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Forensic Analysis of Strontium and Barium Sulphate as a Perceptive Factor by Non-Destructive Method for Tool Paint

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Abstract

New advances in the growth of research methodologies to evaluate among various tools are of crucial to create the best evaluation possible about whether a paint residue seized at a crime scene arises from a tool detected. Standard analytical techniques are not used to evaluate the red tools for the prospective use of X- ray navigators. In this study, the trace amounts of strontium and barium revealed by XRD, the main mineral filler, namely strontium sulphate and barium sulphate, a statistical approach was used, and it can diagnose some forensic tool paint during a home invasion. This work is the best example among others of XRD for an enhanced characterization of tool paints in an effective method.

Keywords: Forensic Tools, Paint Analysis, Discriminate, SEM, Correlation

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Graphical Abstract

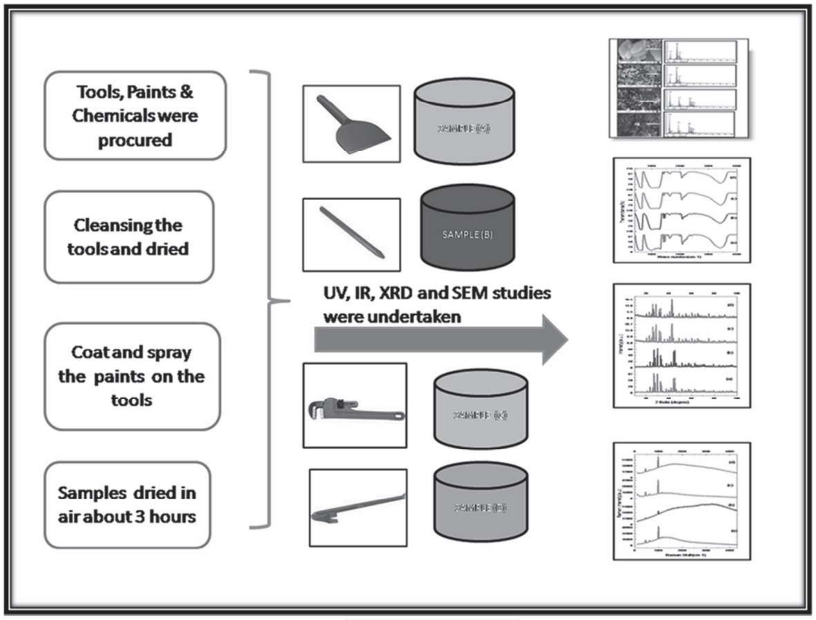

Fig 1. Graphical abstract

1. Introduction

Forensic science is the concept of the application of science in legal disputes. Forensic science has developed to meet new problems and become swifter and precise due to the rising rate of crime. It is challenging to explain the immense amount of crimes undertaken each day and the specifics for every incident. As a result, the forensic investigator dealt with a wide variety of evidence. One case may contain a bloodstained bed sheet, while the other case may contain only produce a single hair. In forensic science laboratories, paint evidence is frequently analysed sorts of trace evidence. Paint evidence like automotive, artistic paints, architectural and automotive paints. It based on the vehicle crashes and running from a collision frequently. A violent interaction through objects as a result in the transfer of paint, either as smears or chips. Paint is a ubiquitous material; it continues to be an essential type of evidence due to its enormous physical and chemical variations. A variety of the core circumstances are the cause of paint evidence must be approached. For instance, forensic experts collected a paint evidence from earlier incidents by a vehicle collision, or it could contain loose paint from damage on vehicles that was never repaired [1, 2]. As a result, the analytical process follows the recognised forensic principles from general to expertise procedures and from non-destructive to destructive techniques. The tiniest paint components are characterised by less sophisticated analyses, than more sophisticated ones that allow a general description of samples. Less harmful approaches will be selected over destructive ones to prevent the samples from unneeded harm methods [3 - 5]. In hit-and-run accidents, paint is frequently transferred and used as forensic evidence, like in the case mentioned above, where a car accident with a bicyclist. Various paint substrates are used in hit-and-runs frequently, it is used in various coating formulations: bicycles, mopeds, motorbikes, boats, vehicles, timber, and traffic signs. In the form of chips, flecks, flakes, powders, smears of paint may be found as evidence or combined form of them. Sometimes, a mailbox or an automobile panel, like a completely painted object may be obtained. Forensic researchers are able to differentiate the unknown substances from paint and are frequently to compare recovered paint from the items found at a crime scene to know the paint source [6]. In other circumstances, it may be to compare two or more unverified samples of paint, which are from different sources of samples that have been suspicion. Based on the paint chemistry, it might be feasible to provide enough information on the colour, model year, model, and making range as a potential investigation lead if automobile paint is recovered [7]. After locating the suspicious vehicle, paint samples can be collected and then it will be submitted for further analysis. Examining works of art for authentication is one of the specific uses of forensic analysis [8]. The identification of the pigment and the data on the pigment's availability, these conclusions are significantly essential [9]. Due to the creation of cutting-edge, effective and user-friendly technology, the adoption of this technique in forensic applications has recently occurred. In break-ins, vandalism, and car accidents, paint droplets are a vital piece of trace evidence that is frequently found. These paints analysis may be used to link a suspect to a specific crime scene [10, 11]. Coating evidence is a great deal of importance in a forensic laboratory. The chemical substance comparison of paints from the site and from the suspect cars or items can assist in identifying the offenders. The automobile coatings are multi-layered, ranging in thickness from a one micrometres to more than ten layers [12- 14]. The main components of paints, which have been employed in classifying and distinguishing paints extensively [15], are pigments and resins. In criminal investigations, paint coat fragments are among the items that are used repeatedly. The paint samples are preserved from the crime scene spot and contrasted with paint from a suspect car. Comparing the colours is the initial criteria of the sample is an assessment [16]. Visual comparison between the colour of an object under investigation and a standard in a colour atlas is the most common method of determining paint colour in crime detection. The findings depend on a number of variables, including the intensity and the kind of the sample's lighting and the expert's eyesight while judging colour. This procedure takes more and more time [17].

Enhancing the analytical approach is required for the study of this kind of material to get a result interesting. Using SEM/EDS through more in-depth research of the inorganic fillers and pigments included in the paint to get a better result [18- 20]. It is used to determine whether a more thorough use of this technique would enable the sample differentiation obtained from various tools indistinguishable - or perhaps not sufficiently distinguished - by the existing analytical strategy is also considerable [21, 22]. In this regard, it is noteworthy that the question of whether or not samples can be distinguished from one another is problematic when it comes to interpretation, especially when homogeneity within the same paint (such as spray paints) needs to be taken in a mind in order to determine whether or not samples have the same origin [23, 24]. Another challenge is when attempting to connect different elements; the beam of electrons may travel beyond the area of interest. Because in order to find any discrepancies or similarities between the samples that will be assessed in every analytical advancement that improves material characterization is undoubtedly. The investigation described here, more particularly, examines tools from personal tool collection with a focus on the presence of barium sulphate and strontium sulphate, two minerals that are typically used as fillers in such paint. Red was chosen since it is the widely used standard colour of the tools that were evaluated in forensic cases. The findings in this research include instances where in-depth XRD and local X-ray microanalysis identified variations in this filler [25]. Given this, the main focus of the current research was to compare the traces of strontium and barium in paint samples as determined by characterising the main mineral fillers, strontium sulphate, and barium sulphate, which facilitated the discrimination of various tools using a statistical approach and could detect some forensic tool paint during a house search.

2. Methods and Materials:

Metal salts were acquired from Merck (Darmstadt, Germany). All the spectroscopic and electrochemical study solvents have been purified according to best practices. After microscopical examinations, all samples were analysed using ultraviolet–visible (UV–Vis), Raman micro spectroscopy and Fourier-transform infrared (FT-IR). These analyses were performed to collect chemical frequency information in addition to evaluating the discriminating power of these techniques.

It is a simple method; some of the slides are coated with metallic salts.

Directly and rest of slides spread out the paints with metallic elements. Non-metallic flakes surface is an important consideration in this methodology. At room temperature, the samples were allowed to dry for a day. As with any non-homogenous sample, a quality analysis depends on the control of preparation and sampling. During sample preparation, consistent thickness and parallel planes are most important. Microscopic comparisons must be dealt under identical conditions, e.g., same instrument and analyst, etc. The only other consideration made during sampling was the avoidance of metallic flakes that efficiently reflect light to produce their effects and interfere with obtaining spectra [26].

The paint layer of these instruments is sampled in bulk with a scalpel into millimetre-sized pieces, which are then placed on stubs, which are aluminium plates covered in a double-sided carbon sticker, for SEM/EDS analysis. Therefore, it is an analysis of paint's external surface, in line with our laboratory usually does when dealing single-layer paint.

Samples (a), (b), (c), and (d) are reported. Samples (a) and (c) are metal-based samples. Sample (b) and (d) are metal based samples along with the paints.

Here, (a, b) - Sr metal is used.

(c, d) – Br metal is used.

(Fig 1). Shows the graphical abstract of the preparation method.

2.1 XRD:

Two Philips X- ray diffractometers were used to create the X- ray diffractograms of the pigment samples given in this work. D8 Advance ECO XRCD Systems with SSD160 1 D Detector (Bruker) by using Cu K(λ = 1.54056 A) which is the most common and widely used X-ray radiation for analysis of powdery and polycrystalline materials. Multiple samples of each pigment from various suppliers were utilised, the best results are provided here. To comparing results from unknown sources or analysing unknown pigment samples, which can be used as a standard for commercial pigments [27-30]. Not experiencing any phase changes in the polymorphic pigments during the grinding operation. It has not needed any additional sample preparation or grinding. Paint samples were stripped of their pigment components b centrifuging and diluting, then cleansing and drying them for analysis to identify the pigment.

2.2. UV–Vis Microspectroscopy:

All the samples were mounted, cross-section, 5 µm thick, in a quartz microscope slide and covered with a quartz cover slip. It was a PERIN ELMER LAMBDA – 35 model. UV–Vis micro spectroscopy analysed Colour coats and clear topcoats. Using a one paint sample Heterogeneity or variability can exist. More than ten spectra from different areas, for each clear coat and colour coat, were gathered to obtain a clear representation of the paint. Using the CRAIC data software, Statistical analyses were performed for every single layer in all the samples. More than, 10 spectra from each layer of each sample were averaged, and calculated. Intra-sample variation was done by spectral comparison. And based on the 2 SD envelope, inter-sample spectral differentiation was examined [31- 33].

2.3. FT-IR Microspectroscopy*:*

The comparison of the sample’s spectral quality to one another and to a reference database was done by the infrared approach. Using an IR Tracer – 100 shimadzu Infrared Microscope FT-IR spectroscopy Analysis of the paint samples was carried out. A micro compression cell II with diamond windows (Kalasalingam University, Virudhunagar) analysed 5 µm thick Cross-sections of each paint measurement. All paint layers of the samples were collected and analysed in multiple times , each part of the paint layer. To identify the chemical composition of each paint layer, including mixtures, by Infrared spectral interpretation [34, 35].

2.4. Raman Microspectroscopy:

The following objectives are suggested for Raman spectra:

- To combine analytical data with discovered data using IR techniques
- To examine the range of characteristics associated with chemical composition that have been observed
- To determine the information that can be gathered;
- To know the technique's ability to discriminate;
- To determine the paint's constituents and create a chemical profile. It has been demonstrated that Raman spectroscopy is a useful tool in forensic pigments analysis. This analytical technique's non destructiveness and the ability to excite different components by using multiple excitation wavelengths make it a substitute for infrared spectroscopy. Further, this method is quite rapid and requires no sample preparation [36, 37]. The paint samples were analysed by Raman spectroscopy using an Imaging spectrograph Raman microscope with a 500 mm laser. 5 µm thick Cross-sections of each paint were placed onto a quartz slide. It undergoing Raman analysis with the colour coats. Using the Raman spectrum, the pigments contained in the colour coating were identified.

2.5. Morphological Studies:

The morphology of as developed Strontium and barium based samples(a, c) and paint based sample(b, d) was observed by Scanning electron microscope (SEM). An Electron Microscope EVO18 (CARL ZEISS) model is used for this analysis. SEM pictures were taken at 1000x and 1500x magnification. Scanning electron microscopy (SEM) plays a vital role in analysis of paint, especially in multi layered paint investigations. It produces an enhanced image of the paint sample, allowing the beam to be focused on a specific paint layer and individual particles for elemental analysis using EDS [38, 39]. Hence, this method is helpful. Because SEM has a significantly greater resolution than optical microscopy techniques, it is highly effective for cross-sectioned and pertinent to trace samples. For non-destructive microscopic investigation in forensic applications, SEM is the optimum instrument, and it has even been used as a reference technique to verify the research. To magnify the sample's physical structures and evaluate the fundamental compositions of the sample, SEM is frequently used with an EDS. It offers elemental information about the sample; it has a certain capacity to convey molecular data. As a result, it is more frequently utilised in conjunction with other molecular information-producing techniques [26]. SEM-EDS is employed to identify the distinctive constituent components of the inorganic pigments by using tiny paint samples.

3.0 Result and Discussion

3.1.XRD:

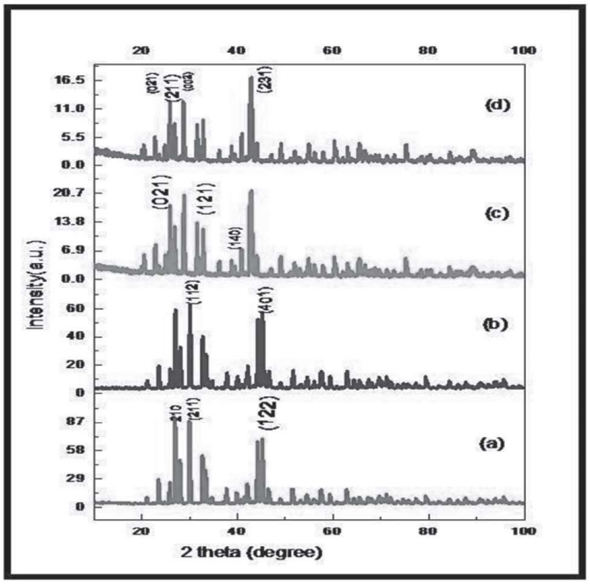

Fig 2. XRD image for metal-based samples (a, c) and paint-based samples (b, d).

The study showed that XRD is useful for mass sample examination and can be utilised for the initial screening of materials without the need for any laboratory sample preparation. XRD patterns of prepared samples are shown several numbers of peaks are identified

(Fig. 2). Sample (a) showed the peaks at 23.24 °, 25.81 °, 27.09 °, 28.06 °, 30.30 °. 32.55 °, 33.19 °, 37.68 °, 41.85 °, 43.77 °. Sample (b) showed the peaks at 23.56 °, 26.14 °, 27.09 °, 28.06 °, 29.98 °, 32.87 °, 37.68 °, 39.93 °,41.85 °, 44.09 ° and 46.66 °. At 45.05 ° the same peaks showed in both the samples (a) and (b); hence it proven the strontium present in the samples. Sample (c) showed the peaks at 20.68 °, 22.93 °, 24.85 °, 25.81 °, 29.02 °, 31.58 °, 32.87 °, 36.07 °, 38.64 °, 40.88 °,43.1 °, 44.09 ° and 49.22 °. Sample (d) showed the peaks at 20.36 °, 22.60 °, 28.70 °, 33.19 °, 36.07 °, 38.64 °, 40.88 °, 42.81 °, 44.09 ° and 49.23 °. According to the earlier researches, Sample (c) and (d) showed the same peak at 26.77 °, it confirmed that the barium was present in the samples. According to the samples (a), (b), (c) and (d), polycrystalline nanostructure was present. The 100 % intensity (maximum) observed at 30.05° for sample (a) and nearly same was shown in sample (b) exhibited that the paint is incorporated with the extract and the plane is (0 0 2). Above 50 % intensity peaks are 32.71°, 44.25°, 45.24° and 26.98°, and their planes are (0 1 2), (2 2 1), (0 4 1) and (0 2 1). Using Debe scherer formula, the crystallite sizes were calculated for the peaks. The crystallite size of the samples is 11.8 and 20.6 nm. The minimum crystallite size was observed for sample (a). The 100 % intensity appears at 42.95° for sample (c) and the same intensity was observed in sample (d). Above 50% intensity peaks are observed at 25.9°, 28.79°,31.57° and the planes are (0 2 1), (1 2 1) and (2 1 1) for sample (c) and 32.85°(0 0 2), 25.87 ° (0 2 1), 28.78 ° (2 1 1), 42.67 ° (1 4 0) for sample (d). Crystallite sizes of the samples are calculated. The crystallite size of the sample (c) and (d) are 50.28 and 61.06 nm.

Plane	**2θ**	**d- spacing**	**FWHM**	**Crystallite size (nm)**
210	30.005	2.97576	0.07	11.8
002	30.08	2.96852	0.04	20.6
012	32.71	2.73623	0.04	20.7
221	44.25	2.04541	0.2	42.9
041	45.24	2.00297	0.23	37.5
021	26.98	3.30167	0.13	62.9
10 0 4	42.95	2.10389	0.002965	50.28
1 0 5	25.9	3.43722	0.001744	81.62
1 2 1	26.88	3.31352	0.001221	11.68
6 0 4	28.79	3.09763	0.000698	20.53
8 0 4	31.57	2.83114	0.000174	82.67

Table 1: Table for strontium and paint based samples crystallite size, 2 theta values, d spacing and FWHM values.

If the size is increased, the tinting strength and the chemical resistance will be increased to the forensic tools. The evidence of the crime scenes have never destroyed by the over heat. It helped to get accuracy in the forensic examinations. Compared all the samples, Sample (a) and (b) is better than samples (c) and (d). It easily binds with the paint to coat. The other one is not fully dispersed. Crystallite size and miller plane values for certain peaks are given in the table. 1.

3.2 UV:

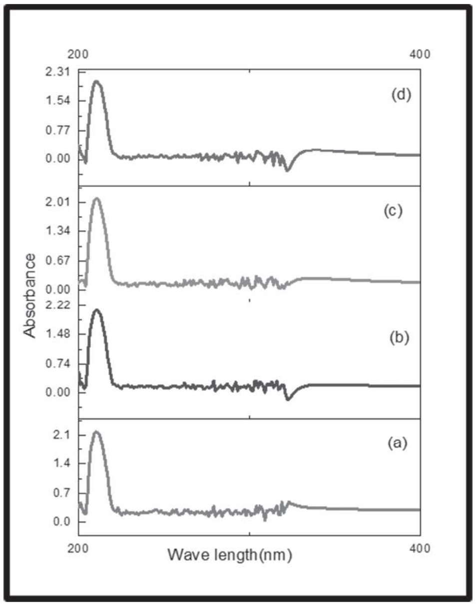

Fig 3. UV image for metal-based samples (a, c) and paint-based samples (b, d).

The maximum energy absorption was reported between 200 and 350 nm, for sample (a) and (b). In the present work, the bands were identified at 210 and 322 nm for the Sr based sample, and at 216 and 290 nm for the paint-based samples are indicated. The energy band gap (Eg) was calculated. The values found were 3.3 and 3.41 eV for paint based (b) and strontium based (a) samples, respectively.

For samples (c) and (d), between 200 to 350 nm, the maximum energy absorption was reported for sample (c) and (d) (Fig. 3). In the present study, the bands were located at 290 and 300 nm for Br based sample (c) and at 210 and 320 nm for paint-based samples with barium (d). The energy band gap was calculated. The highest absorption was noted at 210 nm for all the samples. The measured band gap for (a) and (c) is so close to (b) and (d). It is used to easily identify external compounds. Thus, it will be used to identify the crimes scene by the evidence easily.

3.3. FTIR:

Based on the IR spectra, these tools belong to the epoxy-polyester family containing strontium sulphate as filler. Even some differences are observed, the IR spectra showed similar fingerprint. Still, these differences are related to weak signals or variations in intensities. It is safer to test various independent methodologies to support or disprove these distinctions. X-ray microanalysis spectra (Fig. 4) were collected under the identical circumstances. It showed some changes in peak heights, similar to the IR spectra, although these differences should to be verified by additional analysis. Therefore, XRD was performed on these samples. The primary goal of determining whether any variations in the primary filler, strontium sulphate or barium sulphate, was dispersed.

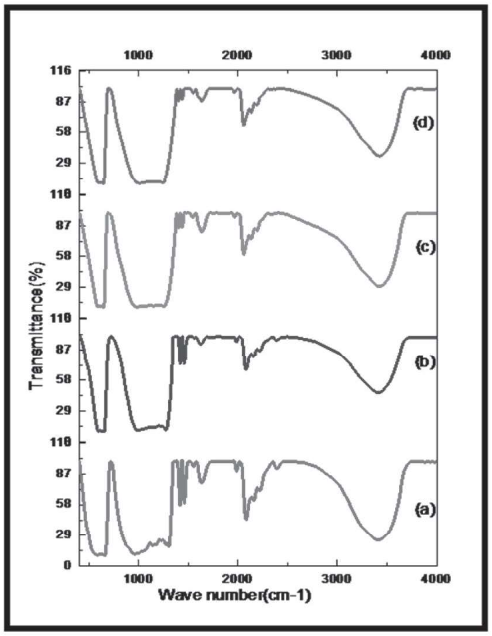

Fig.4. Infra-red image for metal based samples (a, c) and paint based samples (b,d)

The samples (a, b) showed the peaks at 3400 cm^{-1} due to the OH^- stretching. The peaks at 1462.83cm^{-1} and 1411 cm^{-1} was shown. Its due to the CH_3 in O- CH_3 bending and n- formaldehyde resin containing butylated melamine. In addition, the band at 2399cm^{-1}, 2078 cm^{-1}, 2081cm^{-1} and 2078.62 cm^{-1} showed the nitro cellulose paint. Presence of methine bending mode is proved by the peak formed at 1296.05 cm^{-1}. The combination of N- H bending mode and C- N stretching mode produces the peak at 1629 cm^{-1}. The peaks formed at 650- 670 cm^{-1} showed the presence of strontium in both the samples.

The samples (c, d) showed peaks at 550 cm-1 due to the presence of barium in both samples. The peaks at 1420 – 1650 cm^{-1} showed the methyl in methoxy stretching and the presence of calcium carbonate peaks. The peak at 1257.57 cm^{-1}, indicated the alkyd resin is present. Ethyl stretching mode peaks are formed at 3417 cm^{-1}. The peaks at 570- 650 cm^{-1} showed the barium presented in the samples. The peaks at 2057.90 and 2134.87 cm^{-1} showed the presence of nitrocellulose paint in the samples.

IR spectra revealed that sample (a) and sample (b) displayed every component in the paint, however, sample (c) and sample (d) did not. The bands in samples (c) and (d) are not visible. Hence, the components present in the samples are not determined.

3.4. RAMAN SPECTRA:

According to Forensic investigators, Raman spectroscopy to be a priceless and astonishing analysis technique that may be used with large number of different evidence. The typical Raman spectra of samples (a, b, c and d) are depicted in (Fig 5). The most dominating lines of the strontium based(a) and strontium with paint based(b) sample is around 981 cm^{-1} exhibits (C = C stretching area), which are completely same in phase vibration of the thiophene ring and span over the entire component, C– S – H ring deformation exhibits due to the band around 453 cm^{-1}. This vibrational signature shows that most of the electrons are either very confined inside the chain domain or primarily contained in each thiophene ring. The bands strongly located at 661cm^{-1}suggest the presence of S = O vibrational bonds.

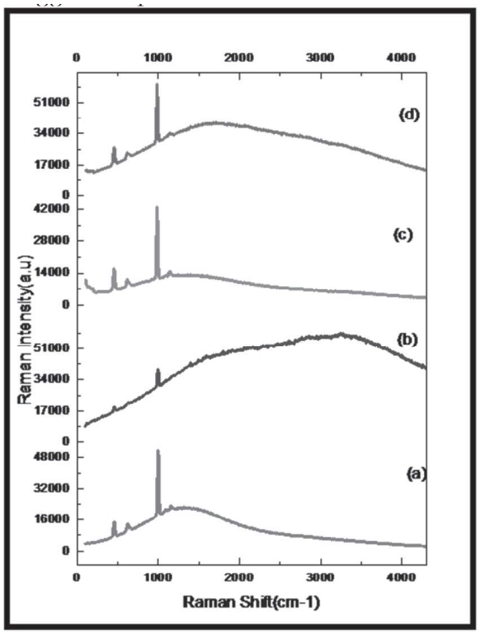

Fig.5. Raman spectra for metal-based samples (a, c) and paint-based samples (b, d)

The most dominating line of the barium based and barium with paint samples (c, d) are formed at 978 cm^{-1} (C- C Stretching). The band at around 440- 500 cm^{-1} formed, which exhibited S- S stretching. The band at 610 cm^{-1} showed the C- O bond. Presence of C= C is proven by the band formation at 1150 cm^{-1}.

3.5. SEM:

The morphology of as prepared Sr based sample (a) and Sr with paint-based sample(b) was investigated by Scanning electron microscope (SEM). Even, not all of the techniques are accessible in forensic laboratories and it is unclear if increased sensitivity would compensate for the local information provided by SEM/EDS examinations. SEM pictures taken at various magnifications (Fig. 6) showed equivalent distribution of charges. (Fig.5) revealed that non uniform square shape particles. The paint-based molecules make surface alterations with grows as heterogeneous long sized rod inside the surface. Each image shows the intensity scale that shows the depth and height along the Z- axis on the left side. Sulphur and oxygen interactions with strontium were proved and it depends upon the level of present in the prepared samples. It proved the sulphoxide paint present in the sample. Samples recorded at various magnifications The SEM images represented. Each images showed distinct and well identified non uniform crystal with different shapes.

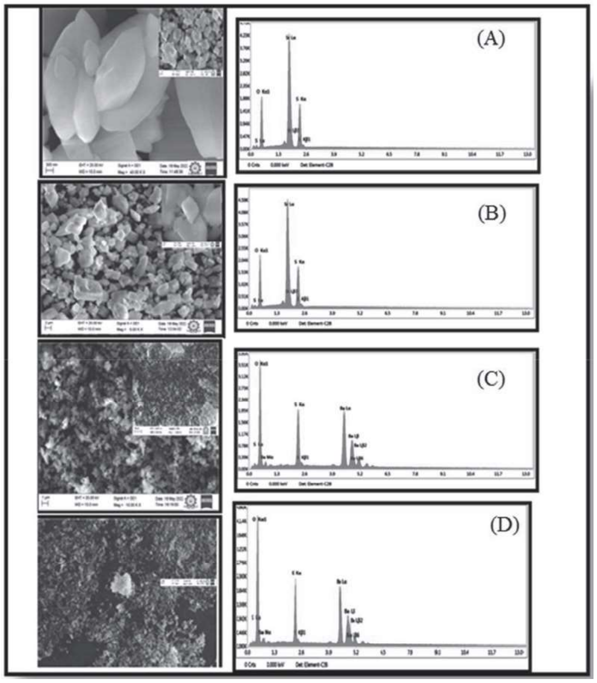

Fig. 6 SEM/ EDS images for metal based samples (a,c) and paint based samples (b, d)

At the same, barium based (c) and barium with paint based (d) samples were charcterised by SEM with EDAX. SEM image revealed the equivalent dispersion of the sample (c). And it was a non-uniform and randomly shaped particle. And, Barium with paint (d) based sample showed a unique spherical-shaped particles. Sulphur is one of the ingredients in the paint. Magnification, take off and live times, and errors ratio are all mentioned in the EDAX.

4. Conclusion

During the comparative analysis of tools from the same chemical family revealed that using statistical tests, this [Sr] % / [Sr] % ratio could distinguish five of the six pairs. The same method is done for barium sulphate samples (c, d). Like other analytical approach this method has limitations and should be used with caution in actual forensic cases, especially statistical tests, Are carry a risk of inaccuracy. To establish an opinion on whether a trace and a reference come from the same source. Overall, this study has demonstrated that XRD significantly improves paint analysis, especially in light of the following: i). Components present in a sample can still be revealed by XRD even if they are over the SEM/EDS limit.ii) the detection of correlations between elements provides further details during the characterisation of the paint, it allows the identification of chemical constituents and/ or the presence of contaminants; iii) the number of samples from the internal collection could be differentiated by XRD, even when they were not done so using other techniques. The findings of this work support a more cautious use of XRD on samples from our own collection than the application of this technology to characterise the real-world samples in the best manner.

5. References

[1] K. J. Kruglak, D. Mara, K. Brooke, V. Maxwell, A. J. Reffner, "The Evidentiary Significance of Automotive Paint from the Northeast: A Study of Red Paint". J. Forensic Sci., 1- 14, Jan 2019. http// doi:10.1111/1556-4029.14007

[2] L. Danny, M. Cyril, E. Pierre, M. Geneviève, "Combining spectroscopic data in the forensic analysis of paint: Application of a multiblock technique as chemomet ric tool". Forensic Sci. Int, vol 263, 39–47, 2016. http://doi:10.1016/j.forsciint.2016 .03.049

[3] Desiderio, Vincent J.; Taylor, Chris E.; DaÃcid, Niamh Nic (2020). Handbook of Trace Evidence Analysis || Paints and Polymers. , 10.1002/9781119373438(), 157–218. doi:10.1002/9781119373438.ch3

[4] K. B. Ferreira, A. G. Oliveira, J. A. Gomes, "Raman spectroscopy of automotive paints: Forensic analysis of variability and spectral quality", Spectrosc. Lett., Vol. 50(2) 102–110, 2017. http//doi:10.1080/ 00387010.2017.1288635

[5] L. V. Jungang, Z. Wen, L. Shuo, C. Rui, F. Jimin, Z. Songdong, L. Yong, "Analysis of 52 automotive coating samples for forensic purposes with Fourier transform infrared spectroscopy (FTIR) and Raman microscopy", Environ 17(1) 59–67, 2015. http//doi:10.1080/15275922. 2015.1091403

[6] Z. P. Janina, T. Beata, K. Paweł, " Comparative Analysis of Car Paint Traces in Terms of Color by VIS Microspectrometry for Forensic Needs". Anal. Lett, 43(3), 436–445, 2010. http//doi:10.1080/00032710903402358

[7] Z. P. Janina, M. Aleksandra, "Characterization of Blue Pigments Used in Automotive Paints by Raman Spectroscopy", J. Forensic Sci, vol 59(4) 943–949, 2014. http//doi:10.1111/1556-4029.12499

[8] R. K. Shelby, A. F. Marisia, M. Ewelina, A. Yasmine, H. Lenka, B. Justin, K. L. Igor, "Bloodstains, Paintings, and Drugs: Raman Spectroscopy Applications in Forensic Science". Forensic Chem., vol 1- 45, 2018. http//doi:10.1016/j.forc.2018.02.002

[9] F. Govaert, M. Bernard, "Discriminating red spray paints by optical microscopy, Fourier transform infrared spectroscopy and X-ray fluorescence". Forensic Sci. Int ,vol 140(1) 61–70, 2004. http//doi:10.1016/j.forsciint.2003.11.015

[10] F. Mylène, M. Vanessa, M. Cyril, "A random object-oriented population study of household paints measured by infrared spectroscopy". Forensic Sci. Int , vol 297, 72–80, 2019. http//doi:10.1016/j.forsciint.2019.01.045.

[11] Sébastien charles, Winterbui, Thomascanler, Alexandrecarnevali, Strontium in barium sulphate as a discriminating factor in the forensic analysis of tool paint by SEM/EDS, Forensic Sci. Int, Volume 331, February 2022, 111127. Https://doi.org/10.1016/j.forsciint.2021.111127

[12] M. Mark, M. James, C. Robert Bernard, B. Candice, "DART-MS: A New Analytical Technique for Forensic Paint Analysis", Anal. Chem., vol 1, 1- 27, 2018. http//doi:10.1021/acs.analchem.8b01067

[13] D. M. Wright, M. J. Bradley, A. H. Mehltretter, "Analysis and discrimination of architectural paint samples via a population study". Forensic Sci. Int., vol 209(1-3) 86–95, 2011. http//doi:10.1016/j.forsciint.2011.01.001

[14] M. Mark, V. B. Wilhelm, W. L. Simon, P. Kari, "Synchrotron FTIR characterisation of automotive primer surfacer paint coatings for forensic purposes", Talanta, vol 118, 156–161, 2014. http//doi:10.1016/j.talanta.2013.10.016

[15] D. J. Melo, S. N. G. Silva, S. M. Henrique, B. Candice, M. Mark, G. J. Andrade, "Automotive paint analysis: How far has science advanced in the last ten years", TRAC-Trend anal chem vol 132 1- 12, 2020. http//doi:10.1016/j.trac.2020.116061.

[16] B. Trzcińska, J. Z. Palus, P. Kościelniak, "Application of microspectrometry in the visible range to differentiation of car paints for forensic purposes". J. Mol. Struct , vol 924-926 , 393–399, 2009. http//doi:10.1016/j.molstruc.2008.10.037

[17] I. Nakai, Y. Ono, Q. Li, Y. Nishiwaki, K. Tanaka, S. Nakayama, "Capability of a TES microcalorimeter SEM-EDS system for forensic analysis of automotive paint and gunshot residue". Surf. Interface Anal ,vol 42(5), 402–410, 2010. http//doi:10.1002/sia.3113.

[18] M. Agnieszka, Z. Grzegorz, N. Tereza, M. Aleksandra, D. Nema, "Hybrid approach combining chemometrics and likelihood ratio framework for reporting the evidential value of spectra". Anal. Chim. Acta, vol 931, 34–46. 2016. http//doi:10.1016/j.aca.2016.05.016

[19] W. T. Chang, T. H. Chen, C. C. Yu, J. Y. Kau, "Comparison of embedding methods used in examining cross-sections of automotive paints with microFourier transform infrared spectroscopy", J. Forensic Sci. pp. 55-60, 2002.

[20] J. Z. Palus, R. Borusiewicz, "Examination of multilayer paint coats by the use of infrared, Raman and XRF spectroscopy for forensic purposes". J. Mol. Struct , vol 792-793, 286–292, 2006. http//doi:10.1016/j.molstruc.2006.03.072

[21] J.M. Challinor, "Forensic applications of pyrolysis capillary gas chromatography", Forensic Sci. Int , vol 21(3), 269–285, 1983. http//doi:10.1016/0379-0738(83)90132-9.

[22] P. Buzzini, G. Massonnet, S. Birrer, N. M. Egli, W. Mazzella, A. Fortini, "Survey of crowbar and household paints in burglary cases population studies, transfer and interpretation". Forensic Sci. Int , vol 152(2-3), 221–234, 2005. http//doi:10.1016/j.forsciint.2004.09.116

[23] A. M. Robert, "(Applications, Theory and Instrumentation) || Gas Chromatography in Forensic Science". Encyclopedia of Analytical Chemistry , 1- 27, 2006. http//doi:10.1002/9780470027318.a9097

[24] K. B Ferreira, A. G. G. Oliveira, A. S. Gonçalves, J. A. Gomes, "Evaluation of Hyperspectral Imaging Visible/Near Infrared Spectroscopy as a forensic tool for automotive paint distinction". Forensic Chem., vol 5, 46–52, 2017. http//doi:10.1016/j.forc.2017.06.001

[25] G. Payne, C. Wallace, B. Reedy, C. Lennard, R. Schuler, D. Exline, C. Roux , "Visible and near-infrared chemical imaging methods for the analysis of selected forensic samples", Talanta, 67(2), 1–344, 2005. http://doi:10.1016/j.talanta.2005.03.042

[26] T. Mukai, H. Nakazumi, S.I. Kawabata, M. Kusatani, S. Nakai, S. Honda, Direct Identification of Various Copper Phthalocyanine Pigments in Automotive Paints and Paint Smears by Laser Desorption Ionization Mass Spectrometry. J. Forensic Sci , vol 53(1), 107–115, 2008. http//doi:10.1111/j.1556-4029.2007.00626.x

[27] N. C. Scherrer, Z. Stefan, D. Francoise, F. Annette, K. Renate, "Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection". Spectrochim. Acta A Mol. Biomol. Spectrosc. , vol 73(3), 505–524, 2009. http//doi:10.1016/j.saa.2008.11.029

[28] L. Huang and D. Beauchemin, "Forensic analysis of Automotive paint chips for the identification of the vehicle manufacturer, colour and year of production using electrothermal vaporization coupled to inductively coupled plasma optical emission spectrometry", J. Anal. At. Spectrom, 1- 7, 2017. http//doi:10.1039/C7JA00196G

[29] K. A. Kopchick, C. R. Bommarito, "Color Analysis of Apparently Achromatic Automotive Paints by Visible Microspectrophotometry". J. Forensic Sci , vol 51(2), 340–343, 2006. http//doi:10.1111 /j.1556-4029.2006.00050.

[30] M. Szafarska, M. Woźniakiewicz, M. Pilch, J. Z. Palus, P. Kościelniak, "Computer analysis of ATR-FTIR spectra of paint samples for forensic purposes". J. Mol. Struct , vol 924-926, 504–513, 2009. http//doi:10.1016/j.molstruc.2008.11.048

[31] M. Bovens, B. Ahrens, I. Alberink, A. Nordgaard, T. Salonen, S. Huhtala, "Chemometrics in forensic chemistry — Part I: Implications to the Forensic Workflow". Forensic Sci. Int , 1- 38, 2009. http//doi:10.1016/j.forsciint.2019.05.030

[32] L. Ortiz-Herrero, I. Cardaba, S. Setien, L. Bartolomé, M. L. Alonso, M. I. Maguregui, "OPLS multivariate regression of FTIR-ATR spectra of acrylic paints for age estimation in contemporary artworks". Talanta, 205, 1- 11, 2009. http//doi:10.1016/j.talanta.2019.120114

[33] M. Aleksandra, M. Agnieszka, Z. P. Janina, Z. Grzegorz, "Application of a likelihood ratio approach in solving a comparison problem of Raman spectra recorded for blue automotive paints". J. Raman Spectrosc., 46(9), 772–783 2015. http// doi:10.1002/jrs.4719.

[34] Abdel-Maksoud, Gomaa; Ibrahim, Medhat; Issa, Yousry M.; Magdy, Mina (2020). Investigation of painting technique of Coptic icon by integrated analytical methods: imaging, spectroscopic and chemometric methods. Journal of Archaeological Science: Reports, 29(), 102085–. doi:10.1016/j.jasrep.2019.102085

[35] Lavine, Barry; Almirall, Jose; Muehlethaler, Cyril; Neumann, Cedric; Workman, Jerome (2020). Criteria for comparing infrared spectra â" A review of the forensic and analytical chemistry literature. Forensic Chemistry, 18(), 100224–. doi:10.1016/j.forc.2020.100224

[36] P. Buzzini, G. Massonnet, “A market study of green spray paints by Fourier transform infrared (FTIR) and Raman spectroscopy” , Sci. Justice., vol 44(3) 123–131, 2004. http//doi:10.1016/s1355-0306(04)71704-9

[37] C. Muehlethaler, G. Massonnet, P. Esseiva, “The application of chemometrics on Infrared and Raman spectra as a tool for the forensic analysis of paints”. Forensic Sci. Int, vol 209(1-3) ,173–182, 2011. http//doi:10.1016/j.forsciint.2011.01.025

[38] L. Danny, M. Cyril, E. Pierre, M. Geneviève, “Combining spectroscopic data in the forensic analysis of paint: Application of a multiblock technique as chemometric tool”. . Forensic Sci. Int , vol 263, 39–47, 2016. http//doi:10.1016/j.forsciint.2016.03.049`

[39] Y. Nishiwaki, S. Watanabe, O. Shimoda, Y. Saito, T. Nakanishi, Y. Terada, T. Ninomiya, I. Nakai, “Trace Elemental Analysis of Titanium Dioxide Pigments and Automotive White Paint Fragments for Forensic Examination Using High-Energy Synchrotron Radiation X-Ray Fluorescence Spectrometry”. Forensic Sci. Int , vol 54(3), 564–570, 2009. http//doi:10.1111/j.1556-4029.2009.01005.x