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An Instrumental Approach for Analysing Automotive Paint – A Review

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Abstract
Hit and Run cases are reporting in almost all the countries with or without intention to cause hurt. In most of the cases eye witness or video documents (CCTV) may neither be visible nor reliable. Paint chips available at the scene of occurrence may only be the piece of information that is available to track down the culprit. The study focused on reviewing automotive paint analysis from 2015-2020 year and assessed various sample collection, technique used for analysing, advancement in technologies, challenges etc. Most commonly used instrument in our study selection is Raman spectroscopy and FTIR in automotive paint analysis. The various advanced instruments and its challenges in the field of forensic investigation has also been reviewed . In summary the given study will provide basic details of paint analysis using various instruments and its effective significancein the field of Forensic investigation.

INTRODUCTION

Accidents involving automobiles is increasing day by day and also crimes involving automobiles get sky rocketed. In Hit-and-run cases, it's been observed that the party responsible for the accident often run off from the place where it occurred, technically from the scene of crime. Therefore, the investigating officer must rely on other information to identify the culprit and vehicle involved in the case. Parts of vehicle such as pieces of bumper, glass pieces (Head/Tail lamp, side mirror etc), skid marks can provide potential information about the vehicle and also eye witnesses, CCTV cameras could provide crucial information about time, colour and other details of the vehicle. However, in many instances only paint chips are peeled off from the suspect vehicle due to collision and recovered from the scene of crime. These trace evidences can provide much information about the vehicle involved in the case such as type of vehicle, company, make and model, year etc. So, paint analysis in Forensic science have a serious role in investigation and prosecution of cases involving Hit-and-Run incidents.

The ultimate aim of paint analysis is to identify and corroborate the suspect vehicle involved in the crime thus, features of paint chips describes the nature of paint on the car that is individualistic in nature. The analysis may either compare the collected evidence sample with control sample or with the content in database. The most extensively used procedure for identification of automotive paint analysis are 1) Preliminary includes a) Optical examination to identify the features, Number of Layers, Original Equipment Manufacturer (OEM) or After Spray, The IR spectrum of each layer of the collected automotive paint is compared with the data of control sample or with the IR Spectrum of added reference paint sample in the database. For example, the Paint Data Query (PDQ) from the Royal Canadian Mounted Police (RCMP), international Original Equipment Manufacturer (OEM) automotive paint

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database having nearly 23000 known paint library and the European Paint Group (EPG) database from the European Network of Forensic Science Institutes (ENFSI). Automotive paints typically have three or four layers and varies from make/model of manufacturer to manufacturer. One or more undercoats, topcoat and clearcoat on the surface and each layer have organic pigments, additive and binders. The components present in the various layers can be identical and thus, individualisation of vehicle by its automotive paint is boon for investigators.

Analytical instruments are well utilized in Forensic Automotive paint analysis especially, vibrational spectra of compound present in the automotive paint is done by FT-IR[11,14,17]. Application in minute sub visible paint particle and its interpretation during Forensic analysis have been practically exposed with a live case in the study using FT-IR by the author[18].For Paint Data Query (PDQ) the author have collected vibrational spectra of 1000+ clear coat samples from various automobile manufacturers with production year 2000-2006 and using search prefilters to identify the details as per its IR spectrum [2]. Pattern recognition prototype is the advanced form to search similar at the same time non identical IR spectral library of paint data query, basic idea was to narrow down the library results also to identify all the details including manufacturing plant, year, model etc. [3,4,6] Fourier Transform Infrared Spectroscopy and Raman Spectroscopy[11,12] are most common used instruments in paint analysis as per literature, but other instruments are also used[17,15]. The combination of traditional instruments is to get appropriate results using already validated technologies to cost minimum in all aspects including time and money[21,25]. The author classified the surface clear coat and characterised using Raman Spectroscopy, also categorized active principle component and linear component for forensic purpose[20], Likelihood Ratio (LR) has been applied in comparing Raman spectra to reduce the issues faced during comparison of blind and normal spectrum of same colour[29]. Features of Raman Spectroscopy and its use in different fields including paint analysis have been discussed by the authors, absolute eye catching nature of the instrument is less sample preparation and mass data of the substrate in short time, its non-destructive nature is highly appreciated in Forensic analysis of paint and dyes[32,33]. Py-GC-MS[24] is another technique used to analyse paint, high discriminating power, ability to distinguish acrylic-melamine coat from other coat is a special feature of Pyrolysis Gas Chromatography and also capable of discriminate five colours of automotive paint with combination of PCA[28]. The only drawback of this method is destructive in nature. Scanning Electron Microscopy (SEM)[17,18,39], energy dispersive X-ray spectroscopy (EDS) and X-ray Fluorescence (XRF) is well known for elemental analysis of paint. Other analytical instruments such as IR Spectroscopy[10,15,39], IR Micro spectroscopy[10], DART-Q-TRAP MS/MS[16,22], ETV-ICPOES[28], OCT[35,40],TOF-Sec-MS[23], HIS[19], HIS Vis/Near IR[19].

METHODS

Search Action

An organized search was conducted for articles related to the particular topic includes ‘Paint, Automotive paint’, Paint Analysis’, ‘chemical paint’, ‘Paint layers analysis’, in ‘PubMed’, ‘Google scholar’, ‘Web of sciences’ and ‘Research gate’. A comprehensive search methodology was used to put together all the criteria included in the review and beside the

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point are excluded. Preliminary investigation in Google Scholar gave up auxiliary unique results respect to particular topic; therefore, the investigation for journal was restricted to PubMed, Web of science and Research Gate and data published year are closely monitored for recent advancement in automotive paint analysis.

Study Selection

The search results from the database gave back 327 articles from PubMed. A supplementary 39 journal reports and articles were received from Web of science and 67 from Research Gate, relevant to the study criteria. These contents were analysed independently. 433 articles were included for the study, and 299 were removed due to their insignificance to the pertained topic. The complete texts of 134 articles were scrutinized for inclusion, and 90 were rejected in final scrutiny, and irrelevant time period by reason of reiteration of information. 44 journal report from the initial search action were used in the study selection.

DATA RESULTS

The articles have been segregated into 12 clusters based on the instrumental techniques used for automotive paint analysis in last five years. The advancement in analytical techniques, complexity of interpretation, etc could be identified from these clusters. Most of the authors used multiple instruments or conducted novel assessments to improve the data quality and identification of components present in the automotive paint sample. The cluster made is independent of selected journal under consideration, ie, Study involved with multiple instruments are selected separately and each instrument are segregated to respective cluster.

Cluster Number	Instrument Used	References
1	FTIR	2,3,4,6,8,9,11,14,17,18,39
2	IR SPECTROSCOPY	10,15,39
3	IR MICRO SPECTROSCOPY	10
4	ETV ICPOES	28
5	OCT	35,40
6	RAMAN SPECTROSCOPY	11,12,14,15,17,20,21,25,29,32,33
7	DART TOF MS	16,22
8	HSI Vis/Near IR	19
9	HIS	19
10	SEM EDS	17,18,39
11	Py GCMS	24
12	TOF Sec MS	23

Table 1

Paint Layers

Modern automotive paint (Original Equipment Manufacturer consist of four layers; primer, surfacer, basecoat and clear coat. The primer surface is close to metallic body of the automobile. Basecoat contain pigments and often metallic parts too. The function of clearcoat is to provide protection to the layers beneath. *Barry K. Levine et. al*conducted their four studies for PDQ search library pre filters using FTIR and Other instruments on clear coat

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samples. Their studies have always been novel for the advancement of PDQ Library. The team have been analyse 1312 clear coat samples from various automotive companies for identification and establishing features of the clear coat layers from automotive companies to companies [2,3,4,6].. Most of the studies under investigation established the elemental composition and features of each paint layers using multiple instrument often with FTIR or Raman Spectroscopy due to their rapid analysis and less sample preparation [11,14,17]

Effect of Weathering

Very few studies only considered the effectiveness of weathering and rusting of sample. The samples might have faced various climatic conditions like extreme temperature, rain, low temperature, snow, humidity etc. The effect may be serious or less. The samples never showed any changes for a year but significant changes have been showed after exposing to extreme climates. The study using rusted and non-rusted blind samples analysed by ETV ICPOES destructive technique but author found different from other. The author suggested that the study in such cases should be considered from inner layers of the paint not from outer due to impact of weathering[28]. Some studies have been suggesting about collecting samples from paint from metallic base (bonnet, roof) than collecting the automotive paint samples from plastic or fibre surface.

COMPARISONS AND FEATURES OF INSTRUMENT

FTIR (Fourier-transform infrared spectroscopy)

The 11 Authors conducted their paint analysis on FTIR and *Barry K. Levine et. al*authored 6novel studies focusing on FTIR (Fourier-transform infrared spectroscopy). The positive consideration of FTIR in automotive paint analysis is due to minimal sample preparation, and a major advantage. The research journal focuses on pattern recognition and search pre filters to assist library search by *Barry K. Levine et. al*adopted three FTIR instruments (Thermo-Nicolet 6700s, BioRad 40A or BioRad 60 FTIR with a DTGS detector)[2,3,4,6]. 1314 clear coat samples were analysed by transmission mode. Slight variations are observed from instruments due to difference in software used in them. The wavelets are analysed by MATLAB Wavelet toolbox 3.0.4[2]. All the study by*Barry K. Levine et. al*ease the investigative procedure for identification of automotive paint by instruments and identifying them by Paint Data Query (PDQ). Attenuated total reflectance FTIR (ATR FTIR) is helpful in rapid analysis due to less sample preparation and use of reflectance needle, the conversation algorithm is much helpful in converting the spectrum obtained in transmission to spectra obtained in ATR mode for comparison. *Jungang LV et. al*conducted 52 sample analysis by FTIR, on their study 8 resin in the paint were identified[14]. All the authors have been stretched on IR Spectroscopy especially FTIR due to its less sample preparation and rapid analysis[11,14,17].

Raman Spectroscopy

Anothercommon instrument used in automotive paint analysis under study is Raman spectroscopy, FTIR and Raman Spectroscopy are frequently used instruments. One study conducted criticized for inability to find resins present but at the same time identified and interpreted the additives and pigment dyes present in the substrate[14]. The exact peak of

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various pigments was accurately found. Some important pigments including Lead chromate that could also create contamination to nature were also identified and discussed[14]. Another study combined with Raman spectroscopy, SEM EDS, ATR FTIR resulted in easy interpretation and analysis of data. Identification of pigments and elemental analysis made easier using combined application on interpreting composition in automotive paint[17]. Major studies compared the discriminating power of FTIR and Raman Spectroscopy, using statistical data of large number of samples analysed it is concluded that discriminating power (DP) is higher in Raman Spectroscopy. An effective identification of vehicle involved in Hit and Run cases were analysed by FTIR and confocal Raman spectroscopy. The study criticized inability of identifying some pigments by FTIR and at the same time identifying and discriminating all pigments present in the study helped in identifying the vehicle involved in the hit and run case samples[12,15,45].

Scanning Electron Microscopy

SEM is having an important role in elemental analysis of paint. The elemental composition on each layer and identification can play a major role in identifying the composition[17,39]. SEM EDS allows easy, effective and rapid analysis without a proper sample preparation[17]. An author details about a case was suspecting a blue car collided with grey surface and task was to analytically prove contact on either of them. The samples were Analysed through FTIR, Raman Spectroscopy and Sem EDX. Elemental analysis of samples gave positive identification of C, O, N, Al, Si, S, Ca, Ti/Ba in the substrate[18]. These gave significant information about positive chances of cross sampling. So location, identification and comparison through SEM EDS can be highly effective in investigation but at the same time combined action with other instruments give authenticate results[18].

Other Instrumental Techniques

Every instrument has its own limitation when it comes to reality. To overcome this issue the forensic experts combines the instrument with other to provide sophisticate nature. This may result in time loss, destruction to sample (egPyGc) etc. Deploying advanced instruments may result accurate result within less time or replace some instrument's deficiency. Direct Analysis in real time-time of flight Mass Spectroscopy (DART TOF MS) could be considered as a substitute of destructive technique Pyrolysis Gas Chromatography [22]. Another study was conducted by Direct Analysis in real time coupled to Q-orbitrap tandem mass spectrometry was helpful in pigment analysis without any pre-treatment at the same time the instrument found to be rapid, effective and even less quantity was identified. The study was also included FTIR which provided information about resin, content and extenders[16].Hyperspectral Imaging Visible/Near IR Spectroscopy enables spatial and spectral information about sample [19]. Slight scratch and impurities can lead to differet results. Fluorescence images are illustrated and observed through the help of instrumentation[19]. Time-of-flight secondary ion mass spectrometry (ToF-SIMS)The instrument is highly chemical sensitive for Principle Component Analysis (PCA)[23]. Electrothermal vaporization coupled to inductively coupled plasma optical emission spectrometry (ETV-ICPOES) the sample under investigation are rusted as well as non-rusted. The author concluded the robustness of the analytical technique by comparing the samples

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with blind samples[28]. The major drawback of the analytical instrument is the sample under investigation is destroyed during analysis ie, destructive in nature and organic compounds does not fall under interest.

DISCUSSION

The ultimate intention behind the study over a particular period to details the advancement in automotive paint analysis over last five years (2015-2020) at the same time introduction of new analytical instruments that are commonly used in other field to automotive paint analysis. By analysing the introduction of new instruments, it is possible to compare the pros and cons of using the instrument and ability to replace the traditionally used instruments. Some factors considered for usage of instrument is less sample preparation, sensitivity, rapid analysis, ease of the access etc. The traditionally used instruments are commonly discussed by authors, the use of FTIR, Raman spectroscopy are discussed often with other sophisticated instruments to check and detail for comparison purpose with criteria. It is been observed that Raman and FTIR spectroscopies are inevitable in research process include any sort of paint analysis, almost all peculiarities of traditionally used instruments such as IR spectroscopy are already been known to public. Most common instruments are highly chosen by forensic practitioner for building up database which is highly useful for identifying vehicle involved in any cases with no control sample for comparison. Some authors have developed algorithm to convert one emission spectrum to ATR spectrum of FTIR that may useful in involvement of two different instruments and to compare with same library spectrum.

Several considerations to be made before selection of instrument, sample of interest and its origin. Layers of paint, weathering are few parameters considered by authors before choosing instrument and comparison. The changes due to weathering is highly important in paint analysis, the extent up to which layers the changes have been occurred, destruction caused to superficial layers are few considerations made by authors.

Most of the samples collection methods are valid, the researcher mostly obtained from Forensic laboratories or police offices, that made authenticity to the samples and indirectly gave supervision to the sample collection from experienced officers.

The journals showed the importance of automotive paint analysis in very crucial circumstances where the paint chips are only link between ‘scene of crime-victim-culprit’ the advancement of analytical instrumentation combined with traditional instruments leads the path for future analysis that would minimize the defects, minimize the laboratory time, less sample preparation and provide accurate results.

Progression of algorithm and employing multi-spectral database (portable field instruments and non-portable laboratory instruments) will definitely improve the accuracy and develop automotive paint analysis section of Forensic Science. Researchers also consider the multi variant standardized analysing methodology to develop new database on emerging instruments in the field of automotive paint analysis and also development of comparing software with different instrument working on same principle even though its hard to develop.

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CONCLUSION

Our study focused to detail recent advancements in forensic analysis of paint analysis in last five years. Raman spectroscopy and Fourier Transform Infrared Spectroscopy is the most common used instruments and considered as traditional instruments used in forensic practise of paint analysis. Other instruments and its applications have been included in the study for better understanding of progress in the paint analysis such as OCT, SEM EDS, ETV ICPOES etc. The commonly used analytical instrument should primarily considered for establishing database however, availability of convenient instrumentation after proper validation must be considered. Challenges like natural weathering, origin of sample that may chemically alter the comparison of paint chips should be separately analysed. Overall, future instruments are more sophisticated and portable, rapid analysis with less sample preparation from the scene of crime itself is a research perspective with respect to making paint database and validation over challenges.

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