DEVELOPMENT OF A METHOD TO CREATE AN AUTOMOTIVE PAINT DATABASE

OPAS THONGNOI

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE (FORENSIC SCIENCE)
FACULTY OF GRADUATE STUDIES
MAHIDOL UNIVERSITY
2011**

Thesis
entitled

DEVELOPMENT OF A METHOD TO CREATE AN AUTOMOTIVE PAINT DATABASE

……………….……….….……..………
Mr. Opas Thongnoi
Candidate

……………………….….….……..………
Assoc.Prof. Nopadol Chaikum,
Ph.D. (Chemistry)
Major advisor

……………………….….….……..………
Asst. Prof. Siwaporn Meejoo Smith,
Ph.D. (Chemistry)
Co-advisor

……………………….….….……..………
Prof. Banchong Mahaisavariya,
M.D., Dip Thai Board of Orthopedics
Dean
Faculty of Graduate Studies
Mahidol University

……………….….…..………
Asst. Prof. Nathinee Panvisavas,
Ph.D. (Plant Molecular Biology)
Programme Director
Master of Science Programme in
Forensic Science
Faculty of Science,
Mahidol University

Thesis
entitled

DEVELOPMENT OF A METHOD TO CREATE AN AUTOMOTIVE PAINT DATABASE

was submitted to the Faculty of Graduate Studies, Mahidol University
for the degree of Master of Science (Forensic Science)
on
March 28, 2011

……………….…………..…..………
Mr. Opas Thongnoi
Candidate

……………………..…..………………
Asst. Prof. Somporn Chongkum,
Dr.rer.nat (Physik)
Chair

……………………..…..…………..……
Assoc.Prof. Nopadol Chaikum,
Ph.D. (Chemistry)
Member

……………………..…..………………
Asst. Prof. Siwaporn Meejoo Smith,
Ph.D. (Chemistry)
Member

……………………..…..……………...…
Prof. Banchong Mahaisavariya,
M.D., Dip Thai Board of Orthopedics
Dean
Faculty of Graduate Studies
Mahidol University

……………………..…..……………...…
Prof. Skorn Mongkolsuk,
Ph.D. (Biological Science)
Dean
Faculty of Science
Mahidol University

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my major advisor, Assoc. Prof. Dr. Nopadol Chaikum, for his excellent advice, valuable time, correcting my thesis, patient teaching and support throughout this thesis completely. He is an excellent advisor.

The thesis cannot be completed without the helpful suggestions and important comments from my co-advisor, Assist. Prof. Dr. Siwaporn Smith. My appreciation is also expressed to Mr. Sit Boonchuchauy for his assistant in using the X-ray diffractometer.

I would like to thank Mrs. Tassimon Kongyoo, Staff of Forensic Chemistry, Central Institute of Forensic science Thailand for supplying the paint samples in this study and Miss Onedee Suprathuk, Technical Manager, at Nippon Paint Company for giving some paint samples and providing the paint information.

My deepest gratitude is expressed to all teachers in the Forensic Science Graduate Program for valuable knowledge.

Finally, I am grateful to my family for financial support, care, and endless love. Moreover, my special thanks are to all friends for their friendship, cheerfulness and precious time.

Opas Thongnoi

DEVELOPMENT OF A METHOD TO CREATE AN AUTOMOTIVE PAINT DATABASE

OPAS THONGNOI 5136977 SCFS/M

M.Sc. (FORENSIC SCIENCE)

THESIS ADVISORY COMMITTEE: NOPADOL CHAIKUM, Ph.D., SIWAPORN MEEJOO SMITH, Ph.D.

ABSTRACT

An automotive paint database for forensic science is mostly useful for case investigations especially in hit-and-run accidents and case linkage. In this study a model paint database was created from powder X-ray diffraction patterns using the MATCH! phase identification program.

Each experimental X-ray diffraction pattern was converted to peak data in the form of a line diffractogram. The resulting line diffractograms were then accumulated to form a database, which could be used to identify paint chips or particles. The program identifies the unknown by comparing peak positions (2θ) and relative intensities (I/I_0) with reference to diffractograms in the database.

KEY WORDS: FORENSIC SCIENCE / AUTOMOTIVE PAINTS / POWDER X-RAY DIFFRACTION / PHASE IDENTIFICATION SOFTWARE

57 pages

การพัฒนาวิธีการที่ใช้ในการสร้างฐานข้อมูลของสีรถยนต์

DEVELOPMENT OF A METHOD TO CREATE AN AUTOMOTIVE PAINT DATABASE

โอภาศ ทองน้อย 5136977 SCFS/M

วท.ม. (นิติวิทยาศาสตร์)

คณะกรรมการที่ปรึกษาวิทยานิพนธ์: นภดล ไชยคำ, Ph.D., ศิวพร มีจู สมิธ, Php.D.

บทคัดย่อ

ในการสืบสวนในทางนิติวิทยาศาสตร์ ฐานข้อมูลของสีรถยนต์มีความสำคัญอย่างยิ่ง โดยเฉพาะในกรณีการเกิดอุบัติเหตุที่มีการชนแล้วหลบหนี หรือการใช้ข้อมูลที่ได้จากสียี่ห้อเดียวกันในการเชื่อมโยงเหตุการณ์เข้าด้วยกัน

ในการวิจัยครั้งนี้ มีการสร้างแบบจำลองฐานข้อมูลของสีรถยนต์โดยใช้โปรแกรม MATCH! ในการสร้างฐานข้อมูลจากกราฟที่ได้จากเทคนิคการเลี้ยวเบนรังสีเอ็กซ์ ซึ่งในสีตัวอย่างแต่ละชนิด กราฟที่ได้จะนำมาเปลี่ยนเป็นกราฟเส้น ผลลัพธ์ที่ได้นี้ถูกนำมาใส่รวบรวมในฐานข้อมูล และสามารถนำไปใช้เปรียบเทียบเศษสีในปริมาณจำกัดได้ ทั้งนี้โปรแกรมยังสามารถวิเคราะห์เปรียบเทียบตัวอย่างสีกับฐานข้อมูล โดยดูตำแหน่ง Peak และความสัมพันธ์ของความสูงของแต่ละตำแหน่งของ Peak (I/I_0) โดยค่า I_0 คือความสูงของ Peak ที่สูงที่สุดในกราฟ ส่วนค่า I คือ ความสูงของ Peak ที่เหลือ ซึ่งจะคิดเป็นอัตราส่วนเทียบกับยอดสัญญาณที่สูงที่สุด

57 หน้า

CONTENTS

CONTENTS (cont.)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (cont.)

LIST OF FIGURES (cont.)

LIST OF ABBREVIATIONS

Abbreviation	**Term**
FOM	Figure of Merit
FWHM	Full Width at Half Maximum

CHAPTER I
INTRODUCTION

Basically the roles of paint coating are decoration and essential protection. Paint applications are generally house decorative, automotive, and industries. Paint components generally comprise 4 parts. First film-formers hold all ingredients in the paint system. Secondly, pigments provide varied color to decorate and protect both the inner paint layer and the substrate surface. If pigments do not provide colors, they are used as extenders which are necessary for physical property improvement such as adhesion, ease of sanding and film strength. Thirdly, liquids are mostly used as solvent for polymer dissolving and to adjust the consistency. Additives are the last base ingredient for improving chemical and physical properties, for example, flow ability and compatibility (Turner, 1967).

Automobile surfaces need both beauty and corrosive protection. In a car coating, paints are commonly applied in three layers. The inner most layer, the primer, is essential to give good adhesion, anticorrosion and smoothness. At the same time, it provides full hiding of the substrate before the topcoat layer is applied. The next outer layer is the topcoat which gives a desired appearance. The outer most layer is the clear coat which gives a glossy appearance (Zeno *et al.*, 1994; Caddy, 2001).

In road accidents, such as a hit-and- run, the offenders sometimes leave the victims irresponsibly at the scene. Nevertheless, paint evidence from the offenders' cars probably remains on the damaged car, the victim's clothes, or sometimes even on the wounds on the victims' bodies. Hence, the duty of the forensic scientist is to examine and identify paint trace evidence for case investigation (Buzzini *et al.*, 2004).

Paint flake examination using the topcoat layer is significant in terms of giving a better view on the color of the suspect's car (Gelder *et al.*, 2005). The result is used as preliminary information for linking other evidences. In daily work, an early step of paint identification is to compare a control paint and the collected paint visually and by using low power visible light microscopy. If they match in color, chemical compositions will be examined further.

Powder X-ray diffraction is a widely used technique in paint integrative examination because it could reveal crystalline materials in paint composition such as pigments and extenders.

Generally, X-ray diffraction is used with dry paint flakes as it could differentiate paint evidence when visual comparison cannot. Mostly X-ray diffraction is a tool for identifying crystalline pigments in paint films (Rendle 2003; Lomax, 2010). In identifying powders, X-ray diffraction is used in the characterization and standardization of crystalline pigments in paint industry. The peak positions (2θ) and relative intensities (I/I_0) of each pigment are each material's characteristics and are therefore collected for making an in-house library (Debnath *et al.*, 2006). Creating a paint database from known sources is necessary for forensic analysis since it could provide useful preliminary information such as the manufacturer, and sellers of paints (Buzzini 2004). When working with the database, a management software is necessary for handling a large amount of data and the software must provide searching and matching of the unknown samples. The analytical result can then be presented in terms of simple statistic matching (Rendle 2003, 2004).

CHAPTER II
OBJECTIVE

In this study the main purpose is to develop a method to create an automotive paint database of 149 samples from Nippon Paint Company. In order to examine paint samples, powder X-ray diffraction technique is employed. All diffractograms were collected as phase pattern to create an automotive paint database using the MATCH! phase identification program.

CHAPTER III
BACKGROUND AND LITERATURE REVIEW

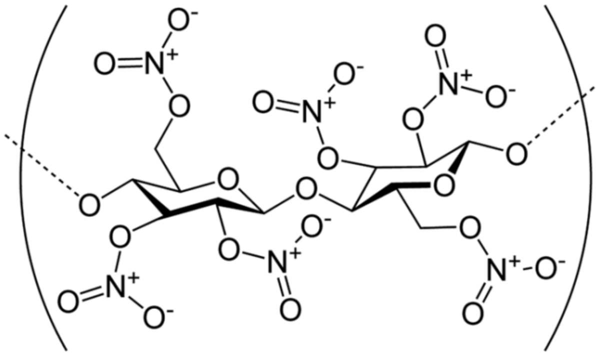
3.1 Paint Principle

The roles of paint coating basically are decoration and essential protection. For the reason, typically, objects are first attractive by their surfaces exterior. Moreover, on each day their surfaces often encounter harsh situation such as accident, scratching by other objects, and acid rain in polluted weather. After that repairing processes are required to renovate their surfaces by paint coating again. Paint applications are generally for house decorative and automotive industries.

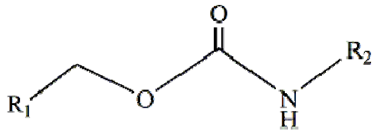
3.1.1 Paint Composition

Paints have been developed continuously for supporting the whole requirement of paint coating. Even though paints have been used for many years, the principal paint ingredients still comprise film-formers, pigments, solvents and additives.

3.1.1.1 Film-formers, sometimes called binders or polymers, hold all ingredients in the paint system either in a container or until a thick film is formed. In a container, they are wet chemical ingredients initially. When applying paint on their object surfaces, the liquid part will evaporate when the paint is used. Subsequently the binders would form a hard thin film. Examples of this kind of binder are nitrocellulose resin and acrylic resin. Nevertheless some binders are forming film through chemical reactions such as alkyd resin in auto oxidative system, and polyurethane in a cross link reaction. A requirement for choosing polymers often is on the basis of their properties, in particular hydrolysis, UV resistance, hardness, adhesion, etc. Examples of film-formers are shown in Figure 3-1.



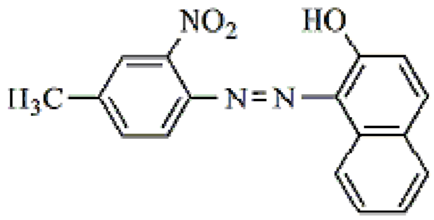
Nitrocellulose



Polyurethane

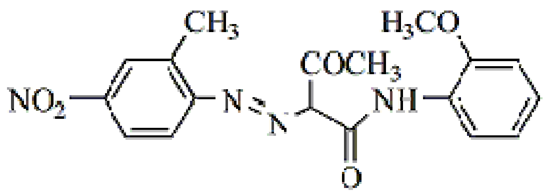
Figure 3-1: Examples of polymers generally employed in paint materials. Adapted from http://en.wikipedia.org/wiki/Nitrocellulose.png and http://en.wikipedia.org/wiki/Polyurethane.gif.

3.1.1.2 Pigments are solid particles suspended in paint solutions. Pigments provide varied color to decorate and protect both the inner paint layer and the substrate surface. Some pigment families are often used as general standard pigments such as phthalocyanine, quinacridone, dioxazine and iron oxide. Examples of pigments are shown in Figure. 3-2. Additionally, in metallic based systems, aluminum flake pigments and mica which are plate-like are mainly essential to give bright appearance during light reflective at their surfaces. If pigments do not provide colors, they are used as extenders which are necessary for physical property improvement such as adhesion, ease of sanding and film strength. Examples of extenders are calcium carbonate and barium sulfate.



Toluidine red

PR 3



A monoarylide yellow

PY 74

Phthalocyanine blue

PB 15

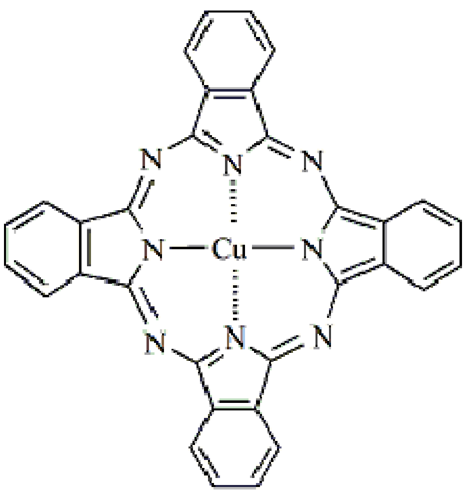
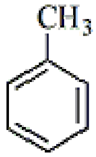


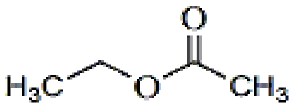
Figure 3-2: Basic pigments commonly found in paints.

3.1.1.3 Liquids are mostly used as solvent for polymer dissolving and to adjust the consistency of paint products. Generally liquid compositions are water, aliphatic hydrocarbon and aromatic hydrocarbon, terpenes, alcohols, ester, ketones, esters, ethers, nitroparaffins and chloroparaffins. Common solvents used in paint system are shown in Figure 3-3.

Toluene



Ethyl acetate



Diethyl ether

Figure 3-3: General solvents used in paint system.

3.1.1.4 Additives are the last small amount base ingredient for improving chemical and physical properties, for example, flow ability, gloss and compatibility.

3.2 Automobile Paints

Automobile surfaces need both beauty and corrosive protection of metal framework and other accessories. Therefore, paint coatings mainly serve all requirements in order to make automobiles more attractive. In a car coating, paints are commonly applied in three layers (Table 3-1).

Table 3-1: Paint layers in automotive system (Caddy, 2001).

<table>
<tr><th colspan="2">Solid color</th><th colspan="2">Metallic</th></tr>
<tr><td>Topcoat</td><td>40 µm</td><td>Clearcoat</td><td>40 µm</td></tr>
<tr><td></td><td></td><td>Metallic base coat</td><td>15 µm</td></tr>
<tr><td colspan="4">Primer surfacer 35 µm</td></tr>
<tr><td colspan="4">Cathodic electrocoat primer 20 µm</td></tr>
<tr><td colspan="4">Pretreatment 2 µm</td></tr>
<tr><td colspan="4">Substrate steel</td></tr>
</table>

3.2.1 Primer

Before going through the process of primer coating, the car body requires to be cleaned to remove all dirt, particularly oils, by using solvents and detergents since they are left from a steel processing. Next, pretreatment, phosphate coating, is done to provide smoother surfaces, followed by cathodic electrocoat primer which gives adhesion as well as protects from corrosion by resisting water replacement into the substrate surfaces. Nevertheless, this is not achieving the smoothness requirement therefore primer surfacer is essential for improvement. At the same time, it presents a full hiding of the surface before an outer layer is applied.

3.2.2 Topcoat

The topcoat or base coat is the next outer layer above the primer layer. It is formulated to give a colorful appearance. It is expected to maintain its appearance for long periods. For this reason, this layer comprises various color pigments and also resists some severe conditions such as photo-oxidation, sunlight, scratching, impact from rock fragment, etc. The top coat system is classified into two systems; the single top coat system, and the base coat/ clear coat system.

3.2.2.1 The solid top coat single system requires a thickness of about 40 μm for glossy appearance and full hiding of the primer layer.

3.2.2.2 The base coat/ clear coat system is a metallic paint as it essentially contains aluminum flake pigment or sometimes mica mineral. Its base coat requires a dry film of thickness about 15 μm. This system is more attractive than the previous ones since its color can change at different viewing angle. For example, at right angle the color is light but at a paralleleangle, a dark color will be seen.

3.2.3 Clear coat

Subsequently the outer most layer, a clear coat, is applied on the metallic basecoat with a thickness of about 40 μm. As a clear coat is mixed with a transparent polymer, it gives a glossy appearance.

3.3 X-Ray Diffraction

3.3.1 Crystal System

Crystals basically consist of the repetitive ordered atom groups so crystal forms are produced in versatile structures. Nevertheless if the chemical compounds contain a disorder group, they are called amorphous (Figure 3-4). In crystallography, the small repetitive unit of crystal structure is a unit cell which is identified by lattice points in three dimensions. The lengths of a unit cell edges and their angles in each axis are called lattice parameters.

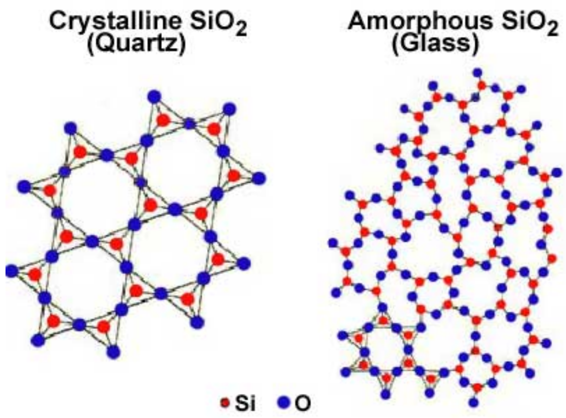


Figure 3-4: Crystalline and amorphous forms of SiO_2 adapted from http://steelguru.com/article/details/MjU%3D/Solid_State_Structure.html.jpg

In Bravais system includes 14 lattices, nine of which are primitive unit cells and the rest are nonprimitive systems (Figure 3-5).

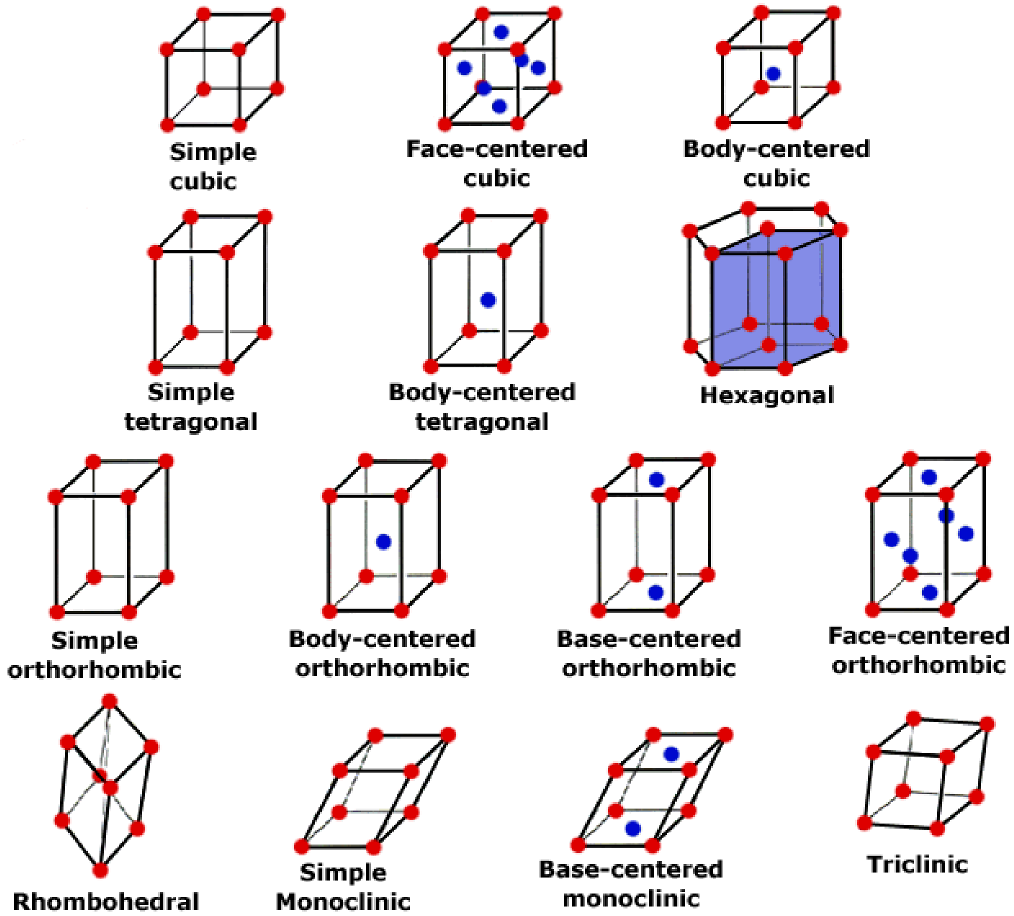


Figure 3-5: Bravais system includes 14 lattices

adapted from http://www4.nau.edu/meteorite/Meteorite/Book-GlossaryB.html.jpg

3.3.2 Miller Indices

In a lattice system, the unit cell edge is naturally cut by a set of planes which is identified by three numbers corresponding to each axis. The interception point at the edge of the unit cell is divided into fractional parts. In a unit cell (Figure 3-6), if a plane cuts the unit cell edge at half of each axis, then their intercepting point is (1/2, 1/2, 1/2). Accordingly the indices are the reciprocal of this number (2, 2, 2). In some cases, if the plane does not cut any unit cell edge or parallel to one or more axes, its means that the intercepting point is infinity. For this reason, the corresponding index is 0. Theoretically, Miller indices is used to assign a set of planes, a particular member of set, or the face of macroscopic crystals parallel to the set as an example of Miller indices of the plane (222) (Figure 3-6).

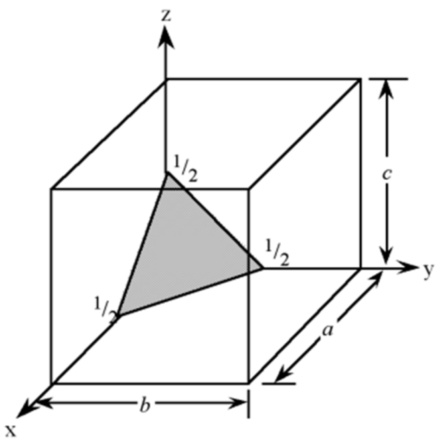


Figure 3-6: Plane (222) in a unit cell adapted from http://cnx.org/content/m16927/latest/graphics11.png

3.3.3 Powder X-Ray Diffraction

Powder X-ray diffraction is a widely used technique in paint integrative examination because it could reveal crystalline materials in paint composition such as pigments and extenders. Since early 1912, X-ray diffraction in crystalline chemical substances was discovered by W.L. Bragg who studied the engagement experiment. Subsequently the diffraction was explained in the form of reflection of the X-ray beam from the planes of the crystal and described by Bragg's equation as below.

$$n\lambda = 2d\sin\theta,$$

n is an integer,

λ is the wavelength of the X-rays,

d is the distance between adjacent parallel planes,

θ is the diffraction angle

X-ray diffraction is based on elastic scattering in crystalline materials. The reflection in two planes is explained in terms of two parallel incident X-rays reflecting from the two parallel planes (Figure 3-7), and during the reflection, the X-rays make an angle (θ) with each plane. At the reflecting area, electrons are forced to vibrate by the oscillating field of the incident beam and radiate in all directions. For that particular direction where the parallel reflected X-ray beam emerge at an angle θ, a diffracted beam of maximum intensity will result if the waves represented by these ray are in phase. (Stout *et al.*, 1989)

$$n\lambda = 2d\sin\theta$$

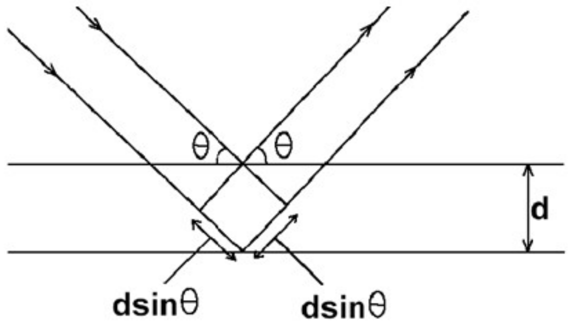


Figure 3-7 Reflection of X-rays from parallel planes
adapted from http://www4.nau.edu/meteorite/Meteorite/BookGlossaryB.html.jpg

Once reflection occurs (Figure 3-7), the fixed incident rays from the X-ray source move through to the fixed material on the flat sample holder and make an reflected angle θ at the planes. The reflected beam is then captured by a detector and the result is read out in the form of a diffractogram. Interpretation of the diffractogram can provide information on the structure of materials.

3.4 Literature Review

Paint identification is important to the forensic scientist when decorated objects for example automobiles are involved. Many methods have been used to examine these evidence continuously.

Infrared spectroscopy is often used for polymer examination in the coating material but other methods, such as Raman spectroscopy is used in pigment identification as a complementary technique.

In 2006, Buzzini *et al.* applied Raman spectroscopy and Fourier Transform Infrared spectroscopy to examine unknown samples in 6 case studies including automotive, household and spray paints. In the case of a road accident, the combination of the two techniques can clarify the point of collision. In the experimentation, they evaluated the paint smears from each car in an *in situ* analysis.

However, the Raman spectroscopic technique was difficult because of the fluorescence of red paint samples obtained from the suspect and the damaged vehicle. For this reason, they used the technique of photo bleaching by leaving the samples irradiated for several hours and subsequently analyzed them by reducing the laser power to 1% to avoid the burning of sample. Although the Raman spectroscopic technique was efficient in this case, longer time was needed than in the conventional method (Buzzini *et al.*, 2006).

In 2004 in Lausanne, a gang of young people vandalized churches and public places using green spray paints. The police requested a laboratory team to examine the paint evidence for obtaining information on the origin of the paint. In this investigation, 40 green spray samples from shops in the Lausanne region were examined by an infrared method to differentiate the polymer groups. Separation of the pigments was done by Raman spectroscopic technique with two laser sources to avoid the fluorescence problem. Another method, visible microspectrophotometry was also used. In this examination, the paint samples were categorized by the difference in intensity. Once again, with the Raman technique, the fluorescence problem still occurred with some green spray paints (Buzzini *et al*., 2004).

Paint examination also employs powder X-ray diffraction because it could reveal details of crystalline pigments and partially crystalline polymer. Recently, the International Centre for Diffraction Data (ICDD) (ICDD, 2010) created the Powder Diffraction File (PDF) which included paint pigment patterns. This PDF file could be suitable for identification of any pigments which are probably involved in forensic science.

In 2006, Debnath *et al.* showed application of X-ray powder diffraction technique for the characterization and standardization of crystalline pigments from various sources. Pigments and extenders which were generally used in paint industry were identified and categorized by *d*-spacing and relative intensity (I/I_0) (Debnath *et al*., 2006). This diffraction technique also could classify the polymorph of synthetic pigments which were commonly found in paints (Lomax, 2010).

In 2003, F. Rendle showed the performance of the X-ray diffraction by comparing the two similar paints with XRD reference patterns, and then the results could distinguish each paint samples based on pigment compositions that gave the color individually. For example, for the similar blue paints, ICI Royal Blue and ICI Admiralty Blue, the first contained Prussian blue while the other contained β-copper phthalocyanine. XRD also provides screening for polymers used as binders in paints. After that other technique such as Pyrolysis Mass Chromatography Pyrolysis Gas Chromatography are required. The order of analysis is also important, in case destructive methods are needed. In paint analysis, for example in a road accident, paints from the scene and that from a suspect car are compared by the naked eye and visible light microscopy. If they match in color, chemical compositions can be analyzed by XRD or FTIR. Moreover, the analytical results of known sources have been added to the database of paint categories such as vehicle as small diffractogram databases. (Rendle 2003, and 2004).

CHAPTER IV
MATERIAL AND METHOD

4.1 Instrumentation

Powder X-ray diffraction analysis was performed on a Bruker AXS D8 X-Ray diffractometer employing $CuK\alpha_1$ (λ = 1.54056 Å) radiation and wide angle Position Sensitive Detector. In this experiment, small amounts of samples were used. Furthermore zero background plate silicon wafer was used as sample holder.

4.2 Paint Samples

149 Automotive topcoat paint samples were supplied by Nippon Paint Company. These were: 9 black samples, 36 blue samples, 12 gold samples, 13 grey samples, 29 green samples, 2 orange samples, 1 pink sample, 18 red samples, 17 sliver samples, 9 white samples, and 3 yellow samples. Each paint had been sprayed on a metal sheet and was then scraped from the sheet for powder X-ray examination.

4.3 Database Software

The MATCH! phase identification software version 10.1a is an easy-to-use database software for phase identification. It is useful for handling large powder X-ray diffraction data. This program provides an essential unknown sample matching mode by comparing the diffractogram of an unknown sample to the reference patterns in the database. To serve the aim of this study, the MATCH! program was employed for transforming the diffractogram of each automotive paint into a peak profile characteristic of the sample. The results were then built up to form a database which could be used to identify paint chips or particles. The program identifies the unknown paint sample by comparing peak positions (2θ) and relative intensities (I/I_0) with those of the reference diffractograms in the database and giving matching result in terms of Figures of Merit (FoM) (Crystal Impact, 2010).

4.4 Method

Initially, each paint sample from the metal sheet was scraped to obtain paint flakes and laid on a zero background silicon wafer. Additionally a few drops of water were added to the sample to form a slurry to increase attachment between the sample and the holder surface. Once the water evaporated, a paint film was formed on this silicon plate (David *et al.*, 2002). Subsequently the sample was examined on a powder X-ray diffractometer. Figure 4-1 shows the flow diagram of the study.

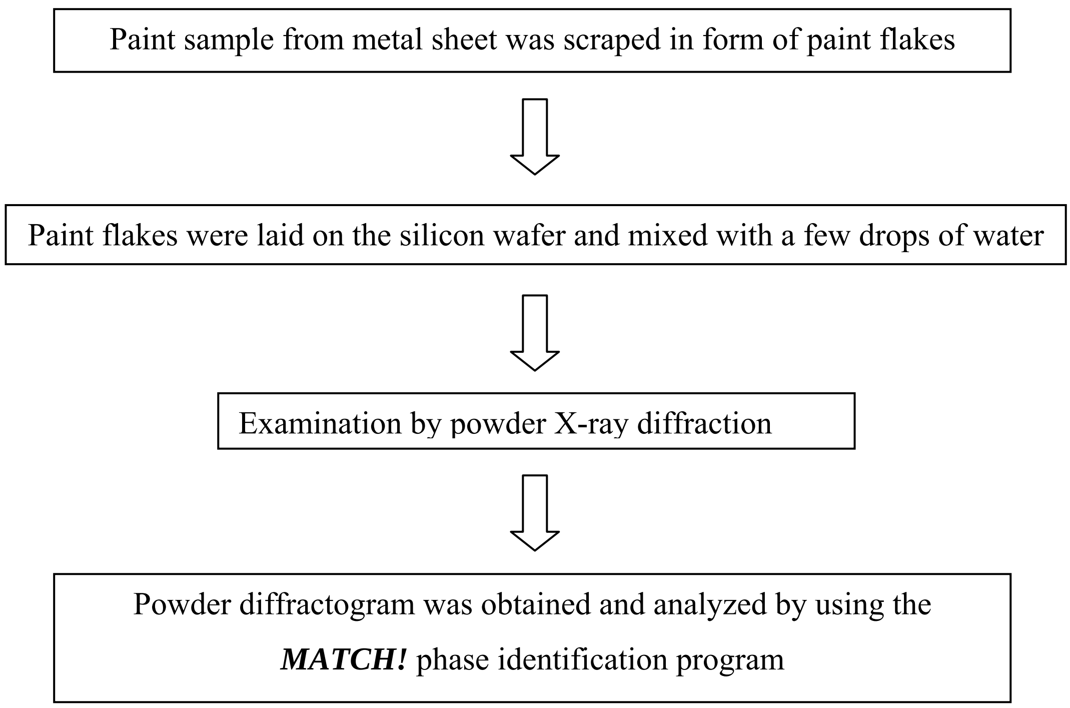


Figure 4-1: Diagram of X-ray diffraction study

4.5 Database Creation

Each diffraction pattern was recorded as a raw data file, with an extension *raw. To create an automotive paint database, each diffractogram was imported to the MATCH! phase identification software (Figure 4-2) by selecting the "File" menu on the toolbar, choosing the "Import" command, and clicking on the "Diffraction data". This procedure is followed by clicking on the desired diffractogram to activate and clicking on "Open" button to upload the diffraction pattern into the program.

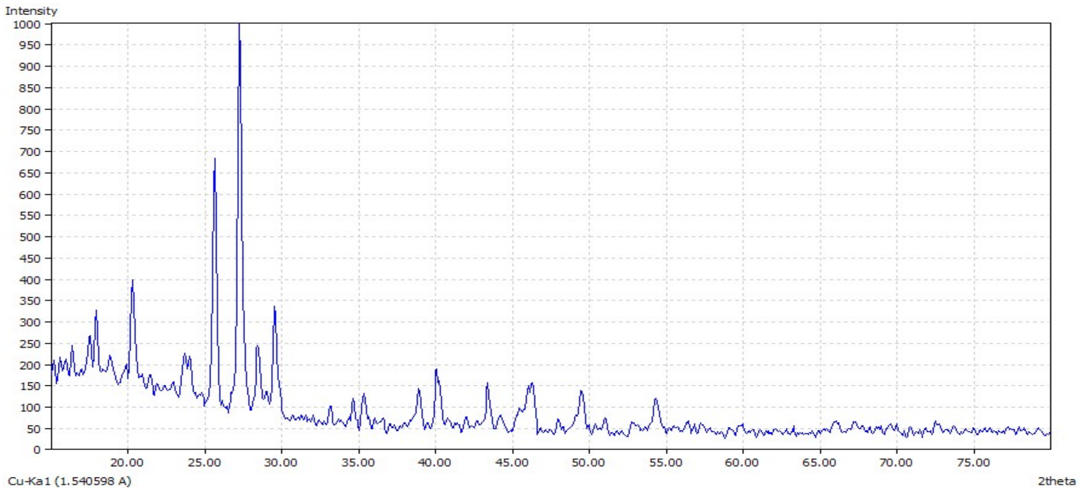


Figure 4-2: An example of diffractogram of an automotive paint sample

The next step is selecting distinct peaks in diffractogram. Before doing the step of peak selection, setting the auto peak searching must be done first. Then going to the "pattern" command at the tool bar and choosing the automatic tab. Next, double click on the "configure" command, the "Automatic Raw Data Processing Options" would immediately appear (Figure 4-3). In this window, it is essential to select the background subtraction and set the peak searching in normal method with the Full Width at Half Maximum (FWHM) about 0.30 2θ. Especially, the normal peak searching mode was set to 65% and correct 2theta error was set as the zero point. These parameters were obtained by trial in the creating database process.

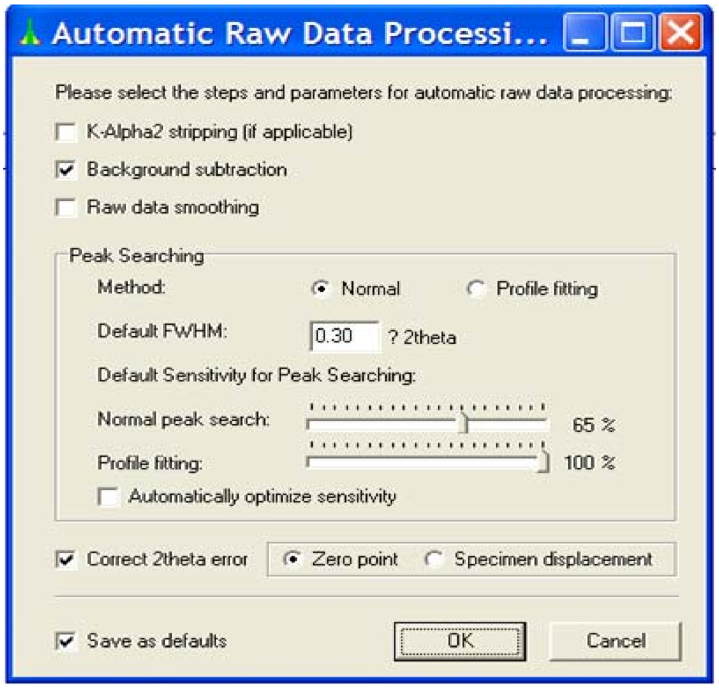


Figure 4-3: "Automatic Raw Data Processing Options" window

Selection of the distinct peaks in the diffraction pattern was done by clicking on the "Automatic Raw Data processing" button in the tool bar, each peak was chosen automatically to produce a fingerprint pattern (Figure 4-4).

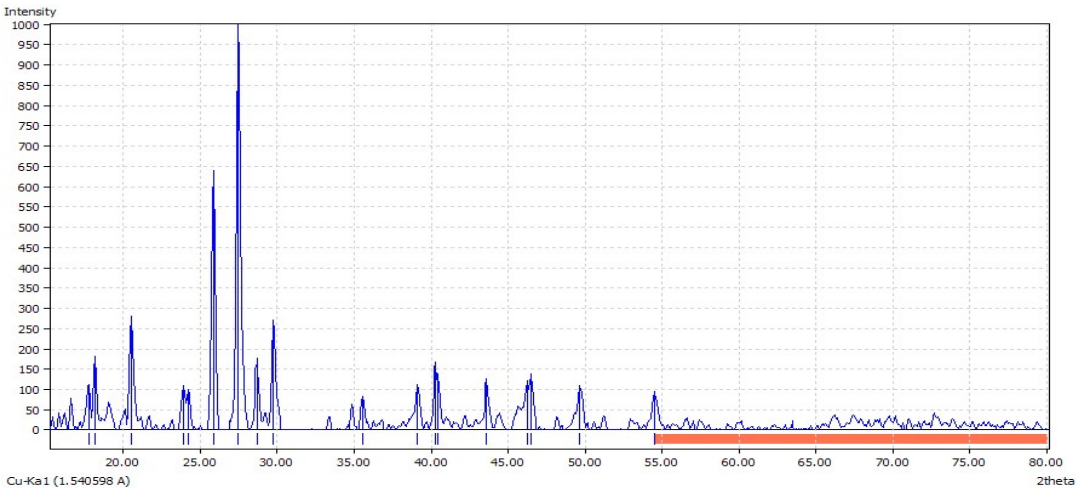


Figure 4-4: Each distinct peak was chosen automatically

This file is then saved by selecting “File” in the toolbar, choosing the command “Export”, clicking on “Peak data” and selecting the desired folder. The result of peak selection was transformed into a vertical line diffractogram being recorded as a diff data file (*.dif) (Figure 4-5).

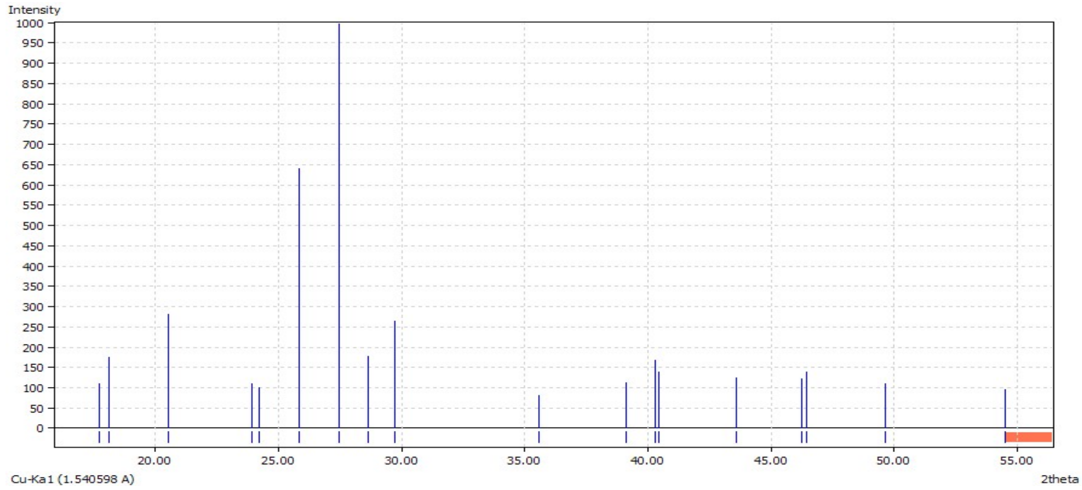


Figure 4-5: Peak data of paint sample in the form of a line diffractogram

When the transformation process of peak data was done, creation of the new user database was carried out as follows. Starting by clicking on the  button in the toolbar, the “User Database Manager” window was displayed (Figure 4-6). Clicking on the “Add” button at the top started a new entry inserting step.

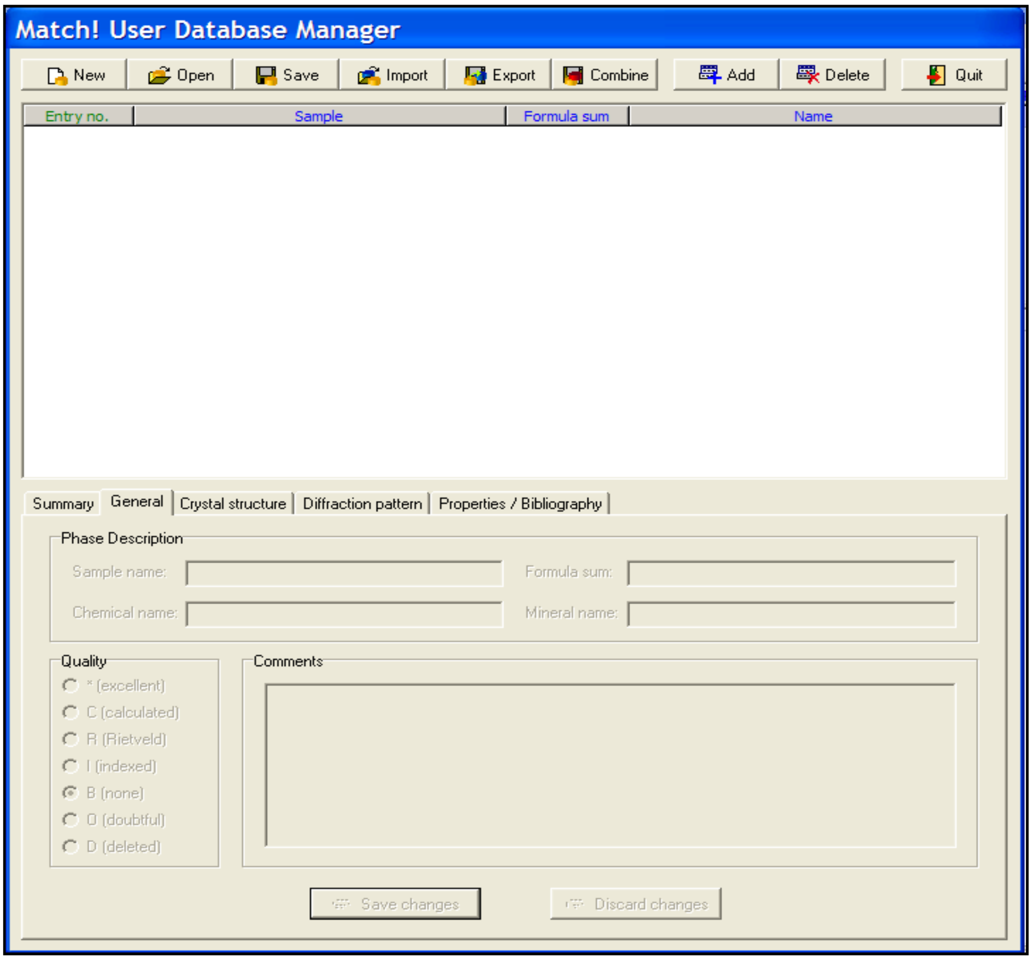


Figure 4-6: First window in User Database Manager as the “General” tab sheet

Immediately, the “General” tab sheet was opened. The necessary information of paint samples could be created in this window such as sample name. However, the diffraction data must be put into this window first, before filling in the pattern detail. Therefore, the next step was importing peak data (.*dif) of the paint samples by clicking on the “Diffraction pattern” tab sheet header and clicking on the “Import” button (Figure 4-7).

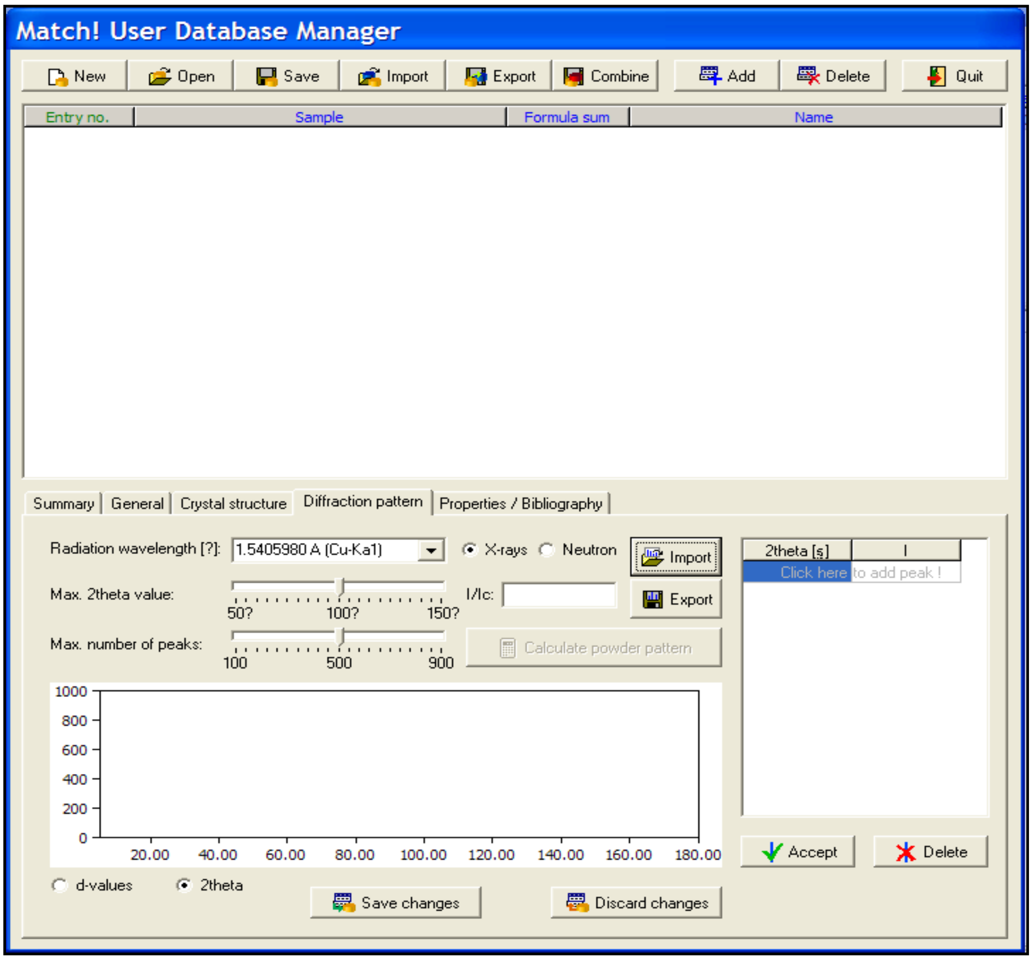


Figure 4-7: Diffractogram imported *via* the "Diffraction pattern" into this window.

A window would then open for selection of the diffraction data file (*.dif) in the folder. This was followed by pressing "Open" button. The desired diffraction would appear in this "Diffraction pattern" tab sheet while the peak list was also displayed in the table to the right (Figure 4-8). It was necessary to choose the Cu-$K_{\alpha1}$ (1.5406 Å) as radiation wavelength and to select 2θ at the bottom of the line diffractogram. Coming back to "General" tab sheet once more, the diffractogram details could now be filled in.

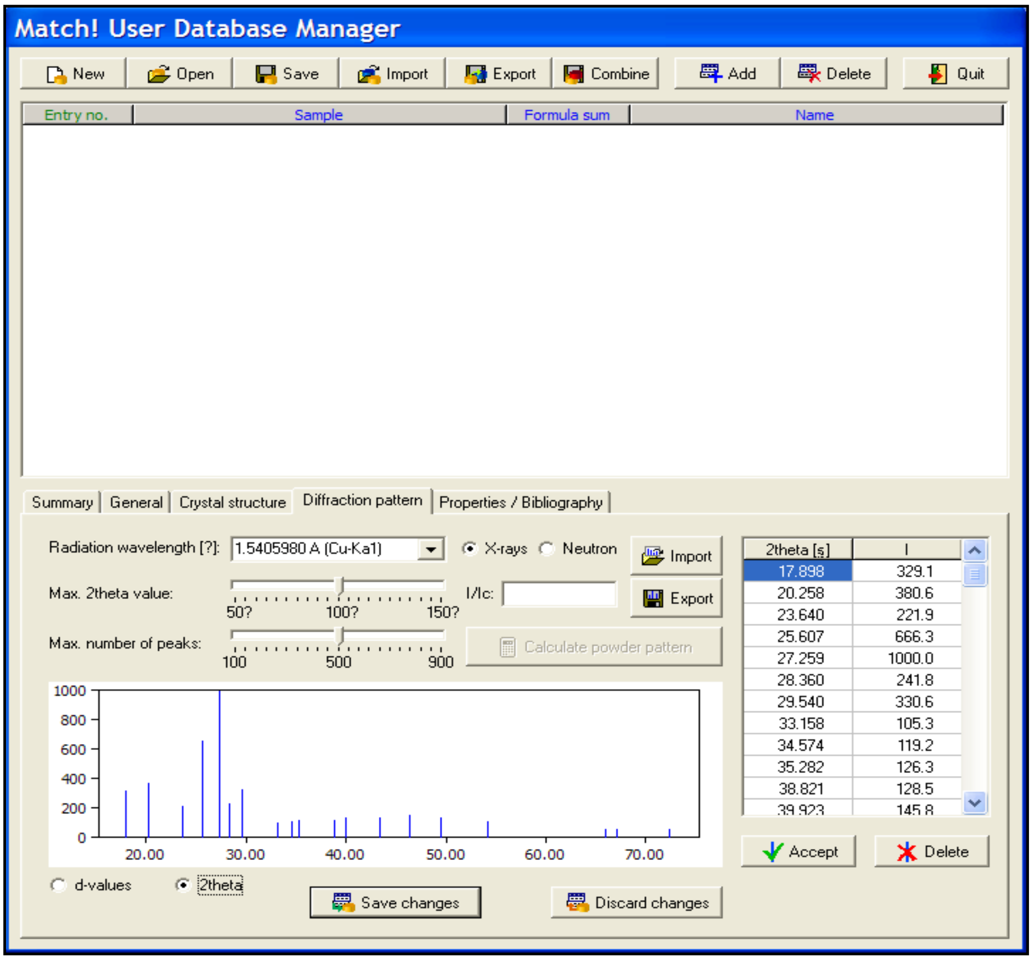


Figure 4-8: Diffractogram of imported reference pattern and a list of intensity for each peak position (2θ)

Finally, when the database creation was finished, it was kept in the user database format (*.mtu) by clicking on the “Save” button to save in the desired folder (Figure 4-9).

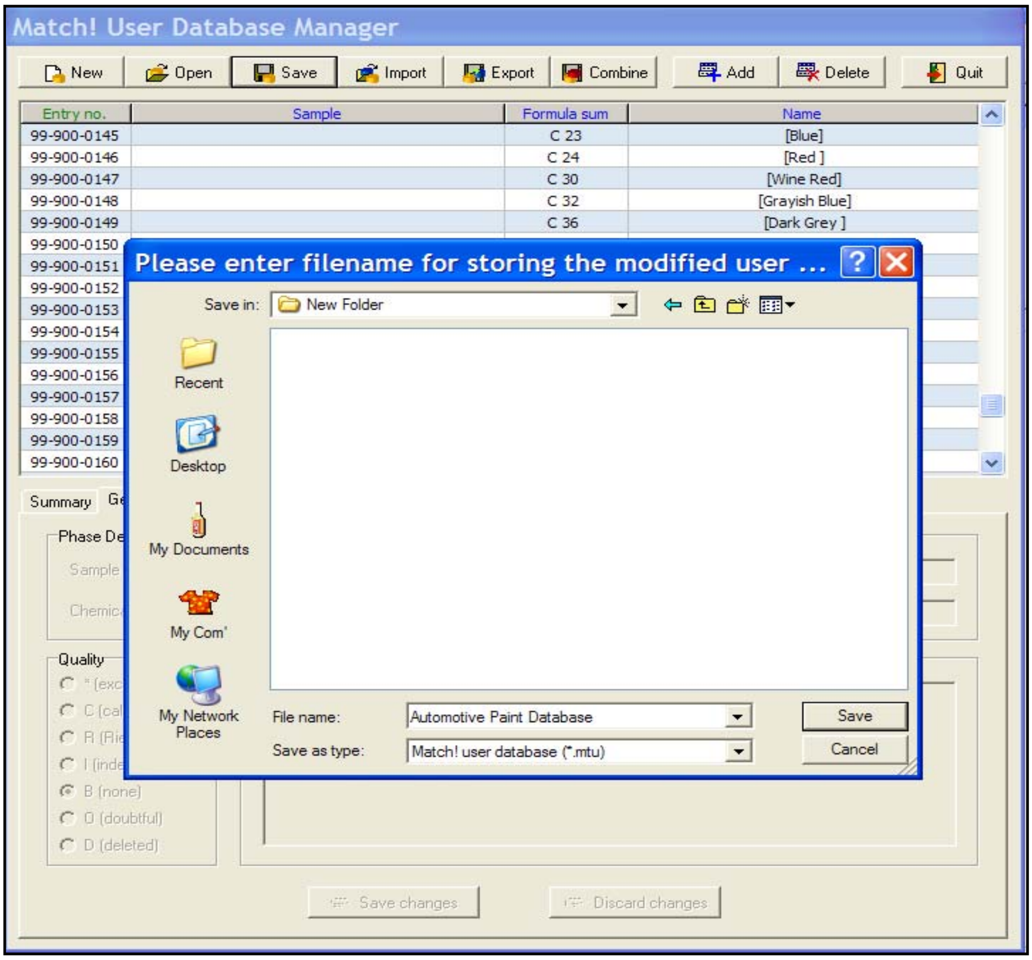


Figure 4-9: Paint sample diffractogram exported and kept in the database

Before using the MATCH! program, the first step was to activate this Automotive Paint database by clicking on the  button in the toolbar. Immediately the "Reference Database Library" dialog would be shown. Then clicking on the "Create" button would put the user database in the "Create Reference Database" window (Figure 4-10).

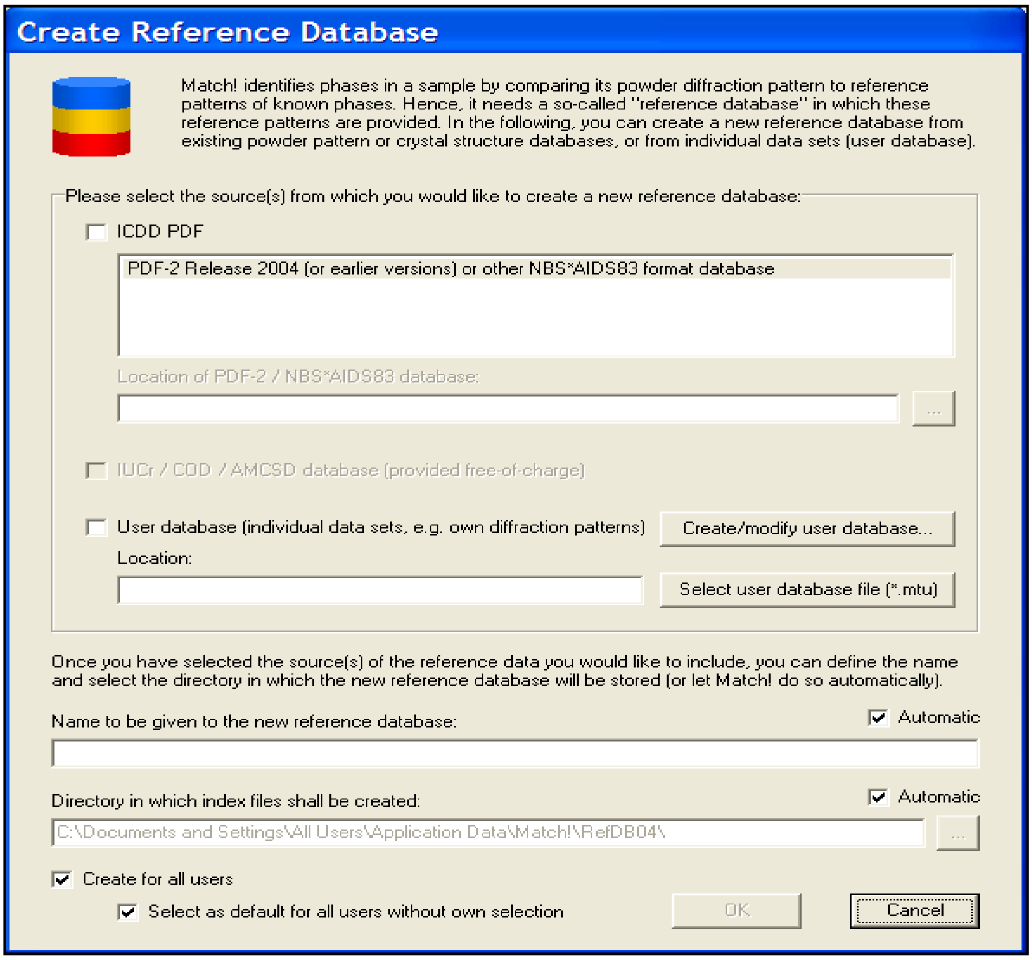


Figure 4-10: New user database selected *via*
"Create Reference Database" window

Then, clicking on the "Select user database file (*.mtu)" button and subsequently clicking on "Create" button would select the preferred Automotive Paint database. The next step was choosing a database file by clicking on the database file (*.mtu), clicking on the "Open" button and clicking on the "OK" button would exit this dialog. At this time, the model automotive paint database was active. Finally, when clicking on the "Quiz" button, the user Automotive Paint database would be ready for the identification of an unknown paint diffractogram matching.

For matching an unknown sample, the search and matching process was started by clicking on the  button on the tool bar. In this step, this program performed an unknown paint sample matching by comparing the diffractogram of the unknown sample to the reference patterns in the model database (Figure 4-11). Next, the MATCH! program expressed the result of matching in the form of a Figure of Merit (FoM) in the last column on the right side of the result list. The Figure of Merit (FoM) was calculated from the various measures of agreement between the database and the unknown pattern such as intensities of each peak position (2θ) and the relative intensities (I/I_0). If they were similar, FoM would be close to 1 while if they were different, FoM would be close to 0.

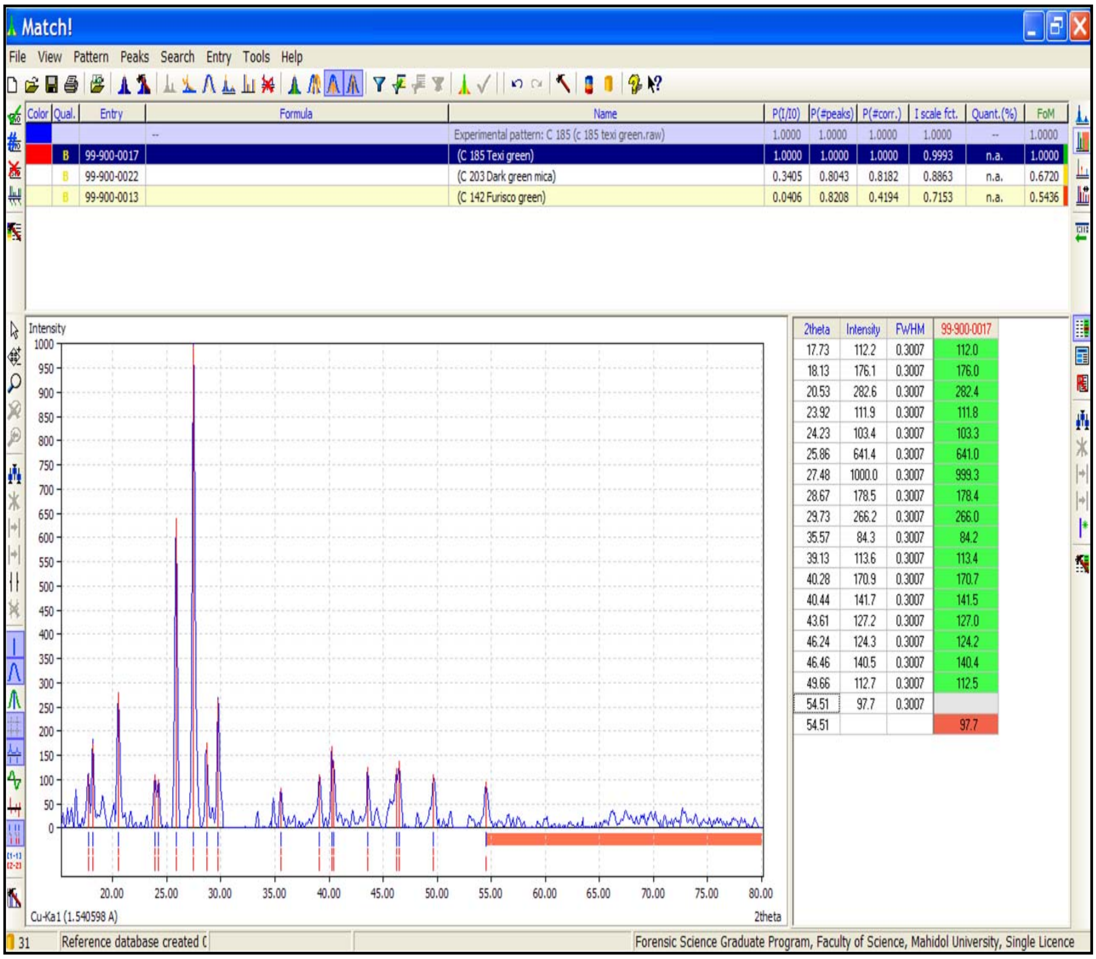


Figure 4-11: The comparison of unknown sample and the highest score FoM reference pattern

In this example of unknown paint sample matching, at the bottom of diffractogram, the upper vertical blue lines were from the diffractogram of the unknown paint sample while the lower vertical red lines were from the reference pattern in the database. The result also shows the list of intensity comparison from both the unknown sample and the chosen reference paint for each peak position. Moreover, visual comparison is still needed to narrow down the number of candidate groups in the FoM column. Finally, Phase identification was finished by pressing the “Ctrl+F” on the keyboard, clicking the corresponding toolbar button, or selecting the “Finished” command from the “File” menu.

CHAPTER V
RESULTS AND DISCUSSIONS

5.1 Automotive paint database

The creating an automotive paint in this model study employed the topcoat paint layer since this layer provides a car's color which can be used as a preliminary information to pursue the suspect's car especially in a case of hit-and run accident. For this reason, 149 samples of the automotive topcoat paint from Nippon Paint Company were examined by powder X-ray diffraction to obtain an XRD fingerprint of the paint samples (Table 5-1). The user automotive paint database was classified into sample group by their varied color.

Table 5-1: Automotive topcoat paints obtained for examination

Color	Paint name	Color	Paint name	Color	Paint name
Black	Black	Gold	Sahara Gold Mica Met.	Red	Brown Met.
	Black Met	(2)	Sand Gold		Canberry Red
	Dark Tur. Mica Met.		Satin Gold Met.		Flaming Red
	Ebony Black		Sebring Met.		Flash Red Met.
	Lamp Black		Sunlight Gold Met.		Foxfire Red Mica
	M-Steen		Wheat Beige Met.		Inza Red
	Sparkling Black Met.	Gray	Blue Gray Met.		Light Vermillion
	Starlight Black P		Brownish gray		Milno Red
	Steel Black Met.		Dark Grey		Monaco Red
Blue	Andaman Blue		Glory Gray		Nifty Red
	Aquerius Blue MC		Golden Gray Mica		Palmp Red
	Blue Mica Met.		Grayish Brown Met.		Rasbery Red
	Cyclone Blue Met.		Grey		Red
	Dark Blue		Hazy Gray Met.		Signal Red
	Dark Blue Met.		Light Quartz Gray Met.		Super Red
	Dark Blue Mica		Magma Gray P.		Taxi Red
	Dark Blue Pearl Met.		Meteor Gray Met.		Vivid Red
	Deep Velvet blue		Misty Gray Met.		Wine Red
	Dynastic Blue Met.		Smoke Gray	Silver	Bluish Silver
	F-series Blue	Green	Chamonix Green Met.		Bluish Silver Met.
	Grayish Blue		Cypress Green Mica		Crystal Silver Met.
	Horizon Blue		Dark Green Mica		Golden Silver Met.
	Ingenerate Blue		Dusk Green Mica		Grace Silver Met.
	Light Blue Met.		Furisco Green		Highight Silver
	Light Blue		Grayish Green Met.		Satin Silver Met.
	L-Blue Met.		Green		Seyfert Silver
	Malacca Blue Met.		Green-Met.		Silver
	Marien Blue		Green Met.		Silver Gray Met.
	Marine Blue Met.		Green Mica		Silver Met.
	Marine Blue Met. (A7)		Green M. Opal		Silver Vouge Met.
	Medium Blue Met		Hanover Green Met.		Sky Silver Met.
	Nares Blue Met.		Heater Green Mica Met.		Sun Beam Silver Met.
	Nautical Blue Met		Jungle Green Mica		Sun Beam Silver Met.
	Pastel Blue		Jungle Green Mica Met.		Titanium Silver
	PB-190 Terra Blue		Light Green		Vogue Silver Met.
	Purple		Light Green Met.	White	Clean White
	Purple Mica		Luna Green MC Met.		Clear White
	Rigid Blue		New Blue Green Mica		Cool White
	Sapphire Blue		Nid Green Mica Met.		Crystal White
	Sihouette Blue		Ocean Green Met.		Dover White
	Sonic Blue		PC Green		Frost White
	Taxi Blue		Tahition Green Met.		Shinny White
	Turquoise Mica		Taxi Green		Sophia White
	Twilight Blue MC		Thyme Green		White
	Twilight Blue Met.		Timber Green Pearl	Yellow	Permanent Yellow
Gold	Amethyst M.		Tropical Green Met.		Taxi yellow
	Fraser Beige		Spruce Green Met.		Yellow
	Fraksen Mica		Y.S. Green		
	Gold Met.	Orange	Orange yellow		
	Lynx Gold Met.		Racing Orange		
	Sahara Beige Met.	Pink	Pink		

These paint samples has been categorized into 11 color groups. According to the list, the largest group is the blue color and the smallest group is the pink color which has only one sample.

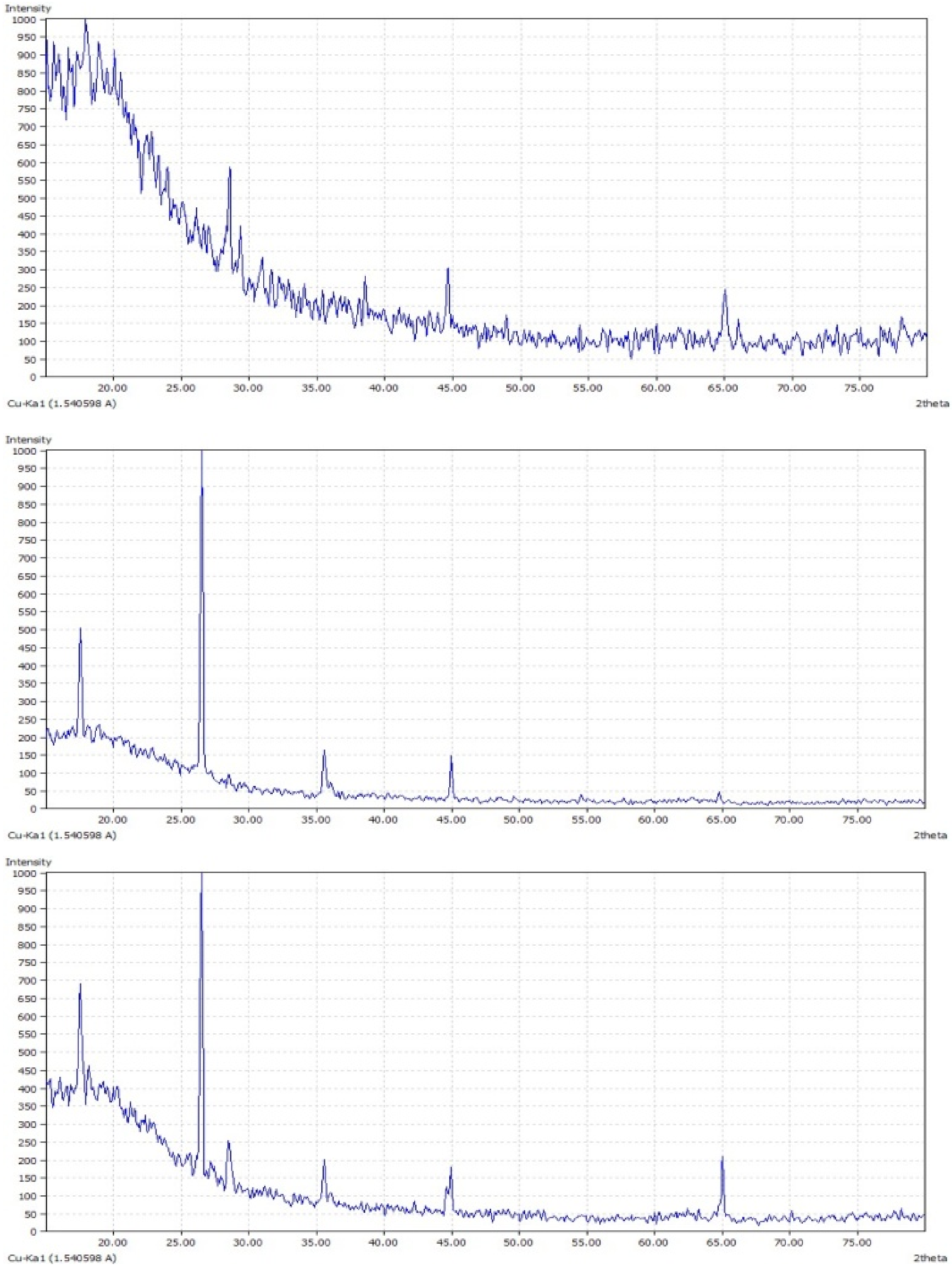


Figure 5-1: Some black paint group

The first group is the black color which exhibited 4-6 distinctive peaks especially the largest peak in the last two samples, located at peak position about 27°2θ and also, several small peaks at about 55°, and 65° 2θ (Figure 5-1). The diffractogram of M-steen expressed a lot of noise and their peaks were not as clear as in the last two samples. However it could be used for unknown paint identification.

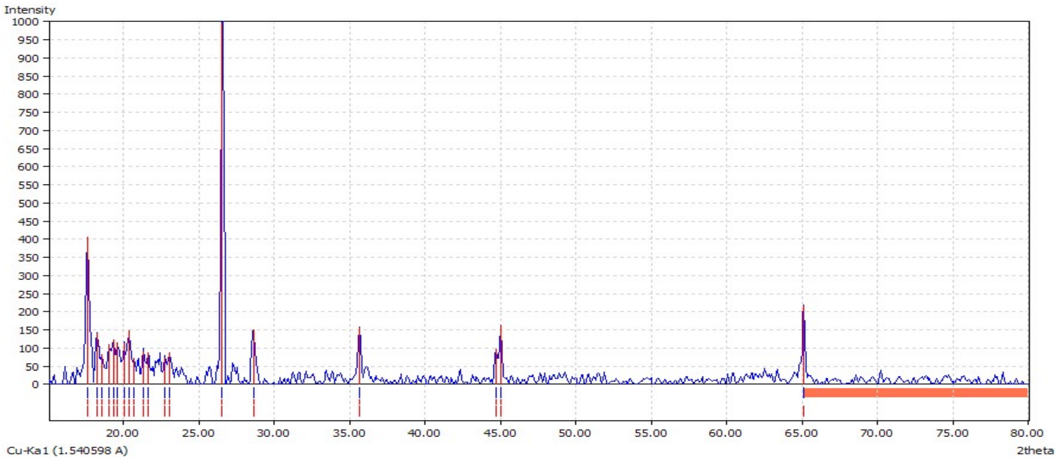


Figure 5-2: Steel Black Met. diffractogram matched to its reference in the model database

As an example, the diffractogram of the black color group (Figure 5-2) in this database was used as an unknown pattern to demonstrate matching between a sample's diffractogram and the references in the black paint database *via* auto searching and matching mode. As a result, when considering the comparison of the vertical blue lines of the sample diffractogram and the vertical red lines of the first candidate from the database at the bottom of the diffractogram, both are alike.

Color	Qual.	Entry	Formula	Name	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	Quant.(%)	FoM
			--	Experimental pattern: C 244 noC (c 244 steel black met pt noc.raw)	1.0000	1.0000	1.0000	1.0000	--	1.0000
	B	99-900-0002		(C 244 steel black met)	1.0000	1.0000	1.0000	0.9994	n.a.	1.0000
	B	99-900-0001		(C 198 Dark tur mica met)	0.8228	0.7344	1.0000	0.9999	n.a.	0.8872
	B	99-900-0000		(C 118 Star light black)	0.9312	0.8596	0.9192	0.9998	n.a.	0.8763
	B	99-900-0003		(C 277 M-steen)	0.0007	0.9566	0.5676	0.1448	n.a.	0.5677

Figure 5-3: Matching result of Steel Black Met. sample

The Figure of Merit (FoM) score of this Steel Black Met paint sample (Figure 5-3) was 1.0000 corresponding to the correct reference at the first entry of all candidates. In this step, one reference was picked up as unknown paint sample for assessment of the matching process of MATCH! phase identification program. As expected, the matching result is accurate while FoM score of the other representative sample, Star light black, was 0.8763 and M-steen was 0.5677 when comparing the similarity to this sample.

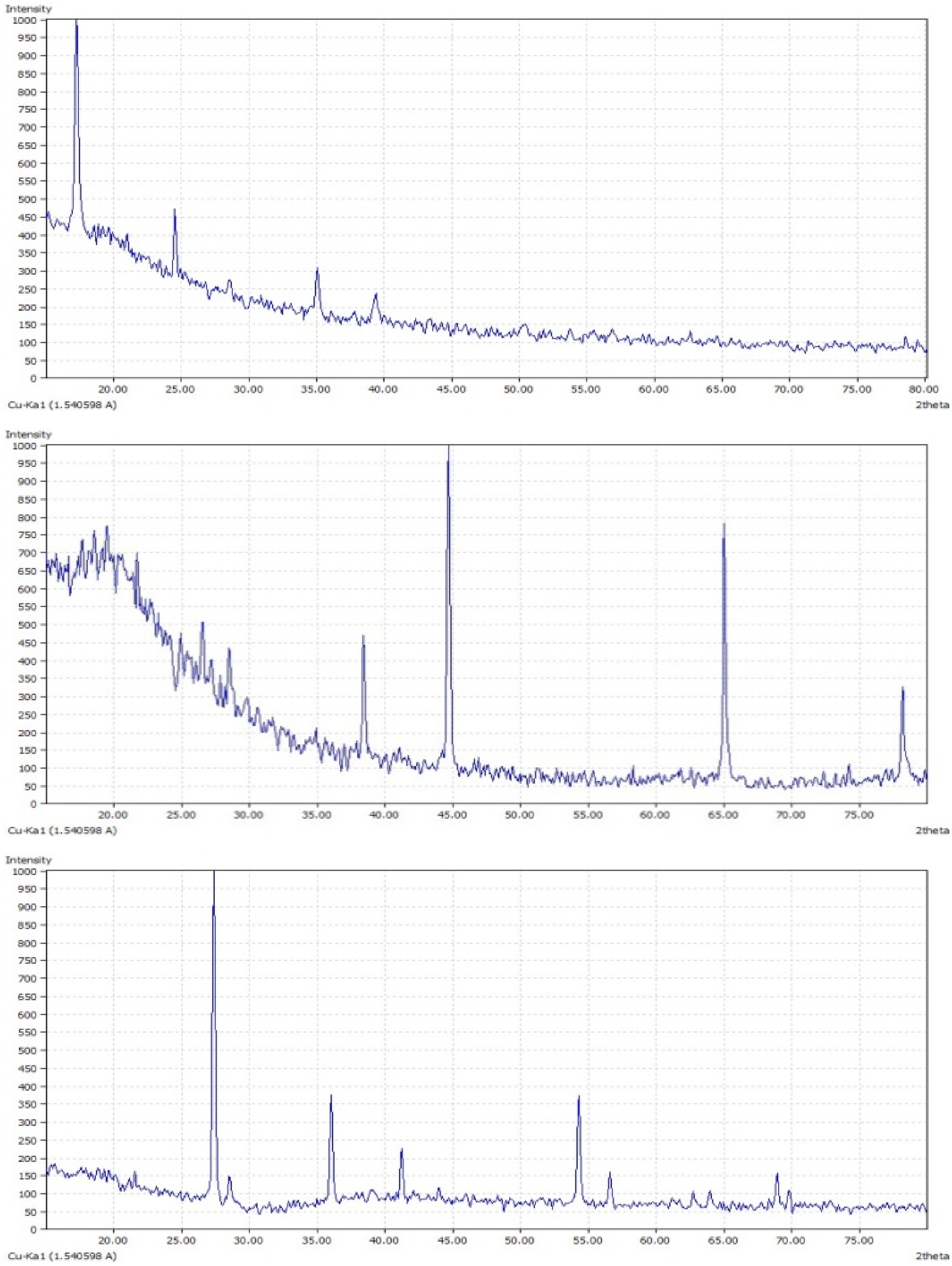


Figure 5-4: Some blue paint group

The diffractograms of the blue group (Figure 5-4) were of various forms as their major peaks were different from each other. The diffractogram of Dark Blue sample had 4 distinct peaks at about 18, 24, 35, and 39 ° 2θ while Light Blue Met.

sample had 4 distinct peaks at about 37, 45, 65 and 78 ° 2θ. The Taxi Blue diffractograms exhibited distinct peaks at about 27, 28, 36, 42, 54, 57 63, 64, 69 and 70 ° 2θ.

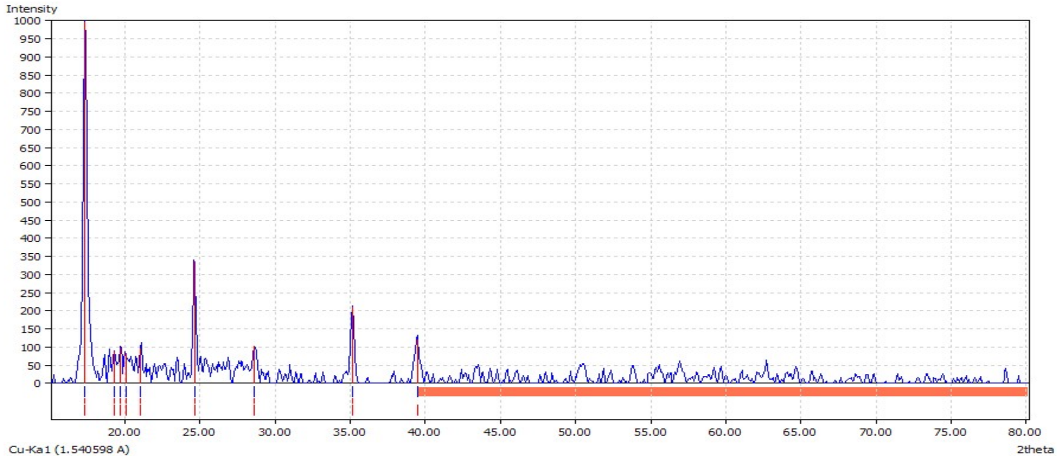


Figure 5-5: Dark Blue diffractogram matched to its reference in the model database

An example of auto matching (Figure 5-5) shows that both the vertical lines of the Dark blue sample and correct reference in the blue paint database correspond to each other.

Color	Qual.	Entry	Formula	Name	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	Quant.(%)	FoM
			--	Experimental pattern: C 11 (c 11 dark blue.raw)	1.0000	1.0000	1.0000	1.0000	--	1.0000
	B	99-900-0001		(C 11 Dark blue)	1.0000	1.0000	1.0000	0.9997	n.a.	1.0000
	B	99-900-0022		(C 210 Medium blue met)	0.8210	1.0000	0.9000	0.9314	n.a.	0.8820
	B	99-900-0007		(C 59 Malcca blue met)	0.0001	0.9518	0.5185	0.1765	n.a.	0.5501
	B	99-900-0028		(C 232 Sihouette blue)	0.0000	0.9518	0.4412	0.1761	n.a.	0.5287

Figure 5-6: Matching result of Dark Blue sample

In matching the result of the Dark Blue sample (Figure 5-6), the FoM score of the corresponding reference as first candidate is quite different from the other candidates because for the second candidate, the FoM is only 0.8820.

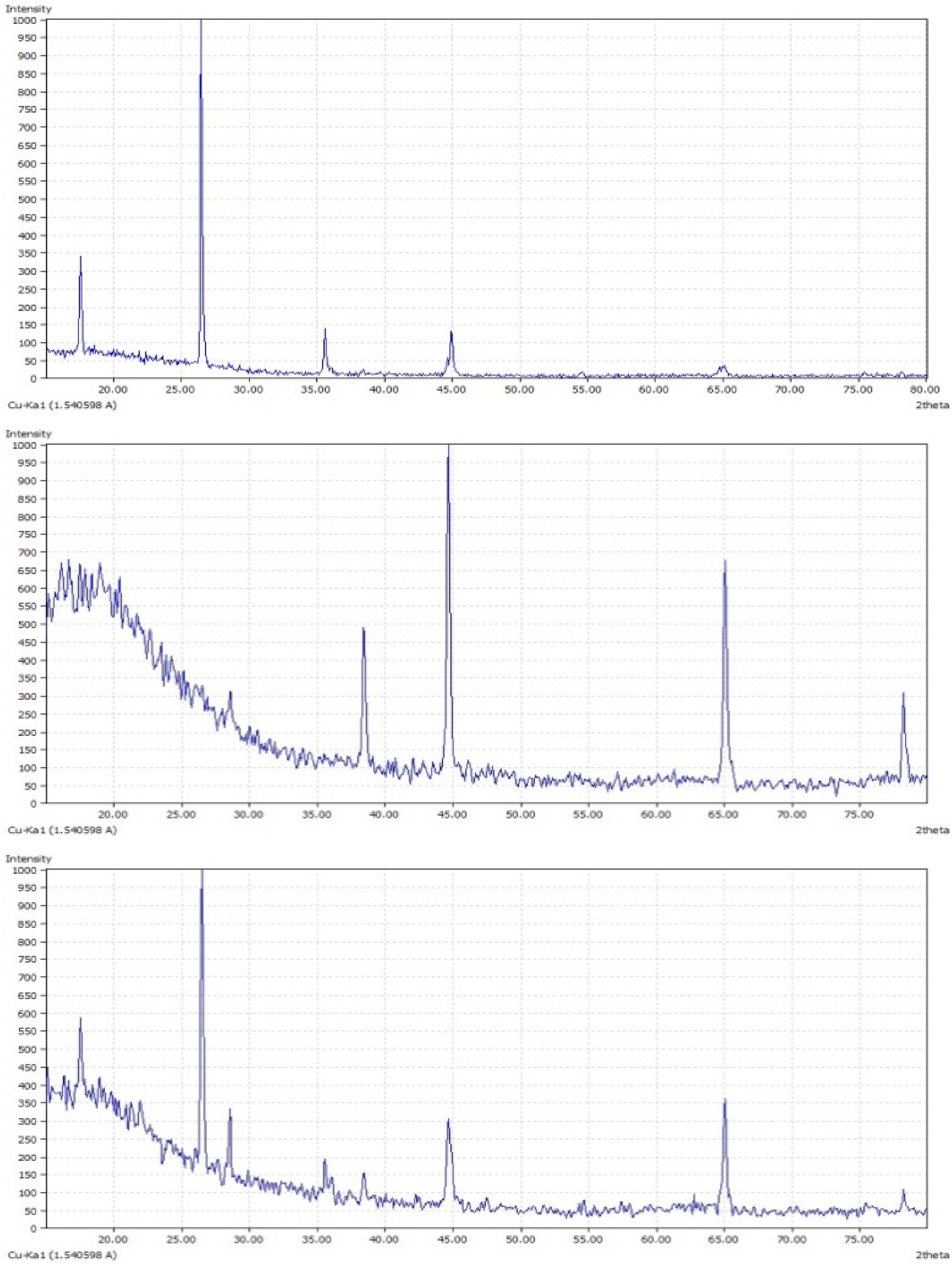


Figure 5-7: Some gold paint group

The diffractograms of gold color group (Figure 5-7) exhibit 5-8 distinct peaks. In the two diffractogram, Fraksen Mica and Sunlight Gold Met., their strongest peaks located at about 27° 2θ, beginning with a peak at about 17° 2θ while another sample shows 5 distinct peaks at about 28, 38, 45, 65 and 78 ° 2θ.

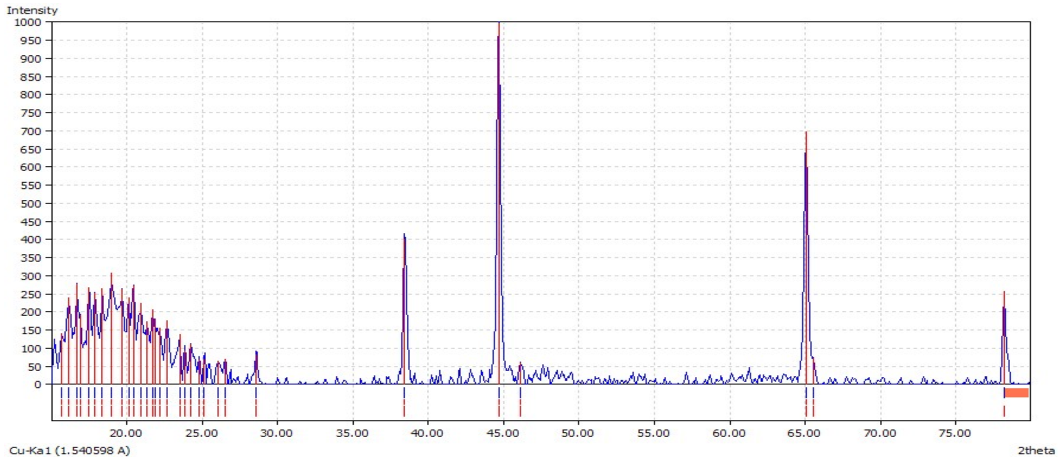


Figure 5-8: Sebring Met.'s diffractogram matched to its reference in the model database

In this group, Sebring Met. diffractogram (Figure 5-8) as unknown paint sample was identified by auto matching mode and the result corresponded to the correct reference pattern with the FoM score 1.0000 (Figure 5-9). Nevertheless other candidates also existed in this matching step since this sample was similar to many references with the FoM scores in range 0.7632 to 0.8760.

Color	Qual.	Entry	Formula	Name	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	Quant.(%)	FoM
			--	Experimental pattern: Metalic Silver C 90 noC (c 90 sebring met hc noc.raw)	1.0000	1.0000	1.0000	1.0000	--	1.0000
	B	99-900-0001		(C 90 Sebring met)	1.0000	1.0000	1.0000	0.9989	n.a.	1.0000
	B	99-900-0008		(C 245 Sahara beige met)	0.9155	0.8742	1.0000	0.8940	n.a.	0.8760
	B	99-900-0010		(C 254 sahara gold mica met)	0.7753	0.9314	1.0000	0.7973	n.a.	0.8612
	B	99-900-0006		(C 218 Wheat beige met)	0.7858	0.9518	1.0000	0.6025	n.a.	0.8452
	B	99-900-0004		(C 178 Amethyst m)	0.7428	0.9581	0.9630	0.7178	n.a.	0.8344
	B	99-900-0007		(C 234 Lynx gold met)	0.5561	0.9824	0.9412	0.4746	n.a.	0.8058
	B	99-900-0009		(C 247 Sunlight gold met)	0.2188	0.8387	0.9545	0.4398	n.a.	0.7847
	B	99-900-0002		(C 138 Gold met)	0.4752	0.9018	0.9259	0.4951	n.a.	0.7632

Figure 5-9: Matching result of Sebring Met. gold sample

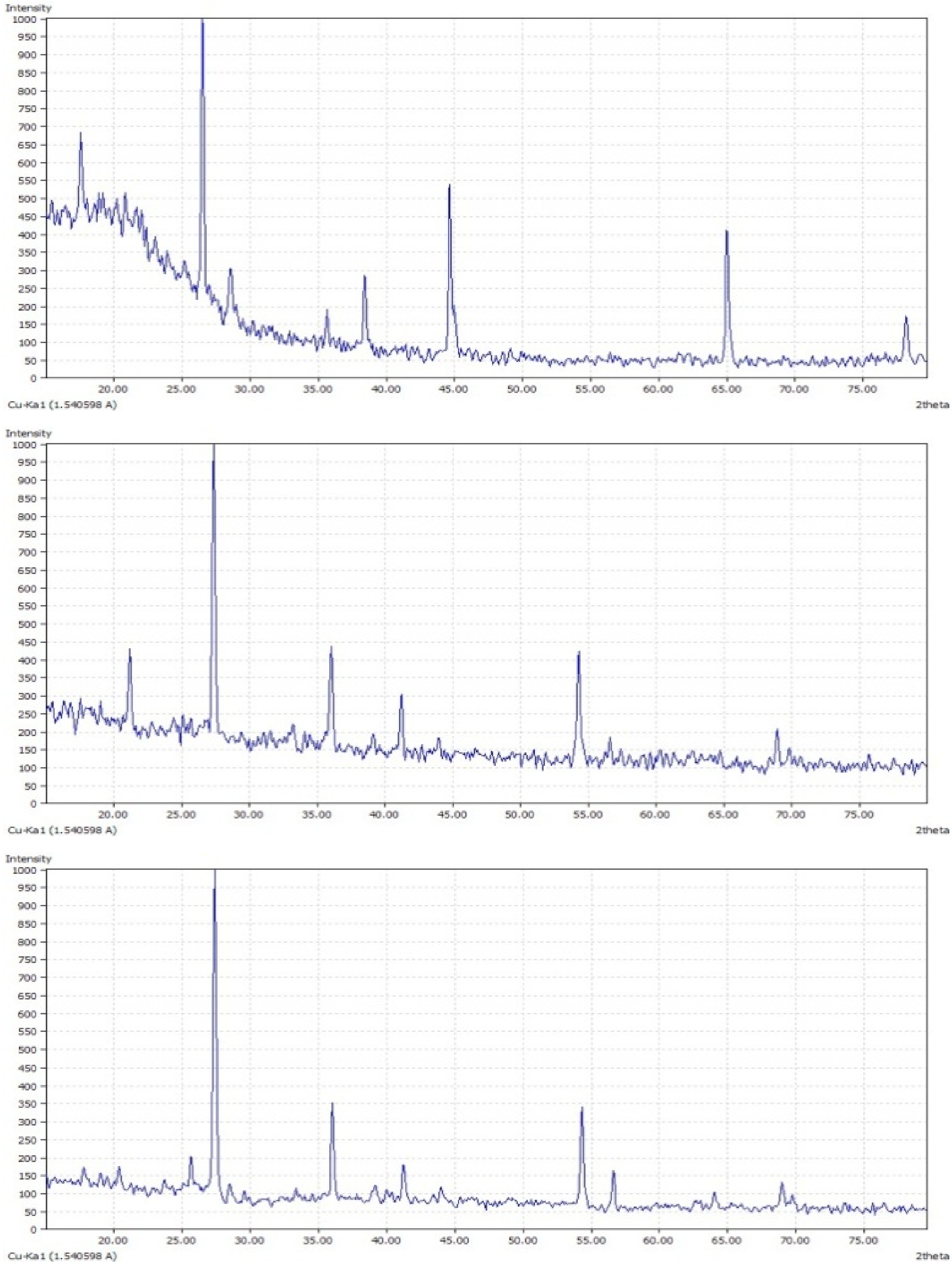


Figure 5-10: Some gray paint group

The gray color samples exhibited similar strongest peaks at 2θ about 27 ° and the smaller peak at about 36 ° 2θ.

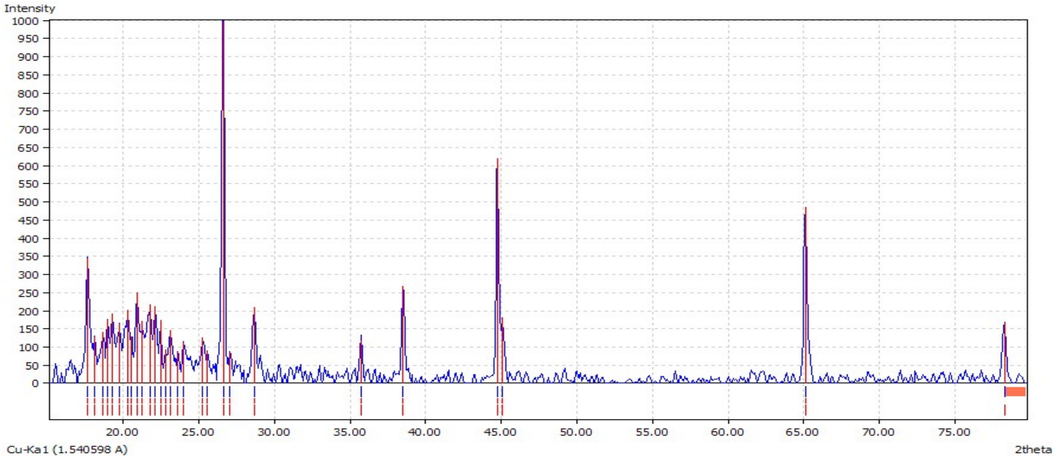


Figure 5-11: Golden Gray Mica diffractogram matched to its reference in the model database

One of gray paint groups (Figure 5-11) was used as an unknown in the auto matching mode. Numerous vertical lines in this diffractogram were obtained and this pattern actually matched the reference correctly in Figure 5-12.

Color	Qual.	Entry	Formula	Name	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	Quant.(%)	FoM
			--	Experimental pattern: C 188 noC (c 188 golden gray mica t noc.raw)	1.0000	1.0000	1.0000	1.0000	--	1.0000
	B	99-900-0004		(C 188 Golden gray mica)	1.0000	1.0000	1.0000	0.9991	n.a.	1.0000
	B	99-900-0000		(C 20 Brownish gray)	0.8537	0.7788	0.9231	0.6175	n.a.	0.8093
	B	99-900-0007		(C 242 Light quartz gray met)	0.5089	0.9518	0.7586	0.6615	n.a.	0.7810
	B	99-900-0006		(C 223 Meteor gray met)	0.7603	0.5612	1.0000	0.9987	n.a.	0.7748
	B	99-900-0008		(C 259 Misty gray met)	0.3576	0.8625	0.9500	0.5067	n.a.	0.7413
	B	99-900-0009		(C 262 Glory gray)	0.2978	0.9518	0.8667	0.4844	n.a.	0.7352
	B	99-900-0003		(C 152 Hazy gray met)	0.0602	0.9481	0.6774	0.4532	n.a.	0.7061
	B	99-900-0002		(C 120 Blue gray met)	0.0244	0.9663	0.7714	0.2841	n.a.	0.6919

Figure 5-12: Matching result of Smoke Golden Gray Mica

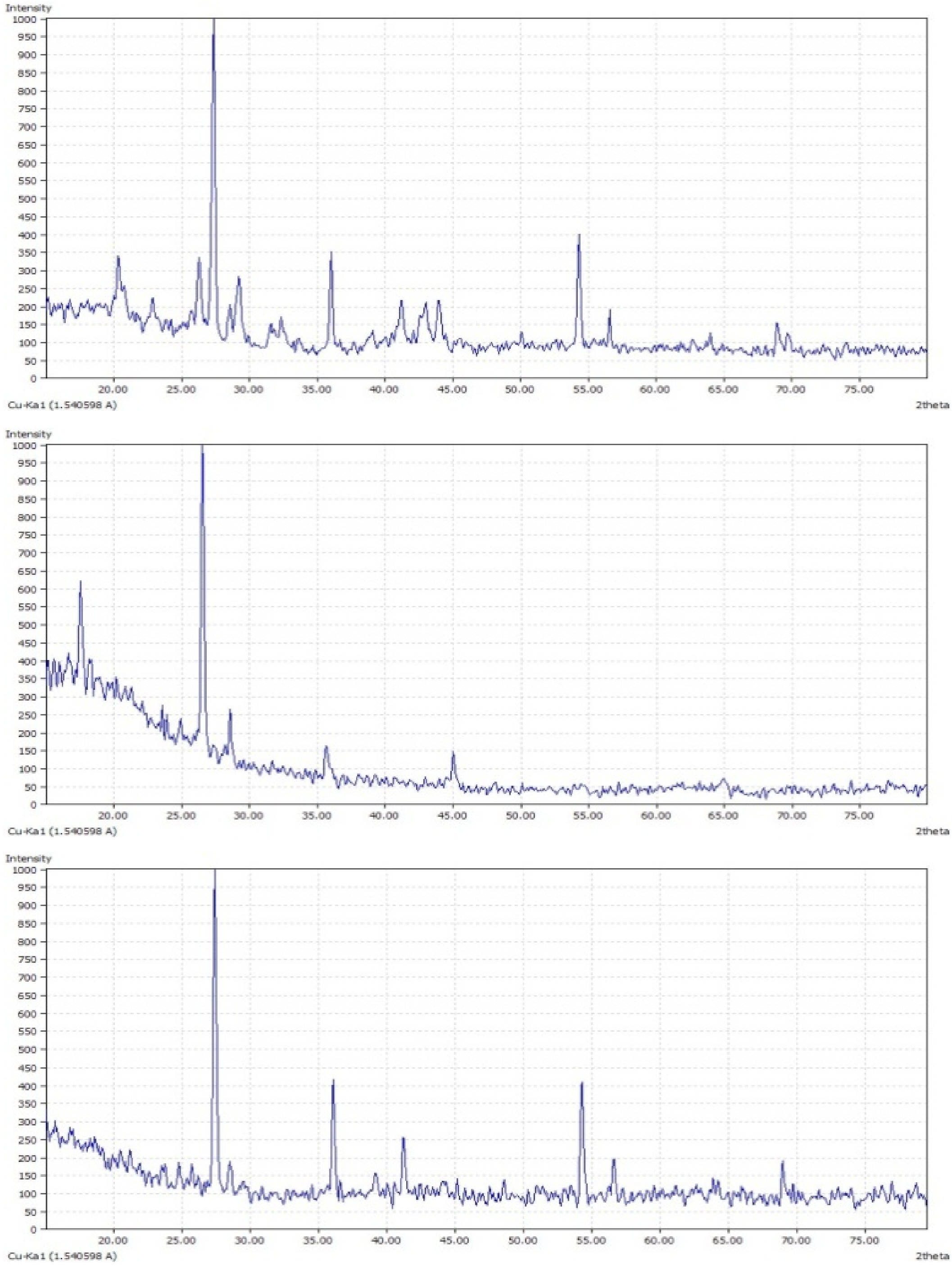


Figure 5-13: Some green paint group

All diffractograms of three representative paints in Figure 5-13 exhibited the highest peak at about 27 ° 2θ while the other peaks did not coincide.

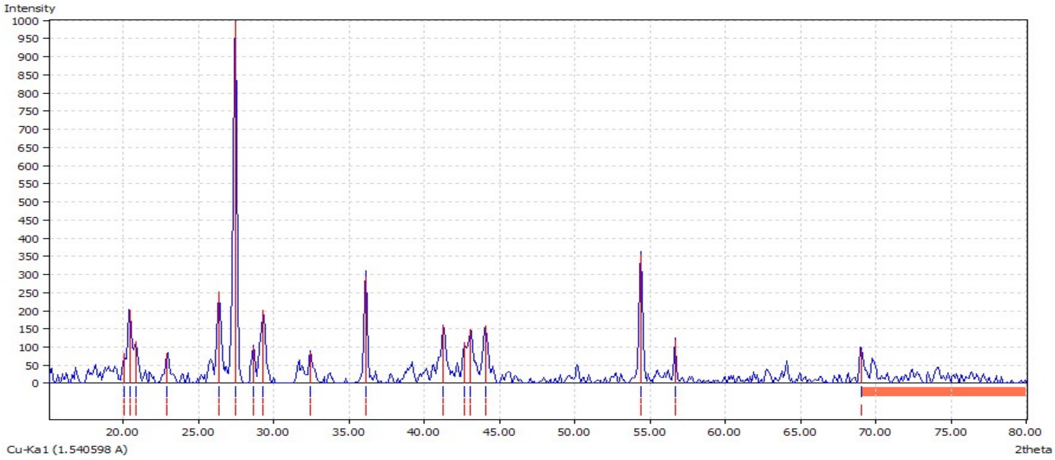


Figure 5-14: Green paint diffractogram matched to its reference in the model database

In the matching step (Figure 5-14), the Green sample could be matched to the correct reference at the first candidate (Figure 5-15). The second candidate was Light Green, one of representative sample, which had similar obvious peaks at 27, 36, 42, 54, 57, and 69° 2*θ.*

Color	Qual.	Entry	Formula	Name	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	Quant.(%)	FoM
			--	Experimental pattern: Solid Green C 44 (c 44 green k.raw)	1.0000	1.0000	1.0000	1.0000	--	1.0000
	B	99-900-0002		(C 44 Green)	1.0000	1.0000	1.0000	0.9992	n.a.	1.0000
	B	99-900-0003		(C 48 Light green)	0.9089	0.8133	0.8572	0.9709	n.a.	0.8777
	B	99-900-0017		(C 185 Texi green)	0.1562	0.7524	0.3889	0.8132	n.a.	0.5626

Figure 5-15: Matching result of Green sample

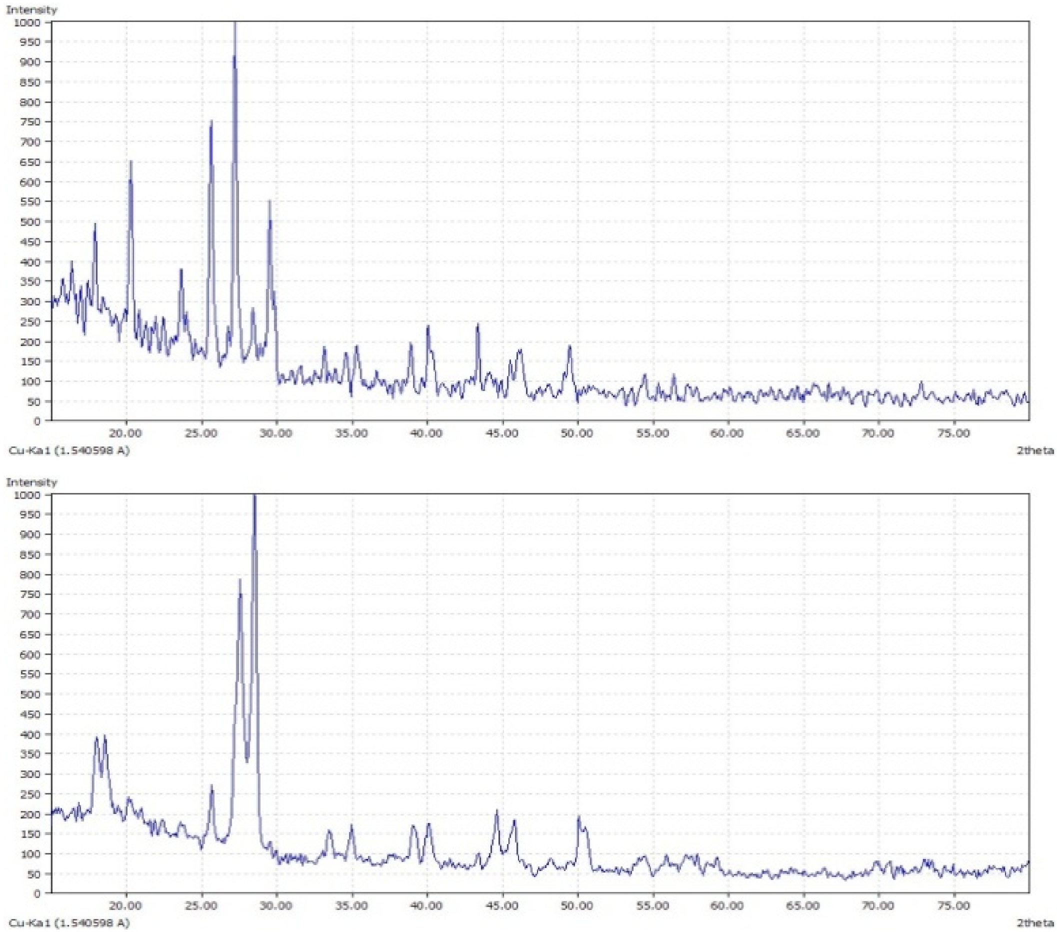


Figure 5-16: Some orange paint group

For the small group of orange color (Figure 5-16), many major peaks and small peaks were found in both samples, giving rise to many high intensity vertical lines when the peak data were created.

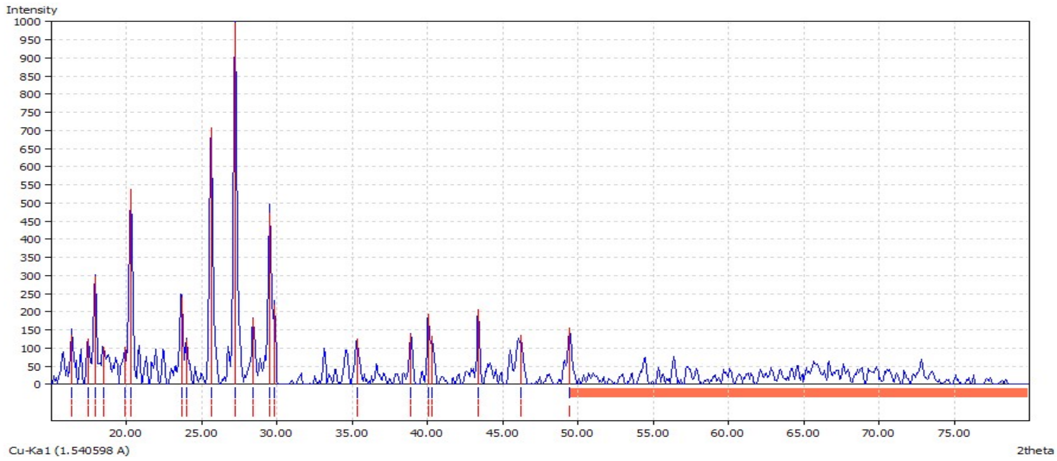


Figure 5-17: Orange yellow diffractogram matched to its reference in the model database

Color	Qual.	Entry	Formula	Name	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	Quant.(%)	FoM
			--	Experimental pattern: TMr4 (c 10 orange yellow.raw)	1.0000	1.0000	1.0000	1.0000	--	1.0000
	B	99-900-0001		(C 10 Orange yellow)	1.0000	1.0000	1.0000	0.9991	n.a.	1.0000
	B	99-900-0000		(C 5 Racing Orange)	0.0390	0.8440	0.8335	0.5188	n.a.	0.6777

Figure 5-18: Matching result of Orange yellow sample

Basically an unknown paint diffractogram could be matched to Orange yellow easily, since there were many clear peaks (Figure 5-17), as the first candidate with 1.0000 score, much higher than the second candidate, Racing Orange (Figure 5-18).

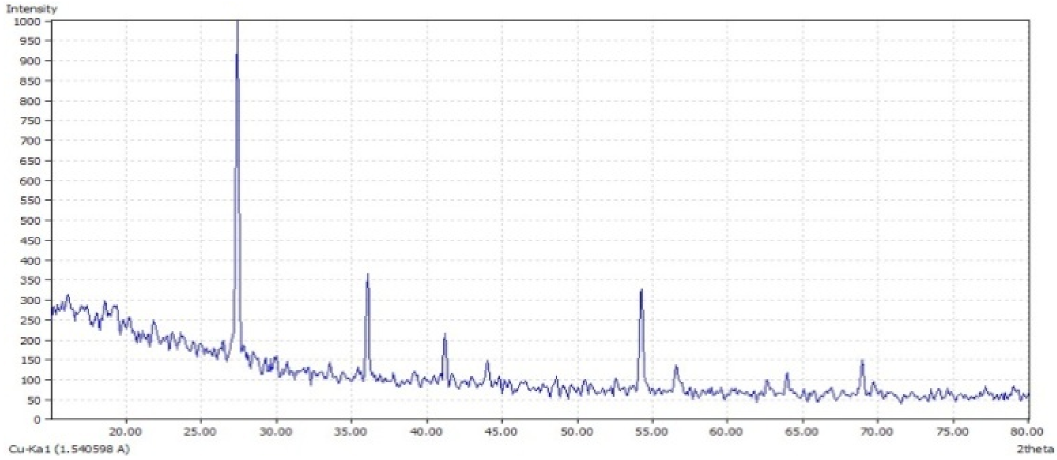


Figure 5-19: Some pink paint group

The smallest group of pink color (Figure 5-19) had only 1 sample in this database. The diffractogram contained about 10 obvious vertical lines when creating the fingerprint (Figure 5-20). Additionally, in a real accident scene if this paint was found, it could be easily to distinguish it from other color by the naked eye.

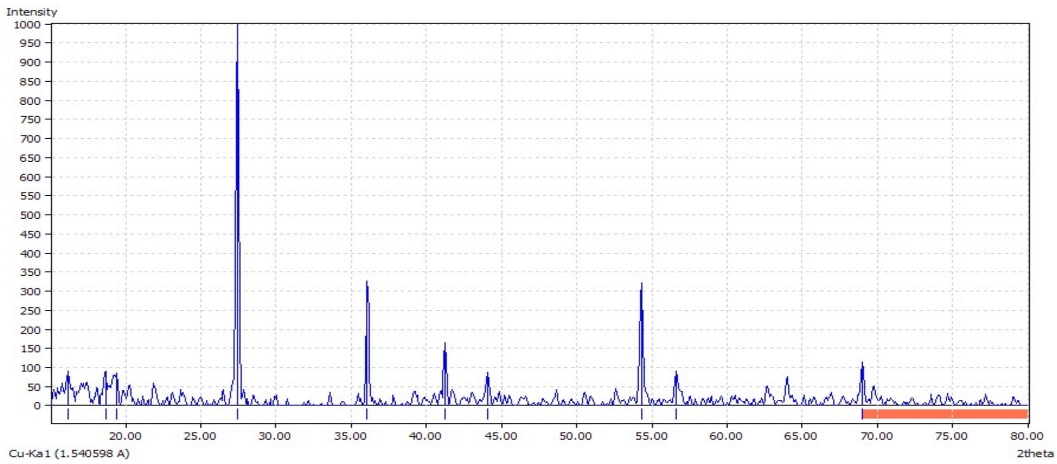


Figure 5-20: Pink diffractogram was created the peak data

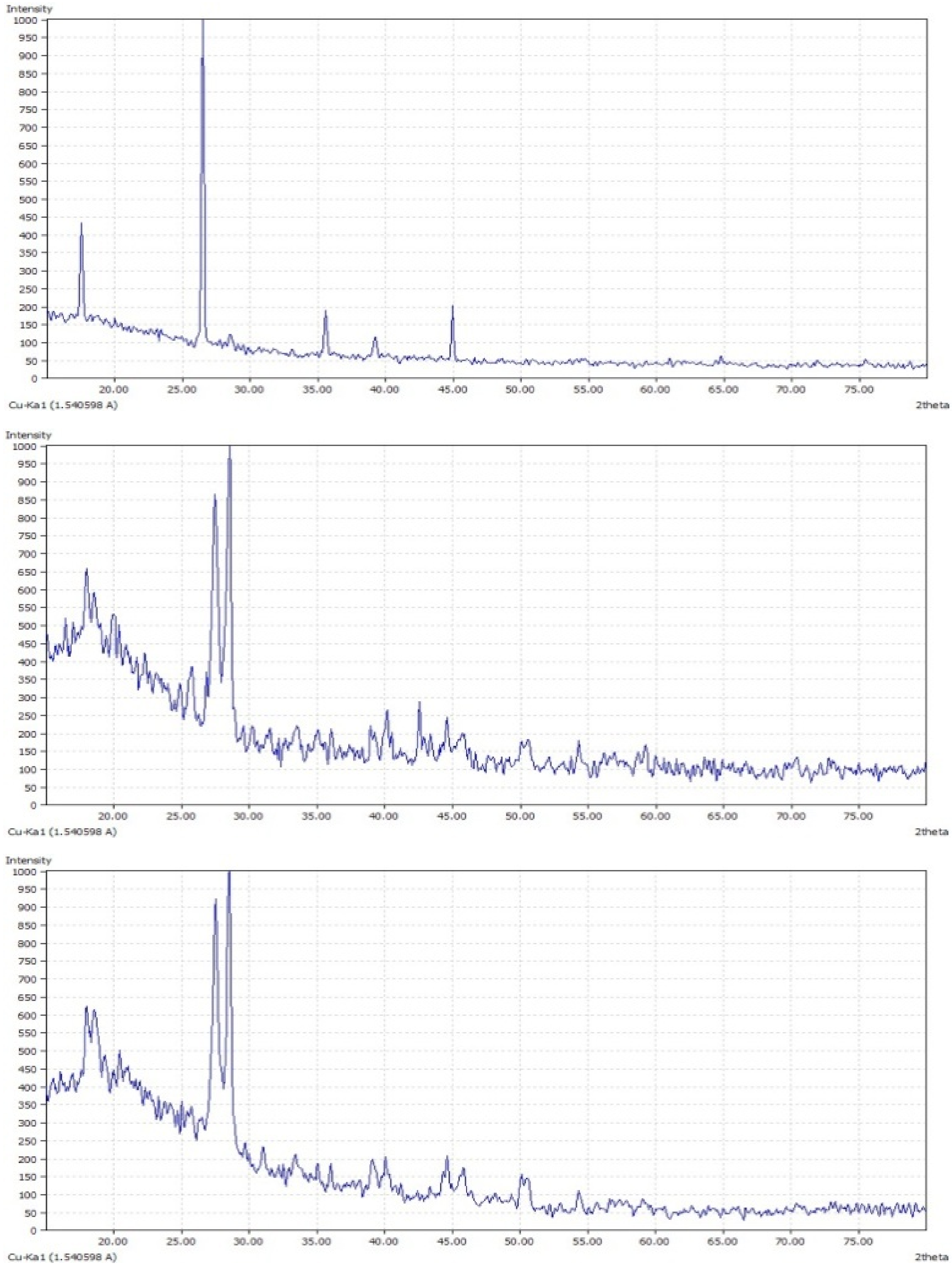


Figure 5-21: Some red paint group

Three example diffractograms of red paints (Figure 5-21) were chosen to represent this group. The first sample showed the main peak at 5 positions while the others two sample were similar since their 2 main peaks occurred at about 27 and 28 ° 2θ.

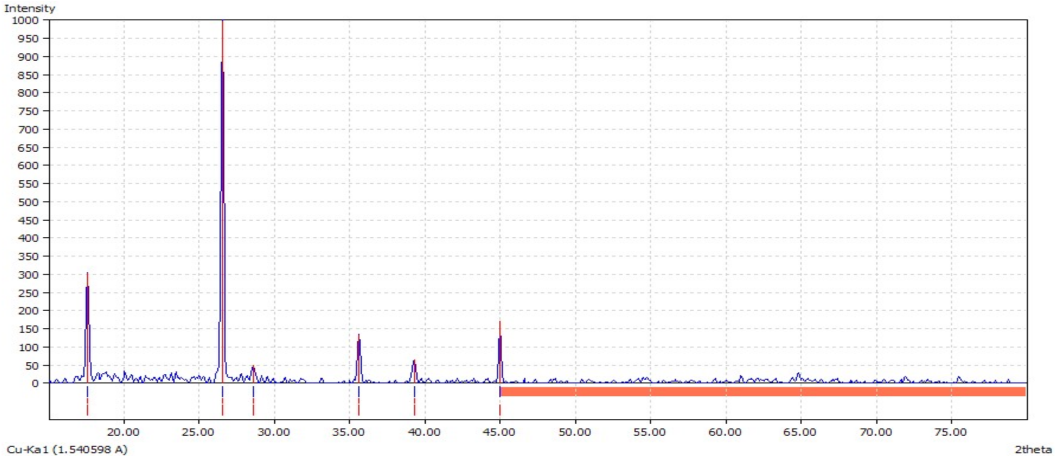


Figure 5-22: Foxfire Red Mica paint sample matched to its reference in the model database

Color	Qual.	Entry	Formula	Name	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	Quant.(%)	FoM
			--	Experimental pattern: C 248 noC (c 248 foxfire red mica pt noc.raw)	1.0000	1.0000	1.0000	1.0000	--	1.0000
	B	99-900-0005		(C 248 Foxfire red mica)	1.0000	1.0000	1.0000	0.9997	n.a.	1.0000
	B	99-900-0002		(C 113 inza red)	0.8305	0.9608	0.4521	0.9758	n.a.	0.8098

Figure 5-23: Examples FoM scores of Foxfire red mica samples

In this group, Foxfire Red Mica was used as the unknown sample to try matching with the database (Figure 5-22). The resulting FoM was 1.0000 for first candidate (Figure 5-23). Although there were 18 reference patterns in this red paint database only two candidates gave close matches.

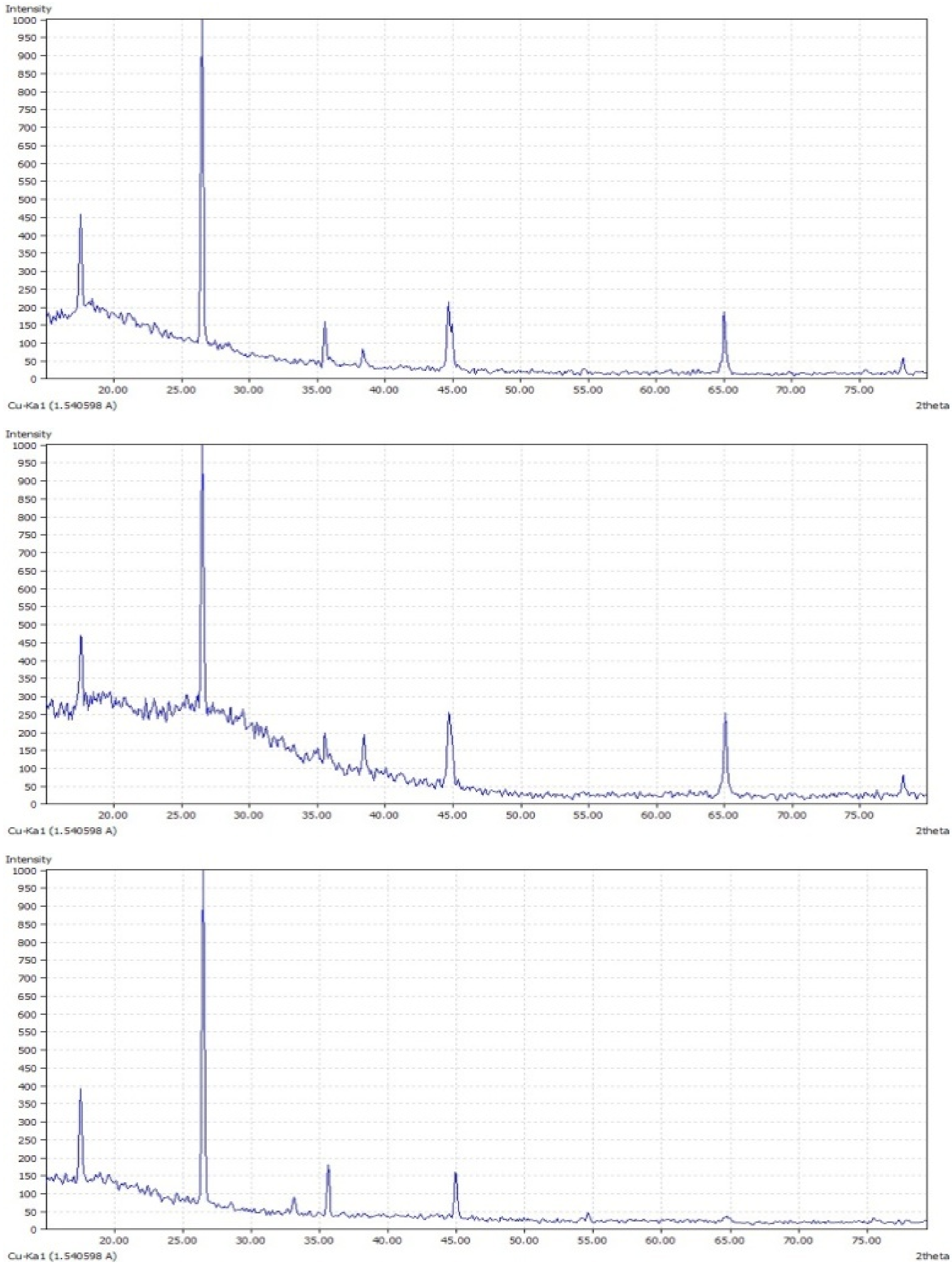


Figure 5-24: Some silver paint group

Silver paint was a one of the large groups. However their main peaks were mostly similar (Figure 5-24). The main peaks occurred at about 15, 27, 36, and 45 ° 2θ while the smaller peaks were spread out.

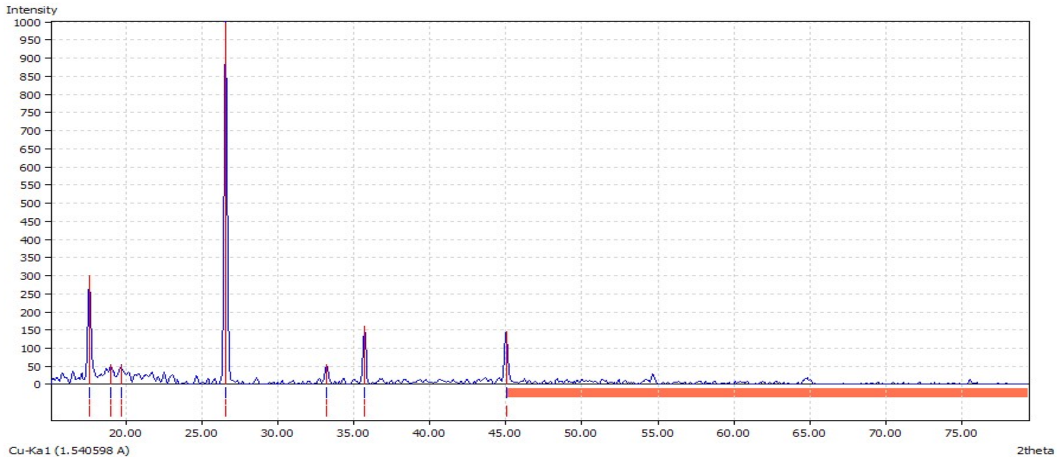


Figure 5-25: Satin Silver Met. paint sample matched to its reference in the model database

Satin Silver Met. sample (Figure 5-25) was identified by using auto matching mode and could be matched to the correct reference with an FoM score of 1.0000 (Figure 5-26).

Color	Qual.	Entry	Formula	Name	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	Quant.(%)	FoM
			--	Experimental pattern: C 198 noC (c 64 satin silver met hc noc.raw)	1.0000	1.0000	1.0000	1.0000	--	1.0000
	B	99-900-0003		(C 64 Satin silver met)	1.0000	1.0000	1.0000	0.9999	n.a.	1.0000
	B	99-900-0018		(C 177 Sun beam silver met)	0.9191	0.8948	0.8008	0.9998	n.a.	0.9138
	B	99-900-0019		(C 213 Bluish silver met)	0.8939	0.9798	0.7019	0.8930	n.a.	0.7760
	B	99-900-0001		(C 58 Grace Silver met)	0.3990	1.0000	0.2772	0.9339	n.a.	0.6170
	B	99-900-0011		(C 131 Silver met)	0.0893	0.9798	0.5263	0.5327	n.a.	0.5995
	B	99-900-0004		(C 65 Satin silver met)	0.0170	0.9216	0.3750	0.4737	n.a.	0.5075

Figure 5-26: Examples FoM scores of Satin Silver Met. sample

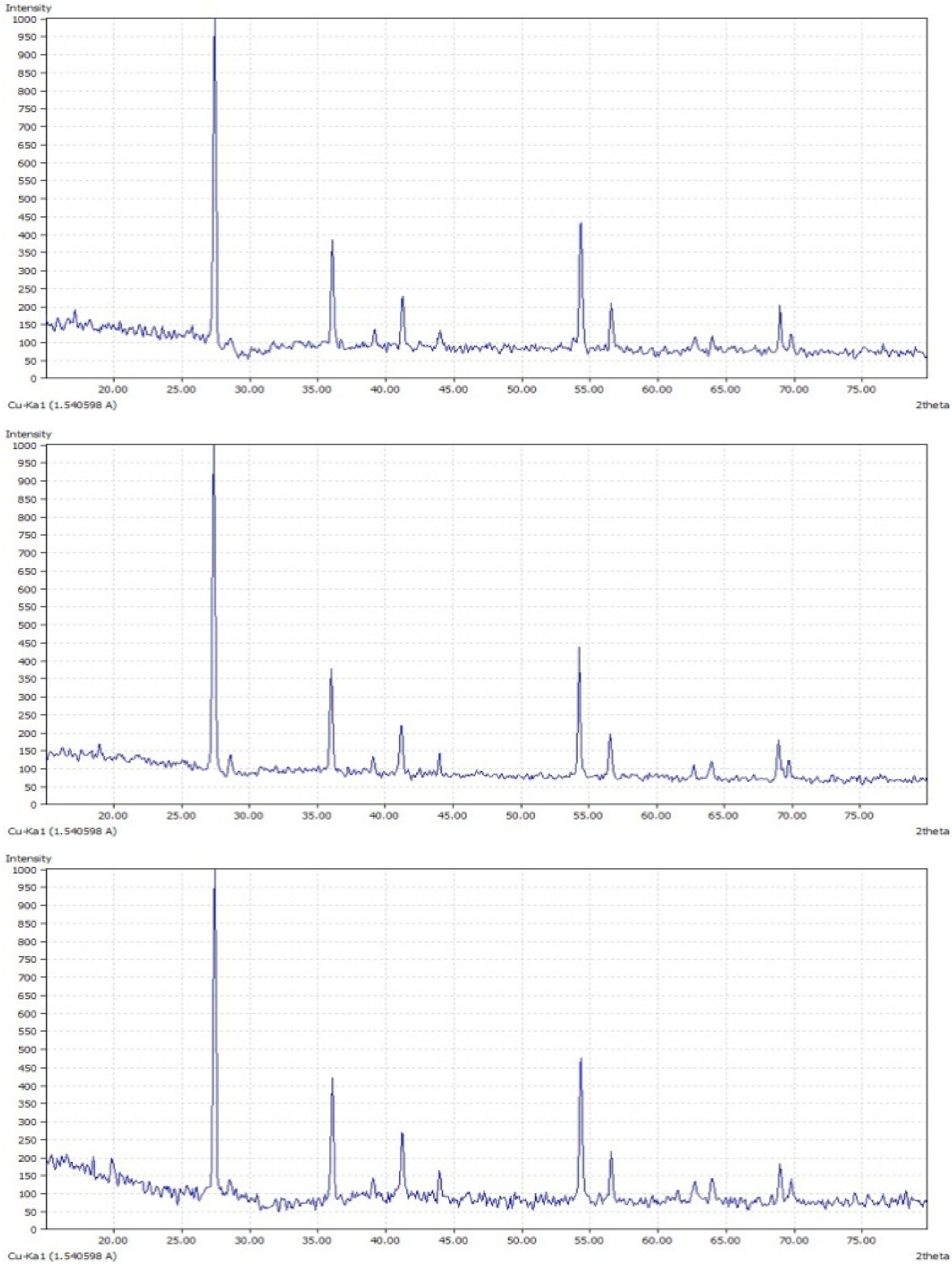


Figure 5-27: Some white paint group

The representative of white paint diffractograms (Figure 5-27) showed similar XRD patterns, the main peak appearing at about the same position while several small peaks make each diffractogram different from the others.

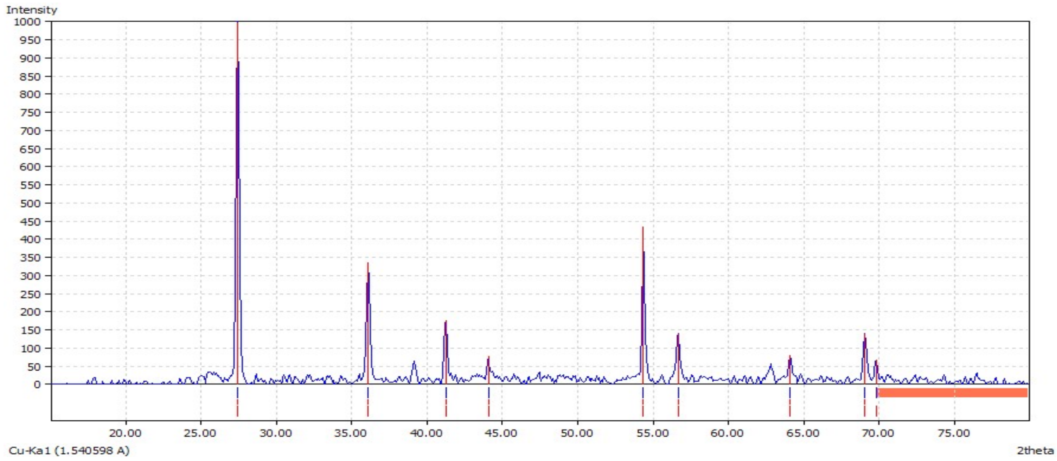


Figure 5-28: Sophia White paint sample matched to reference in the model database

In this group, Sophia White was used as the unknown (Figure 5-28) and its diffractogram matched correctly (Figure 5-29) although the FoM scores for other candidate were also close to the first accurate candidate. This was probably due to the main peaks being in similar positions.

Color	Qual.	Entry	Formula	Name	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	Quant.(%)	FoM
			--	Experimental pattern: C 75 (c 75 sophia white ac.raw)	1.0000	1.0000	1.0000	1.0000	--	1.0000
	B	99-900-0002		(C 75 Sophia white)	1.0000	1.0000	1.0000	0.9997	n.a.	1.0000
	B	99-900-0006		(C 216 White)	0.9457	1.0000	1.0000	0.9997	n.a.	0.9902
	B	99-900-0000		(C 21 Frost white)	0.9893	1.0000	1.0000	0.9996	n.a.	0.9841
	B	99-900-0003		(C 108 Clear white)	0.8348	0.9798	1.0000	0.9996	n.a.	0.9760
	B	99-900-0004		(C 109 Clear white)	0.9864	0.8948	1.0000	0.9952	n.a.	0.9727
	B	99-900-0008		(C 249 Dover white)	0.9503	0.9798	0.8894	0.9997	n.a.	0.9522
	B	99-900-0009		(C 250 Shinny white)	0.9051	1.0000	0.8750	0.9905	n.a.	0.9505
	B	99-900-0001		(C 69 Sophia white)	0.9545	0.9798	0.8890	0.9800	n.a.	0.9404

Figure 5-29: Examples FoM scores of Sophia White sample

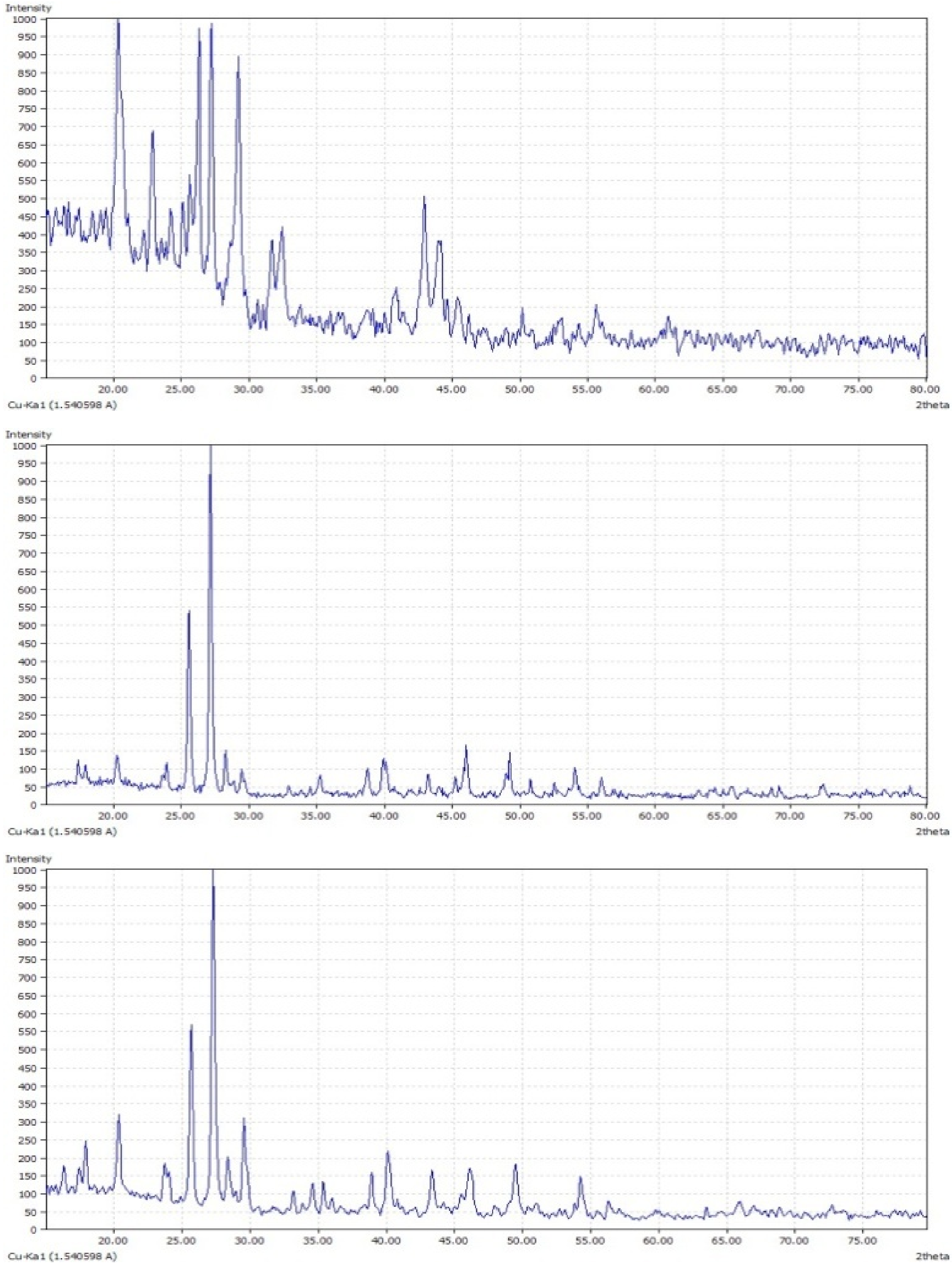


Figure 5-30: Some yellow paint group

Figure 5-30 shows the XRD patterns of paints in the yellow group.

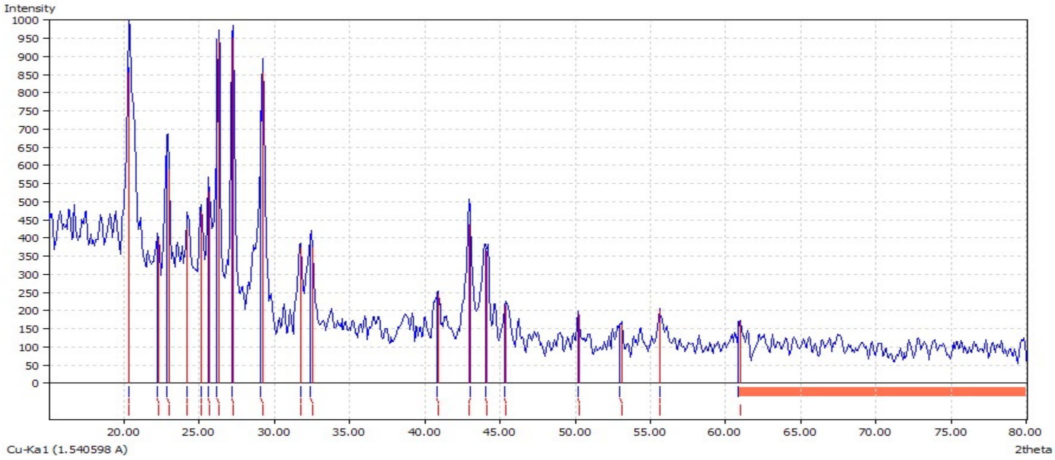


Figure 5-31: Permanent Yellow paint diffractogram matched to reference in the model database

Permanent Yellow was used as the unknown (Figure 5-31). It was correctly matched to the first candidate with an FoM score of 1.0000, much different from the second candidate (Figure 5-32).

Color	Qual.	Entry	Formula	Name	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	Quant.(%)	FoM
			--	Experimental pattern: C 275 (c 13 permanent yellow.raw)	1.0000	1.0000	1.0000	1.0000	--	1.0000
	B	99-900-0000		(C 13 Permanent yellow)	1.0000	1.0000	1.0000	0.9992	n.a.	1.0000
	B	99-900-0001		(C 141 Yellow)	0.0128	0.6977	0.4213	0.9496	n.a.	0.5553

Figure 5-32: Example FoM scores of Permanent Yellow sample

All these example of searching and matching steps by MATCH! phase identification program could match an unknown paint sample to reference in the database satisfactorily even though many references were extremely similar such as in the white paint database .

5.2 Forensic paint study

As car surfaces are usually coated with several layers of each type of paint, a sample with layers of the topcoat and the clear coat was examined for comparison with the single layer topcoat (Figure 5-33).

The two diffractograms were not much different from each other except for the intensities of the small peaks at about 65 and 75 °2θ. Matching unknown paints to the database was therefore not affected by the presence of the clear coat.

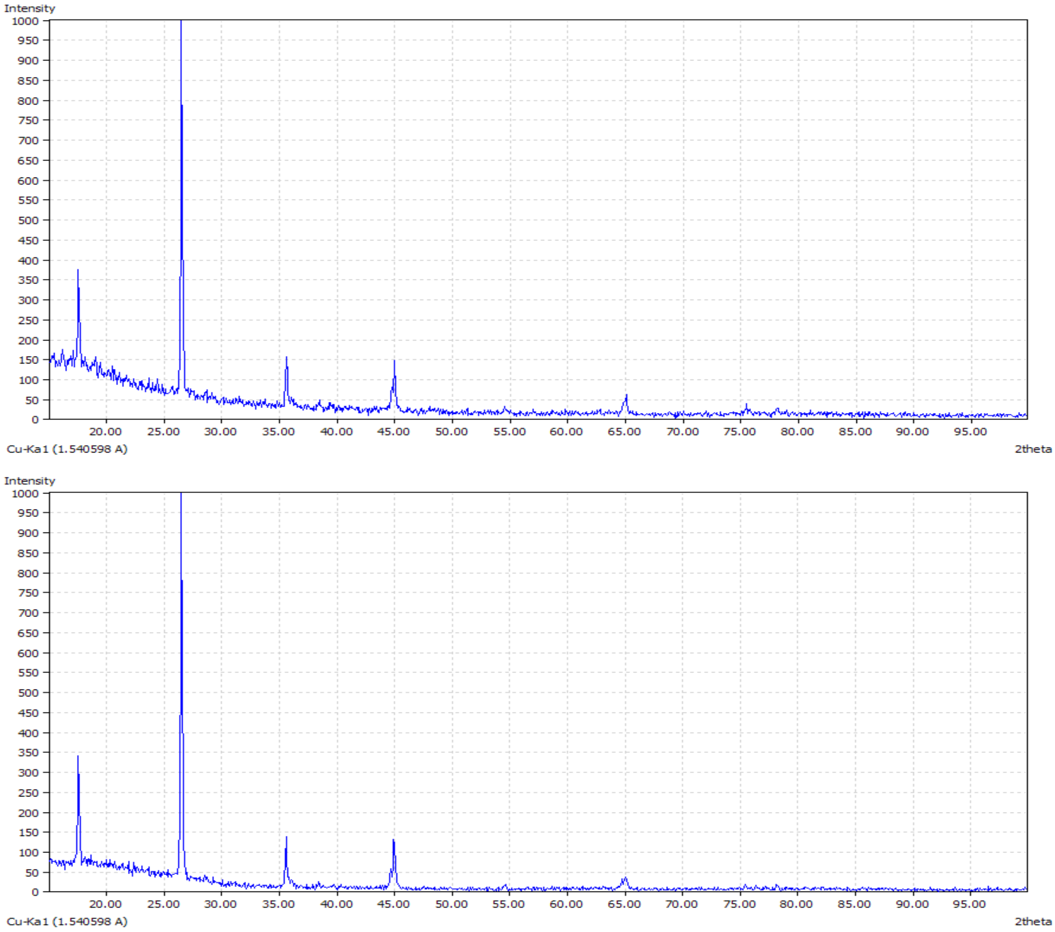


Figure 5-33: Single layer Met Silver Bronze topcoat diffractogram (upper) and two-layer Met Silver Bronze (topcoat layer and topcoat clear layer) (lower)

Forensic analysis often rely on comparing a sample from the scene with references in a reliable database. Comparison of XRD patterns is a qualitative process.

It does not depend on the amounts of a constituent in a sample. Variations in intensity, therefore, are not as important as peak position.

Since paints are mixed systems, identification by using the Powder Diffraction File (PDF) from the International Centre for Diffraction Data (ICDD) version 1999, is not possible because the pigments have to be matched to each standard diffractogarms in the PDF file (Debnath *et al.*, 2006). Some peaks may overlap and some peaks may disappear (Figure 5-34). As a result, the only appropriate way is to create a paint database by collecting reference patterns as the fingerprints for the samples.

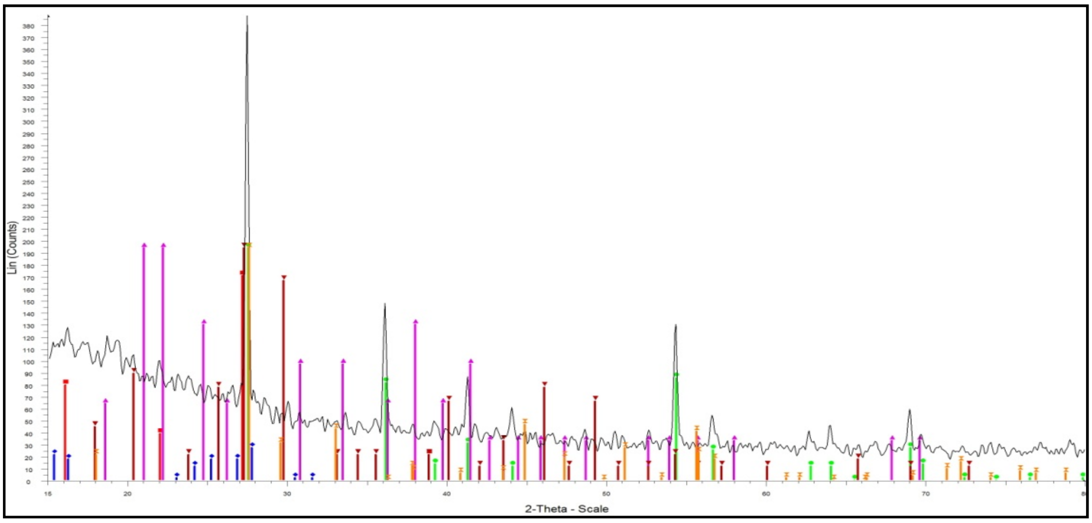


Figure 5-34: Pink paint sample indentified its pigment by using DIFFRAC*plus* EVA program with PDF (1999); green line is rutile, red line is PV 19, Blue line is PB 15:2, pink line is PbS_2O_3, brown line is $PbCrO_4$, and Light brown line is $PbMoO_4$

Some paint groups were amorphous to X-Rays and did not give well defined diffraction patterns. For example, amorphous pattern Palmp red paint (Figure 5-35) which contained PR 221, PR 170 and rutile, did not exhibit distinct peaks even though polycrystalline pigment were present. In these cases, the amount of pigments in paint compositions may not reach the detection limit of this diffraction technique (Lomax, 2010).

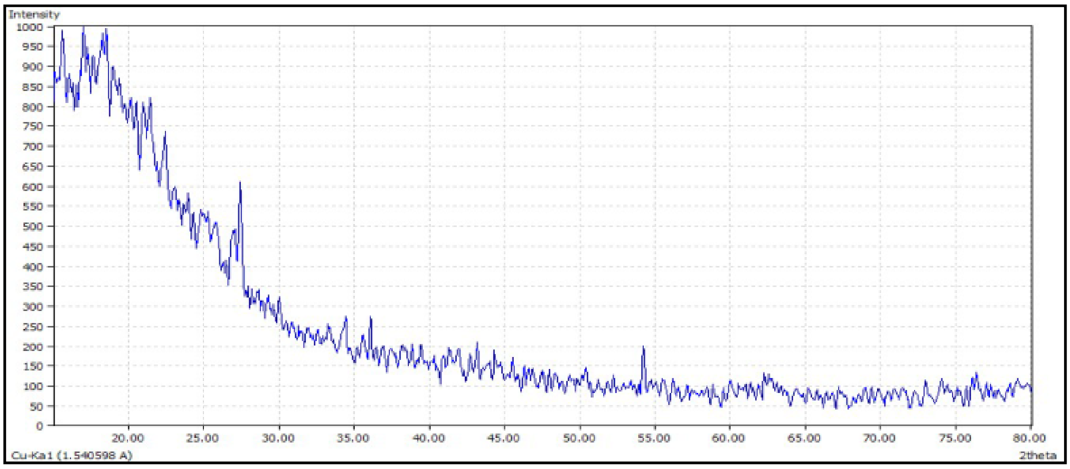


Figure 5-35: Pattern of Palmp red paint

In reality, paints on a car surface may be subjected to severe environments such as strong UV radiations from sunlight, acid rain in polluted areas or sometimes the suspect car is left abandoned for long periods of time in an isolated place. Therefore, paints could disintegrate since their pigments deteriorate by incident daylight which plays an important part in the degradation process (Snickt *et al.*, 2009). Subsequently, the forms in crystalline pigments could be transformed. If the degraded paint is brought to analysis by X-ray diffraction, the diffractograms may be different from the original pattern.

CHAPTER VI
CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

This study is an attempt to create a database of X-ray diffraction patterns of automotive paints for use in investigations involving cars. For example, road accidents and hit-and-runs. A software program, MATCH! Was used to convert peaks in each diffractogram into vertical lines and the line diffractograms were accumulated to form a database of some 149 paints. 'Unknown' paint sample, presumably collected from crime scenes or accident scenes could be examined by X-ray diffraction, the diffractograms converted to line diffractograms and matched to those in the database. Success of the matching was indicated by the Figure of Merit being closes to 1.

5.2 Suggestions

This study is an early step to create an automotive paint database which could be applied the method to other types of paint or other crystalline materials. For example, house hold paints and drugs. Furthermore, paints from other company could be examined by this method and add more population in the database. As some paints may degrade in severe environment such as UV degrading, fading paints should be examined too.

REFERENCES

Bell S. Forensic Chemistry. New Jersey: Pearson Education, Inc.; 2006.

Buzzini P, Massonnet G. A market study of green spray paints by Fourier transform infrared (FTIR) and Raman spectroscopy. Science & Justice 2004; 44 (3): 123-131.

Buzzini P, Massonnet G, Sermier FM. The micro Raman analysis of paint evidence in criminalistics: case studies. Journal of Raman Spectroscopy 2006; 37: 922-931

Caddy B. Forensic Examination of Glass and Paint. London and New York: Taylor & Francis; 2001.

Crystal Impact. Match! Phase Identification from Powder Diffraction http://www.crystalimpact.com/match/Default.htm; 2008.

David WIF, Shankland K, McCusker LB, Baerlocher C. Structure Determination from Powder Diffraction Data: Oxford University Press; 2002.

Debnath NC, Vaidya SA. Application of X-ray diffraction technique for characterisation of pigments and control of paints quality. Progress in Organic Coatings 2006; 56: 159–168

Gelder JD, Vandenabeele P, Govaert F, Moens L. Forensic analysis of automotive paints by Raman spectroscopy. Journal of Raman Spectroscopy 2005; 36: 1059-1067.

Lomax SQ. The application of x-ray powder diffraction for the analysis of synthetic organic pigments. Part 1: dry pigments. J Coat Technol Res, 7 (3) 2010: 331-346.

Lomax SQ. The application of x-ray powder diffraction for the analysis of synthetic organic pigments. Part 2: artists' paints. J Coat Technol Res, 7 (3) 2010: 325-330.

Rendle DF. X-ray diffraction in forensic science. The Rigaku 2003; 19 No.2, 20 No.1.

Rendle DF. DATABASE USE IN FORENSIC ANALYSIS. Crystallography Reviews 2004; 10(1): 23-28.

Snickt GVd, Dik J, Cotte M, Janssens K, Jaroszewicz J, Nolf WD,. Characterization of a Degraded Cadmium Yellow(CdS) Pigment in an Oil Painting by Means of Synchrotron Radiation Based X-ray Techniques. Anal Chem 2009; 81: 2600-2610.

Stout GH, Jensen LH. X-RAY STRUCTURE DETERMINATION. 2 nd ed. New York: John Wiley & Sons, Inc.; 1989.

Turner GPA. Introduction to PAINT CHEMISTRY. London: Cox & Wyman Ltd.; 1967.

Zeno W. Wick J, Jones FN, Pappas SP. Organic Coating: Science and Technology Volume II: Applications, Properties, and Performance. New york: John Wiley & Sons, Inc.; 1994.

BIOGRAPHY

NAME	Mr. Opas Thongnoi
DATE OF BIRTH	21 May 1982
PLACE OF BIRTH	Pattani, Thailand
INSTITUTIONS ATTENDED	Prince of Songkla University, 2001-2005 Bachelor of Science (Chemistry) Mahidol University, 2008-20011 Master of Science (Forensic Science)
HOME ADDRESS	3/1 Moo 4, T. Kuan, Panare, Pattani 94190 E-mail: oa_etc@yahoo.com