base coat 15µm</td></tr>
<tr><td rowspan="2">Undercoat</td><td rowspan="2">40µm</td><td colspan="2">Primer surfacer 35µm</td></tr>
<tr><td colspan="2">Cathodic electrocoat primer 20µm</td></tr>
<tr><td>Primer</td><td>20µm</td><td colspan="2">Pre-treatment 2µm</td></tr>
<tr><td colspan="2">Substrate (e.g. Wood)</td><td colspan="2">Substrate (e.g. Steel)</td></tr>
</table>

Table 2.2 indicated the decorative and automotive paint systems have different layers and thicknesses with some different nomenclature but similar in function. The primer coat functions to stick to each of the substrates where the substrates are metallic which includes anticorrosive pigments to the part of the corrosion protection system and make it more needed in the paint systems. In automotive paint systems, the pre-treatment layer appears very thin, but has good adhesion to the substrate and is relatively inert, making the metal surface less susceptible to chemical attack than untreated metal. It converts into a smooth material and also provides a uniform fine coating porous surface to which the rest of the paint system can adhere (Xu et al, 2015). The corrosive nature of the surface material is important to take into account when treating it, as it is susceptible to

exposure to air and moisture. Primers and primer finishes are important to ensure that thicker layers are fully opaque, or that the undercoat is opaque, and that the base of the topcoat is smooth. The gloss on the top layer requires not total opacity and just enough pigment to give colour to the paint system. Clearcoat/basecoat system produces metallic and pearlescent automotive and refinishes systems that contain aluminium or mica platelets which give the required appearance, durability and improve gloss by applying the clear unpigmented acrylic or polyurethane-based varnish (Bently, 2001).

2.3 Heavy metals in Paints

According to Emanuel et al. (2005), paint manufacturing use in their process pigments, which contain mineral elements such as copper (Cu), Pb, Cd, mercury (Hg) and Zinc (Zn). Some of those elements have been measured in wastewater generated by this industry. Indeed, concentrations of 1670 g/L of Pb and 105 g/L of Hg have been found in wastewater coming from paint manufacturing in Port-au-Prince (Emanuel et al., 2005). At high concentrations, metallic pollutants could provoke a biological imbalance in aquatic ecosystems. The study was to explain the ecological risk of heavy metals in Port-au-Prince paint manufacturing, where the marine ecosystem was considered the target to protect. The effects of Pb, Cu and Hg, contained in these wastewaters, have been studied on the embryonic development and the growth of two levels of the marine food chain namely algae (Asterionella glacialis and Asterionella japonica) and crustacean (Cancer anthonyi). Wastewater samples were collected in 2004 and 2005, on the collector of paint manufacturing. A maximal concentration of 500 g/L Cu and 700 g/L Pb, respectively, were measured (Emanuel et al, 2005).

Khan et al. (2021) performed a study about the contamination of heavy metals in acrylic colour paints commonly used by school children. Composition of heavy metals such as manganese (Mn), cobalt (Co), Ni, Zn, arsenic (As), Cd and Pb were assayed from a different colour of acrylic paints using microwave digestion and inductively coupled plasma mass spectrometry (ICP-MS) system. The optimised method involved the paint digestion reagents hydrofluoric acid (HF, 40%, 2 mL) and nitric acid (HNO3, 65%, 5 mL) which has offered excellent method performance with recovery values ranged between 99.33% and 105.67%. Elements were identified in all samples analysed, with levels of each element ranging from 0.05 to 372.59 µg/g. Zn had a high proportion (68.33%) and Cd had a low proportion (0.05%). Furthermore, paint contamination was also color-specific, with amber having significant total heavy metal concentrations (526.57 µg/g), while scarlet contained low levels (12.62 µg/g) (Khan et al, 2021).

In a study by Wang et al., (2020), paint samples from 91 different paint brands and colors were analyzed for the presence of eight heavy metals and lead. The results showed that the average concentration of heavy metals and lead in paint used by Chinese opera actors was 16.2 µg/g. The average amount of As (1.8 µg) was analyzed. /g), Cd (0.6 µg/g), Cr (23.1 µg/g), Co (4.4 µg/g), Cu (610 µg/g), Zn (10415 µg/g), Ni (7.6 µg/g) were detected in face paints and at least 4 of the 8 heavy metals were detected in all samples analysed. Car paint dust contains Cd, Cr and Ni which could be released into the environment during scraping off the old paint from a vehicle before repainting (Nduka et al, 2019).

2.4 Pigment and colour composition related to forensic examination

Pigments shows the colour of the paint, which provides opacity and occasionally prevents corrosion. Pigments must scatter light with a different refractive index as compared to that of the resin and be of optimum particle size. Pigments can be divided into organic pigments and inorganic pigments. These pigments are composed of small solid particles less than 1 μm in diameter and can refract light (Ravikumar et al., 2012). Pigment particles are crystalline solids that appear in cubes, rectangles, needles, and other flat shapes that can reflect light (Bently, 2001). A full spectrum of colours and different finish patterns can be archived using a variety of natural and synthetic pigments in the paint (Ravikumar et al., 2012).

According to Bently (2001), pigments was chosen based on the various effect as following: hue clarity and brilliance (organic pigments produce the most interesting and clean colours), white and black colours (white pigments come from titanium dioxide, the deepest blacks are inorganic carbon, organic blacks and whites, etc.)), non-bleeding pigments (inorganic compounds are sparingly soluble in organic solvents, some organic compounds are very sparingly soluble, and some organic compounds are more soluble in stronger solvents. Lightfastness (Inorganic compounds are more stable to UV light due to their chemical structure), heat resistance (inorganic pigments and very few organic compounds are stable at high temperatures above 300 °C, but some decompose and melt at low temperatures) , anti-corrosion (all anti-corrosion pigments are inorganic), UV-absorbing (titanium dioxide and fine iron oxides protect from binders and substrates and block UV radiation), pearlescent and reflective effects (treated mica And metallic aluminum is used to get the reflective effect, aluminum flakes are generally smooth or may be colored.They are coated with pearlescent mica pigments to create an interference effect on the reflected light give as a further enhancement).

Decorative paints require organic pigments that have the right properties of ultimate color fastness and do not require heat stability, whereas automotive paints require inorganic pigments to achieve very high standard quality colors. pigments are used. (Bently, 2001). The optimal pigment formulation for all paints can achieve the desired color effect (Rayland, 2012). Paint samples can be useful as forensic evidence in a number of situations, especially in the area of colour recognition. Images from surveillance cameras or witnesses can be useful to identify the vehicle involved in the crash and run incident, especially the determination of colour are a priority to help the investigation (Duarte et al., 2022).

Automotive paints generally consist of the toxic metals Pb, Cr, and Cd, which are the building blocks of coloured pigments. Cadmium sulfide (cadmium yellow), lead chromate (chrome yellow), chromium oxide (chrome green), and lead oxide (lead red) are examples of metallic pigments found in automotive paints. Cd is released in the manufacture of cadmium pigments. Cadmium pigments are stable inorganic colorants that produce vibrant shades of yellow, orange, red and maroon. These pigments produce golden yellow pigments based on cadmium sulfide (CdS) (US EPA, 1993). Measurements of ambient concentrations of his three metals at an auto repair shop in Hat Yai City, Songkhla Province, Thailand have been reported (Vitayavirasuk et.al, 2005). Grinding, welding, and painting of auto parts was also an activity that released metal and scraped off the car's paint dust during the refinishing of used cars (Nduka et al, 2019).

2.5 Forensic analysis of paint related evidence

Paint can be powerful forensic evidence or evidence that can be utilized to solve the crime when it is involved for most hit-and-run incidents and vehicle crashes and death accidents. Crime scene paint such as from the suspect's car on the victim's body, clothing, and belongings are important evidence to help locate the vehicle involved. Paints swatches come from a type of force used to transfer paint from one object to another and can be found in a variety of shapes and sizes (Muro et al., 2014). Through forensic comparison, similarities and differences in appearance, layer sequence, size, shape, thickness, or some physical or chemical characteristics of paint from the two samples in question and references could conclude that the samples are of the same origin. Proper paint analysis can help investigators prove or disprove a suspect's involvement in a crime and determine if the paint is real or fake (Muro et al., 2014).

In general, reaching the strength of a conclusion depends on the nature and number of relevant features included in the evidence. A good comparison could be carried out if multi-layers of paint are present in the evidence and are found with other paint sources with similar characteristics depending on the sequence of layers and components. Passing comparisons of such paint related samples are important in criminal forensic investigations, but only if there are matching samples for investigators and forensic analysts. e.g. the suspect’s car has been confiscated and used as a reference.

Automotive paint is one of the most common forms of trace evidence found in car crash, hit-and-run accidents or most found in any incident involving a vehicle. In the forensic examination, each layer of automotive paint is both visually and chemically analysed. Usually, samples are taken from the vehicle or clothing of the victim involved in an incident or at the scene. Often, there are no witnesses to hit-and-run incidents, and investigator are difficult to locate the suspect to compare samples with automotive paint from the suspect's vehicle. Therefore, the analysis of the automobile fragments or paint chips left at the scene becomes sometimes the only link to start the investigation. For example, car components, make, brand, and year of manufacture were determined using paintwork collected at crime scenes or car crashes. Manufacturers tend to use different paints and ingredients in their products, so know paint formulations and processes, paint standards, and the availability of paint databases to get details on paint proofs, especially for unknown proofs was important. Paint strips recovered from crime scenes and victims' clothing are analyzed, and an automotive paint database can be used to correlate the data to specific lines and vehicle models within a limited range of manufacturing years (Lavine et al., 2016).

Paint chips can provide important information and be strong evidence to solve a criminal case so the evidence must be analysed with appropriate and accurate methods and instruments. ASTM International has come out with some documents of standard guidelines on current forensic paint analysis, including Forensic Paint Analysis and Comparison (ASTM E1610-2014), Infrared Spectroscopy in Forensic Paint Examinations (ASTM E2937-13), Scanning Electron Microscopy/X-ray Spectrometry in Forensic Paint Examinations (ASTM E2809-13), Microspectrophotometry and Colour Measurement in Forensic Paint Analysis (ASTM E2808-11).

2.5.1 Stereomicroscopy

Stereomicroscopy is a physical matching procedure routinely used in the examination of paint schemes. The determination of the number, order, colour, thickness, and texture of each layer in a paint system can be conducted using a stereomicroscope (Caddy, 2001). Identifying and physically inspecting the outermost layer and any possible layer sequence for paint-related evidence can provide an indication of the type of paint obtained. When a paint sample matches physical characteristics such as the multiple matchable layers and the same colour, it poses the most likely come from a common origin (Caddy, 2001).

Based on Wilfried Stoecklein's study (2001), an examination of microscopic color specimens using a stereomicroscope with fiber optic tungsten filament illumination with a reflected light source against a neutral gray background was recommended. Determination of colors in three-dimensional color spaces using the Munsell coordinate system, the standard DIN 6164 color chart, the natural color system, and the Methuen color manual, providing color labels or coordinates for color samples. Although there is no universally suitable color system for determining the color of effect paints, which comprise the majority of automotive paints, automotive paint colors are described and classified using color collections sold by the most important paint manufacturers (Stoecklein, 2001). The Comparative colour examination is carried out by individuals with good colour vision, since the visual assessment could be subjective and therefore fraught with uncertainty. Objective and colorimetric-based colour measurements were also established by the subjective single observer as an alternative such as 'Standard Observer' colour measurement (Stoecklein, 2001). The human eye can measure such colors, which are directly related to the process of color vision. Experimental results have shown that proper mixing of three monochromatic emissions, called the trichromatic theory, can also adequately match three different types of cones sensitive to different wavelength ranges with specific color vision. rice field. Retinal color perception cones were standardized on a quantitative scale to determine the color stimuli that determined responses to different wavelengths of light (Stoecklein, 2001).

Palus et al. (2000) described that optical microscopy, infrared spectrometry and elemental analysis could be routinely applied in paint examination to give the information on both layer structures and chemical compositions of the examined samples. In Poland's car paint examinations, paint chips coming from repainted and repaired cars were examined. The examinations aimed at sample comparison, especially in hit-and-run cases which might lead to conclusions that are formulated in the category of probability. The determinations of morphology and chemical composition of the examined paint samples were proved valuable in all presented cases, enabling the comparison of paint samples and to deciding whether they may have a common origin (Palus et al., 2000). In addition, a comprehensive laboratory collection of reference paint samples, as well as color and molecular information, may greatly facilitate the identification of car crashes and accidents with paint, especially known paint debris. Brands, make and year information adds weight and credibility to comparative evidence, whether originally developed for vehicle identification or to show uniqueness (Palus et al., 2000).

According to Kruglak et al. (2019), valuable analytical data was provided by population studies of trace evidence for suspects of crime to evaluate the evidentiary significance through the assessment of the frequencies of physical, microscopical, and chemical properties of automotive paint chips. This study collected two hundred automotive paint chips from auto body shops, and then all samples were analysed using stereomicroscopy, brightfield, and polarised light microscopy. a sequence of modern instrumental techniques used by forensic paint examiners namely the Fourier-transform infrared (FT-IR), Raman, and ultraviolet-visible (UV–Vis) microspectroscopy to analyse the red paint. Paint samples were compared to each other to assess the discriminatory potential of each analytical method. From these studies, the results show that macroscopic and microscopic properties were able to differentiate up to 99.995% of the population. All paints could be differentiated, when there is a combination of instrumental techniques either FT-IR or UV–Vis microspectroscopy. One would not expect to encounter two indistinguishable paint chips originating from different sources during the investigation of a single event can be concluded (Kruglak et al., 2019).

2.5.2 Microspectrophotometry

A microspectrophotometer (MSP) was used to measure the intensity of light transmitted, absorbed, or reflected by the sample at each wavelength in the visible or ultraviolet regions of the spectrum. MSP was used to compare paint samples by measuring colour. Most paints contain 2 or 3 pigments, and especially in reflection mode, the spectrum is a combination of all spectra, in addition to the few features of the MSP spectra of the pigments, so the pigment determination is difficult (Muehlethaler et al., 2013). MSP can distinguish between optically identical samples and provide an objective measure of colour. The effect-coating procedure is more challenging due to the large variation in spectral sensitivity, requiring measurements to be performed on clean, undamaged sample areas of similar size and morphology (Muehlethaler et al., 2013).

2.5.3 Polarised light microscopy (PLM)

Polarised light microscopy (PLM) is usually used to determine particles in the paint samples. According to Wilfried Stoecklein (2001), PLM allows up to ×1000 magnification and uses incident and transmitted light to examine paint samples. Plane polarized light is incident light/bright field and fluorescence can help in determining the shape of particles especially crystalline materials that include the majority of pigments in such samples using PLM and also accomplish the specific effect of pigments such as metal and pearl. PLM is also used for the examination of layers of paint samples and also the measurement of the thickness and uniformity of each layer. The observation of the morphology and physicochemical features of coloured pigments and extenders in the composition of the paint used magnification ranging between 250× and 1000× in transmitted light/bright or light/dark field. The analysis needed only a small-sized paint sample, at approximately 3 μm section which had been embedded to surface resin parallel or perpendicular (Stoecklein, 2001).

2.5.4 Fourier transform infrared (FTIR) Spectroscopy

Infrared (IR) spectroscopy is a useful and powerful tool to produce important information from microsamples like example small chips or smears of paint samples. Paints layers have microsampling capabilities that provide molecular structural information on organics and inorganics. The probable source of the paint can be ascertained by using a database and also to compare samples from different sources to determine if they can have the same origin can be done by using IR Spectroscopy (Beveridge et al., 2001). Dispersive and FTIR analysis was the two primary instrumental methods for the analysis of paint fragments. FTIR spectrometer is the primary method of analysis conducted on each topcoat and primer layer due to its sensitivity, speed, and discriminating ability and examines all the frequencies of radiation emitted by the source. It is also a non-destructive method available for the analysis of paint because it helps rapid identification of the binder, resin, and additive components in the sample (Muro et al., 2014). It analyses samples in a clean, fast, and non-destructive manner (Duarte et al., 2022), allowing the examination of the physically remove of thin paint smears from the substrate (Rayland & Suzuki, 2012). It can be used to determine the organic components of binders and pigments and also to classify the various types of general binders present in the sample. Infrared absorptions can be produced by all components of paint, and aid in determining the overall composition of paint. The binders and the pigments that are present in higher concentrations could be identified with FTIR (Rayland & Suzuki, 2012).

Jungang et al. (2016) conducted a study using FTIR and Raman Spectroscopy to analyse 52 automotive coating samples. Compounds in the pigments or additives were titanium (Ti), iron (Fe), Cu, Pb, and Cr were used for coatings. FTIR was used to identify resins and additives, and Raman microscopy was used to detect additives and pigments in automotive paints. FTIR and Raman microscopy work better together than individually for identification. Combining these two non-destructive methods can effectively identify different paint samples for environmental and forensic purposes (Jungang et al., 2016).

2.5.5 Pyrolysis gas chromatography - mass spectrometry (PyGC-MS)

Pyrolysis is the use of thermal energy to break chemical bonds. Temperature, heating rate, and time are factors for the degradation of macromolecules such as analgesics into smaller volatile fragments, separated by GC and identified or characterised using MS. (Muehlethaler et al., 2013). Using these techniques, paint samples were analyzed for different compositions. A trace sample of 10 µg was required to determine the monomers of the binding system, while the identification of several additives and pigments was used to improve the discrimination of chemically similar paints. The advantage of PyGC-Ms was the high selectivity with which trace components can be detected and compared. On the other hand, the drawback of this technique is that it is destructive, requires a sample preparation step, and is time consuming. Therefore, due to the limited number of samples available for forensics, analytical methods should be carefully planned and selected (Muehlethaler et al., 2013).

The PyGC-MS was the combination of gas chromatograph or a mass spectrometer to detect and identified the pyrolysis products. The analytes can be compared and the reliable data can be produced by using PyGC-MS. PyGC can identify the types of the automotive paint binder on microgram-sized samples of topcoat paint samples and also can be distinguished among acrylic lacquer, acrylic enamel, and alkyd enamel which are the organic binder in paint found in original paint systems (Henson et al., 2001). It also could be used for the identification of additives, such as coalescing agents, flow promoters and organic pigments and discrimination of polymers in surface coatings. The pyrograms can indicate the compositional data of paint samples within a class (Caddy, 2001).

2.5.6 Scanning electron microscopy - energy dispersive X-ray spectroscopy

Scanning electron microscopy/energy dispersive x-ray (SEM/EDX) spectrometry is an ideal tool for performing non-destructive analyses on small and also large single or multi-layered paint fragments, it is used for the elemental analysis of paints and coatings (Henson et al., 2001). Section 2.1 described that the composition of the paint contained pigments and extenders. The compositions of automotive paints are varied and different elemental profiles are determined. For example, non-toxic titanium dioxide (TiO_2) in the common white pigment as compared to some lead-based predecessors. Decorative pigments are added to coatings to produce a glittery or flamboyant appearance. Water-borne coating was substituted the aluminium metal flake put the metallic appearance in an automotive finishing coat (Henson et al., 2001).

SEM/EDX is primarily used to compare qualitative or semi-quantitative modes with elemental detection through indirect identification of inorganic content in paints (Muehlethaler et al., 2013). Since the periodic table can detect a wide range of elements, it is used to study the elemental composition of paint samples layer by layer. Additionally, each paint layer could be identified and pigments compared (Henson et al., 2001).

2.5.7 X-ray powder diffraction (XRD)

According to Henson et al., (2001), XRD is an elemental analysis used by forensic paint inspectors to analyse the crystal structure of materials. A glass capillary tube with petrolatum or other amorphous glue was used to attach a small piece of the paint sample examined by XRD. Moreover, the XRD inspection required a long time to perform, about several hours. Discrimination of two types of titanium dioxide (rutile and anatase) was an application of XRD in forensic paint inspection. (Henson et al., 2001).

2.6 Elemental determination of paint related evidence

The choices of analytical methods to measure heavy metals in paints could be due to many factors such as the number of samples, cost, analysis purposes, and rapid measurement determination. Flame Atomic Absorption Spectrometry (FAAS), Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Inductively Coupled Plasma Atomic

Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was a commonly used method in elemental determination. Comparatively, ICP-AES poses a lower limit of detection, but it could be more costly. According to the Element Profile Determination Guidelines, an international method for paints and varnishes to determine total lead concentrations from 0.01% to 2.0% using the FAAS method. ASTM D3335-85a (2014) is the standard test method for low levels of lead (0.01% to 5.0%), cadmium, and cobalt in paints using AAS. ASTM E1613-12 (2012) states that the analytical technique contributing to differences in lead concentration measurements is inductively coupled plasma atomic emission spectrometry (ICP-AES), flame atomic absorption spectrometry (FAAS), or graphite furnace atomic absorption spectrometry. I'm explaining. (GFAAS) technology.

2.6.1 Flame Atomic Absorption Spectrometry (FAAS)

WHO (2011) described that AAS operates based on the free atoms that absorbed light at wavelengths characteristic of the element. For instance, 283.3 nm is the wavelength for the absorption of the ground-state atoms of lead. The amount of light absorbed can be linearly correlated with the concentration of the analyte in the sample. To perform an AAS measurement, a lead-bearing sample must first be processed by the instrument, producing ground-state atoms as a vapor in the instrument's optical path through a process called atomization. FAAS uses air-acetylene or layered oxide-acetylene-air flames to atomize lead at temperatures up to 2600°C. FAAS detection limits were found to be moderate, but still adequate in most cases this is because the sample had to be aspirated directly during analysis. At least about 5 mL of digestate can be introduced for aspiration and measurement of a stable signal. FAAS measurements are subject to interference by light scattering and molecular absorption by matrix components, which can be adequately compensated for by various approaches. FAAS devices, which require laboratory knowledge to operate, are widely available with or without an autosampler. The initial cost of equipment is relatively low, and consumables such as acetylene gas are also relatively inexpensive. The instruments also require low frequencies, and the samples productions can be several samples per minute (WHO, 2011).

Ogilo et al. (2017) evaluated the levels of Pb, Cr, Cd, and Zn in settled indoor dust and paint debris. Samples were collected from 12 selected houses in Nairobi County, Kenya between February 2016 and November 2016. Samples were digested using a modified version of EPA method SW846 3050B and analyzed for metals using FAAS (Shimadzu AAS-6200). Pearson correlation coefficients were determined for various metal pairs in the paint chip and dust samples. The average concentrations of metals in both dust and paint chip samples were repeated in the order Zn>Pb>Cr>Cd. Mean concentrations of Zn, Pb, Cr and Cd were 366.14 µg/g, 129.12 µg/g, 82.65 µg/g, 27.40 µg/g, 321.77 µg/g, 289.59 µg/g and 77.54 µg/g in the dust samples. did. 73.45 µg/g of the paint chip sample, respectively. In the correlation, Pb, Cd and Zn in the paint chips showed a negative correlation, and Cr showed a positive correlation. Although the study found that the metals in the paint fragments had a common origin, correlations between the different metal pairs in the dust suggested different origins (Ogilo et al., 2017).

Dhakal (2018) who have studied the elements Cd and Pb suggest that these two elements are dangerous heavy metals that can damage multiple organs even at low exposures. Paint is a major source of environmental contaminants such as Cd and Pb, with 100% of samples of stripped paint on the walls of shipping containers having at least

0.25ppm Cd and Pb ranging from 150ppm to 482ppm. reported to be in the range of Sample solutions were prepared by acidolysis using the 3050B method. Acid Digestion of Sediments, Muds and Soils, Revision 2 (USEPA, 1996) and Cd and Pb metals were analyzed by FAAS. 100% of the samples were contaminated with Pb, which was above the WHO toxicity range, while 80% of the samples were contaminated with Cd, which was below the WHO toxicity range. This result was of great importance to officials and citizens as they recognized that the city could be exposed to toxic metals. (Dhakal, 2018).

2.6.2 Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

GFAAS is an AAS technique that uses electrically heated graphite tubes to vaporize and nebulize analytes at temperatures up to 3000 °C prior to detection, resulting in very low detection limits and no required decomposition. The volume is only very small (approximately 20 μL) (WHO, 2011). GFAAS measurements can also be subject to significant interference from light scattering and molecular absorption from matrix components, which can be appropriately corrected with various approaches, including the use of matrix modifiers. The GFAAS device must be operated by a trained laboratory technician. Such instruments are ubiquitous and require an autosampler to improve accuracy and throughput, with a sample throughput of approximately 1 sample every 2-3 minutes (WHO, 2011). The initial equipment cost is moderate, and maintenance and consumption costs are relatively high compared to FAAS (WHO, 2011).

2.6.3 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

WHO (2011) explained that ICP-AES uses an inductively coupled plasma source (a very hot ionized gas composed of electrons and positively charged ions) to dissociate the sample into its constituent atoms or ions. did. Under these high-energy conditions, lead