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Evidence Type
Paint and Glass

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Introduction

The importance of paint and glass as physical evidence, has been recognised for quite some time. In fact, these are one of those forensic materials which have engaged the attention of crime investigators and concerned scientists since inception of the forensic science laboratories, and have always played important and crucial role in crime investigation. The physical and chemical methods of analysis of paint and glass have been improved, revised, and updated with the advancements in instrumentation and technology, from time to time. The clue materials paint and glass, in general, are used to connect the criminal with the crime, by linking the crime scene/victim and the suspected person/vehicle/tools. This is achieved by comparing two or more samples to establish their source correspondence. The desired characterisation/individualisation of glass and paint is the ultimate goal of their forensic analyses. The advances made in this direction during the period between the 11th and 12th Interpol Forensic Science Symposia have been reviewed. This review is based on literature search covering articles published in core forensic journals during this period, and on the responses from scientists working on evidence types paint and glass. The advances reported here under the heads 'Paint' and 'Glass' are further grouped. The grouping is not very rigorous, these are instinctive groups, for the sake of convenience of presentation.

Paint

Paint as a physical clue is frequently encountered in hit-and-run, burglary, art forgeries, and other offences. A paint chip or a paint smear may be transferred to the victim or left at the scene of accident, or paint smear could be transferred on to a tool during commission of a burglary. There are numerous possibilities and situations under which a transfer of paint from one surface to another could occur. Routine forensic examination of paint enables identification of organic and inorganic composition of each paint layer. The recent trends in forensic examination of paint is summarised below.

Infrared Spectroscopy

Microspectroscopy in infrared has come to play a very important role in the examination of paint samples. It has been used in the past also by many workers to generate chemical compositional data on automotive paints. A survey of U.S. automobile original topcoats (1974-1989) for binder and pigment compositions has been conducted using infrared spectroscopy (1-7). Data were obtained from panels of the Reference Collection of Automotive Paints for single layer topcoats, excluding base coat/clearcoat finishes. The FT-IR instruments were used for recording the absorption spectra.

Suzuki (1) studied occurrence of acrylonitrile, a copolymer used in some acrylic melamine enamels, and iron ferrocyanide, an inorganic pigment used in some blue and green paints. Both of these components produce characteristic C≡N stretching fundamentals, which occur in a spectral region devoid of other significant absorptions, and hence they are usually easy to detect and assign. Acrylonitrile absorptions occur predominantly for some topcoats, used on certain make of vehicles manufactured in U.S. before 1985. This may be of particular significance in some cases. Polyurethane isocyanate N=C=O stretching absorptions, which also occur in this same spectral region, were not detected for any of the topcoats of this study.

During the course of the above study a number of prominent unidentified absorptions were observed in the infrared spectra of some automobile original topcoats from the reference collection. These absorptions did not appear to arise from binders or binder related components. Often, a particular group of unknown absorptions appeared only in the spectra of some topcoats having certain colours, which suggested that they arose from pigments responsible for, or contributing to, those colours. Also, in some cases, same absorptions occurred in the spectra of topcoats of different colours suggesting a combination of two colours to produce a third one. Thus, most of the unidentified absorptions appear to arise from specific colour imparting pigments, but with the exception of ferric oxide, talc, and diatomaceous silica, they could not be attributed to any pigments previously identified in automobile paints using infrared spectroscopy. All of those previously identified, however, were pigments used in undercoats. The unidentified absorptions were analysed and several inorganic pigments used in automobile topcoats were identified (3). These are ferric oxide, hydrous ferric oxide, Chrome Yellow, Molybdate Orange, and silica-encapsulated lead chromate pigments. Three extender pigments used as flatting agents, talc, diatomaceous silica, and synthetic silica were also identified in a few black semigloss non-metallic topcoats. Lead chromate (Chrome Yellow) pigments, which were found in many reference collection yellow, orange, and red non-metallic topcoats, are no longer used in U.S. original finishes. Their presence can thus serve as both a means to differentiate between topcoats and provide some indication of when certain topcoats may have been produced. Simultaneous identification of both binders and pigments was possible for many topcoats. The far infrared region below 700 cm^{-1}, which cannot be observed when using a narrow band mercury cadmium telluride (MCT) detector, was found to be important for the analysis of topcoats containing certain inorganic pigments.

It was further observed that inorganic pigments were responsible for only some of the unidentified absorptions in the infrared spectra of topcoats from the reference collection. Unlike the inorganic pigment absorptions, which were usually broad and a few in number, the remaining unidentified absorptions were sharp and numerous, indicative of organic compounds. Because these peaks are narrower than most binder absorptions, the method of spectral subtraction was used to help delineate pigment peaks obscured by binder features (5). Using this technique, several organic pigments were identified in some yellow, orange, red, and brown non-metallic topcoats, and a few brown metallic ones. Four of the benzimidazolone pigments were identified in single layer topcoats from the reference collection of automotive paints. The pigments and the types of finishes in which they were identified (given in parentheses) are: Benzimidazolone Orange (non-metallic orange, red, and brown), Benzimidazolone Yellow 3G (non-metallic yellow and orange), Benzimidazolone Yellow 4G (non-metallic yellow), and Benzimidazolone Brown (metallic brown). Benzimidazolone Orange is the most common of these. In cases in which the pigment peaks are prominent, the specific pigment responsible can usually be identified based on the peaks observed between binder absorptions or superimposed upon them, without having to use spectral subtraction. This is possible even when absorptions of two or

more pigments are present. Absorptions of benzimidazolone pigments were not observed in the spectra of any reference collection topcoats produced before 1977. Use of the benzimidazolones, especially Benzimidazolone Orange, increased in the 1980s because they were common replacements for lead chromate pigments, which were phased out of use in U.S. automobile original finishes during this period. Topcoats containing some benzimidazolone pigments may exhibit band broadening and other changes when subjected to excess pressure, and this possibility should be considered when such topcoats are analysed.

The technique of subtracting spectra of closely matched topcoats lacking pigment features from the spectra of topcoats containing the pigment of interest, for isolating pigment peaks, was further extended to identify several different quinacridone pigments used in red and brown non-metallic and metallic monocoats (7). Four of the quinacridone pigments were identified in some U.S. automobile original finishes from the reference collection. These are: Quinacridone Red Y, Quinacridone Violet, Quinacridone Magenta, and Quinacridone Magenta B. The Quinacridone Red Y and Quinacridone Violet are two polymorphic forms of the same unsaturated quinacridone ring structure, but they have noticeably different colours and distinguishable spectra. These were found to be common in red non-metallic topcoats. Quinacridones were also identified in brown non-metallic, and red and brown metallic finishes.

Elemental analyses using XRF spectrometry were also performed on most of the topcoats together with infrared spectroscopy. For inorganic pigment identification, elemental analyses provide information that is particularly appropriate to confirm, clarify, or augment the infrared results. In the case of organic pigments as well, the elemental analysis is quite revealing because inorganic pigments are frequently used with organic pigments.

The survey has focused on some spectral features that may be used to rapidly and unambiguously classify topcoats. As a prerequisite to the analysis of pigments using this in situ method, analysts should be very familiar with the absorptions of automotive topcoat binders. Analysts who use infrared spectroscopy for paint examination on a regular basis and who routinely identify binders by this means are likely to find this an easier task than those who rarely use this technique, or those who use infrared absorption patterns in strictly a comparative mode without attempting to identify binders and pigments.

The method of spectral subtraction was used to help visualise and clarify pigment absorptions and distinguish them from those of binders. This method may be useful tool for identifying unknown pigments in reference collection (known) topcoats, but this would probably be less useful for actual case samples because the binder composition itself is usually in question and choice of an appropriate subtrahend spectrum becomes much more of a problem.

Zieba-Palus (8) used FT-IR Microspectrophotometry and SEM-EDX for the examination and discrimination of multilayer fragments of automobile paints.

Chromatography and UV/Vis Spectroscopy

In forensic examination of paints, the identification of organic pigments and their semi-quantitative analysis is necessary for comparison of paint samples from the suspect vehicle and paint fragments from victim/place of occurrence. The separation of pigments by chromatographic techniques and their identification by UV/Vis spectroscopy have been attempted by several workers.

Massonnet and Stoecklein (9) developed a procedure for chromatography of light-fast polycyclic pigments (phthalocyanines, quinacridones, perylenes, perinones, dioxazines, indanthrones, isoindolinones, benzimidazolones). The pigments are converted into mobilizable

onium compounds with trifluoroacetic acid/water and separated onto C_{18}-reversed phase plates. Organic paint pigments mainly used in the automotive industry are separated by thin layer chromatography and identified by means of their respective rf values. The visible spectrum of each pigment recorded directly on the TLC plate (TLC spot) gives complementary information. A computerised database including the rf values and the visible spectra of each pigment was also created in order to help their identification. The use of HPLC and TLC methods for the analysis of automotive paint pigments have been investigated by others (10,11) also.

Voskertchian (12) used visible spectrophotometry to determine qualitative and quantitative composition of small paint fragments (7-15 micrograms) containing different phthalocyanine (copper and metal-free) pigments and their mixture. The results show that spectrophotometry offers a high degree of identification for phthalocyanine pigments in paint fragment.

The use of microspectrophotometry in the UV range (240-400nm) has been explored by Stoecklein and Fujiwara (13) to distinguish clear coats from 2-coat metallic and non-metallic paint systems by tracing UV-absorbers down to the nanogram range. The light stabilisers (UV-absorbers and radical scavengers) are used by the paint manufacturers in 2 coat systems for automotive paints to protect the paint against gloss reduction, cracking, delamination, yellowing and blistering. At the same time, the weather resistance of organic pigment is improved. The car manufacturers use paints with different UV absorbers. The migration of the UV-absorber into the basecoats in connection with the wet in wet applications adds further to the distinctive features of the light stabilisers, as this changes the absorption characteristics. Additional possibilities of differentiation are provided by the varying decrease of UV-absorber concentrations with time. The analysis of UV-absorbers allows the possibility of distinguishing between vehicles which were originally painted in an identical manner and which were indistinguishable by methods like IR-spectrometry, pyrolysis GC-MS and SEM/EDX. This method yields informative data suitable for comparative study of paint fragments.

Colour Comparison

The colour, structure, and texture are three of the parameters used in microscopic comparison of paint fragments. The potential use of image analysis to evaluate these parameters was explored by Munro (14).

A digital imaging system for colour measurement and comparison of motor vehicle topcoat paints was explored by Cappelli (15). Imaging software can provide histogram for a given colour image. A histogram gives the frequency distribution of intensities of image's colour channels (Red, Green, Blue, Hue, Saturation, Value, Intensity). Histograms and Accumulated Histograms were developed from acquired colour images in order to compare paint samples and confirm visual colour matches. This technique can be used to remove the subjectivity associated with the human perception of colour.

Thornton (16) reviewed the fundamental elements of colour perception and colour comparison systems. The pitfalls in colour perception and colour discrimination were also discussed to illustrate the application and limitations of colour comparisons.

X-ray Fluorescence and X-ray Diffraction

The X-ray Diffraction technique was used to examine inorganic crystalline materials form the bulk of repaint primer by Edmondstone (17) to evaluate its potential to discriminate

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between different inorganic pigments and extenders. Fifty-three samples of repaint primer were examined, either as intact chips or as a small (50μg) amount of primer scraped from a paint chip and pressed flat onto the sample support. Talc was identified in all the samples. The following components were identified in more than one sample: kaolin, rutile, $BaSO_4$, $Zn_3(PO_4)_2.4H_2O$, $MgCO_3$, dolomite, chlorite, calcite, red iron oxide, yellow iron oxide and zinc oxide. The minerals magnesite ($MgCO_3$), dolomite ($MgCa(CO_3)$) and Chlorite (Hydrous magnesium aluminium silicate) are difficult to identify by elemental techniques in the presence of a large amount of talc (magnesium silicate). It was observed that the identification of crystalline materials by XRD provides a simple and non-destructive method of characterising automotive repaint primers in a manner that other techniques cannot.

Massonnet (18,19) analysed samples of metallic automobile paint in the form of multilayer chips, collected from 51 vehicles involved in traffic accidents over a period of two years, by energy dispersive X-ray microfluorescence (XRMF) and X-ray diffraction (XRD). The relative discriminating power of each technique was evaluated. The results indicated that these two techniques are well adapted to the analysis of metallic automobile paint and have the advantages of being non-destructive, relatively rapid, and complementary. Of the 51 samples analysed, only two pairs could not be differentiated by both instrumental methods. In addition, the results appeared to be independent of the make and model of vehicle. As a single technique, the semi-quantitative analysis by X-ray microfluorescence proved to be a very powerful tool for the forensic examination of metallic automobile paint and it is suggested that further work be conducted in this area.

RamJanam et al.(20) analysed fragments of red paint collected from various sources, by X-ray Diffraction technique to evaluate its discrimination potential. It was observed that XRD could be a complementary technique used together with other methods of analysis for comparison and discrimination of paint samples.

Miscellaneous

Mccrone (21) has described the history of titanium white pigment used by artists, and its importance in the examination of art forgeries. Titanium white is one of the most important pigments used by artists. Its presence in different polymorphic forms and as co-precipitates or pure, make it a most useful substance for microscopists interested in art forgeries. The presence of submicron titanium white pigment in a painting ensures a post-1920 painting. By noting the presence of barium sulfate as a co-precipitate and the crystal form, anatase or rutile, then permits further delineation of the time period that painting was produced.

The layer sequence of multilayered white and off-white paint chips is sometimes difficult to discern when employing usual microscopic methods. The commonly used techniques may not provide the needed discrimination, since only a limited number of pigments and extenders are used in white and off-white paints. The cathodoluminescence microscopy (CLM) may provide the needed layer sequence information and discrimination when analysing and comparing multilayered white and off-white paint samples. Cathodoluminescence is the emission of radiation from the sample in the visible light region following excitation by electrons generated from a cathode electron gun. CLM provides further discrimination of the layer sequence of multilayered white and off-white paint samples since cathodoluminescence is sensitive to phase differences, trace foreign atoms, and other lattice imperfections. Analysis of polished cross-sections by CLM was accomplished utilising a light microscope coupled with a vacuum specimen chamber and a cold-cathode electron gun. The information obtained by CLM with

darkfield reflected light microscopy, fluorescence microscopy, and scanning electron microscopy coupled with energy dispersive X-ray spectrometry were compared by Hopen et al.(22).

The application of Raman Spectroscopy to the examination of paint samples has been described by Brissaud (23). Coloured coats of the paint fragments are analysed by Raman spectroscopy to identify pigments for their comparison and differentiation.

The degradation of two automotive coatings, an acrylic melamine and an acrylic urethane clear coat was studied by Wernstahl (24). The influences of light intensity, temperature and air pollutants on the degradation of the coatings were studied. The results indicate that it is important to include the effect of air pollutants when evaluating the service life of acrylic melamine clear coats by accelerated test methods. A coupling of IR measurements with measurements of gloss retention show that there is correlation between loss of cross-linker from the coating and loss of gloss.

The influence of relative humidity on the rate of isocyanate functionality depletion at the film-air and film-substrate interfaces of a urethane coating was examined by Ludwig and Urban(25), using attenuated total reflection FT-IR. The effect of relative humidities ranging from 0 to 80% on crosslinking reactions was examined. The results indicate that reactions of isocyanate groups with OH functionalities are inversely proportional to the relative humidity. The results are discussed in terms of the reactions which occur between water and isocyanate, as well as the plasticization effects of water and solvent molecules. These studies indicate that the presence of competing reactions within the system may result in various degrees of crosslinking.

Tanabe et al. (26) have reviewed the application of neural network technique to the forensic analysis of IR spectra of car paint samples. IR spectral data of 222 paint samples were classified by the Cohonen self-organizing feature map network, and were classified into 6 groups. 2-Step neural network system was trained, and paint samples gathered at real car accident places were tested.

Automotive paint formulations undergo constant evolution and revision based on the needs of the industry, including appearance, longevity, repair, and economics. Recently, environmental concerns have been added to the mix, with the mandate to reduce volatile organic emissions from paints. Newer formulations may include a higher solids load, changed polymer chemistries, water-based products and the results of other new technologies. How these formulation changes present themselves when the dried paint is examined as forensic evidence has been discussed, together with comparisons of older formulations, by Wampler et al. (27). The fragments of paint recovered during forensic investigations were analysed using Pyrolysis-GC/MS. Pyrograms generated from intact fragments or separated layers were used to match paint evidence to known paint formulations in an effort to narrow the scope of the search, help identify involved vehicles, and exclude others. The peaks which appear in any pyrogram of an automotive paint may be a complex mixture of polymer pyrolyzate, additives, plasticizers and other ingredients, each of which has a specific function in the performance of the paint as a product.

The old lead-based paints mobilise as dust during renovations, leading to a potential for high exposures to lead. Hence, it is desirable to develop techniques that can be used on-site to rapidly identify lead-containing paint on walls. A simple fibre-optic probe suitable for remote elemental analysis using laser-induced breakdown spectroscopy has been developed for this purpose (28), and is used to determine the lead concentration in samples of dry paint. Optical fibres transport the laser pulse to the sample and transfer the emission signal to the spectrometer. The use of separate excitation and collection fibres allows coupling of the probe to a

conventional spectrometer using simple optics. The measurement takes less than 1 min to perform, requires no sample preparation, and can be made through overlayers of non lead containing paint.

A method for isolation and identification of paint pigments by sublimation has been described by Palenik (29). Since many organic pigments sublime under atmospheric pressure at reasonable working temperatures, this appears to be an attractive procedure and has been successful for many pigments. The sublimation apparatus, procedure for charging the sublimation tube, heating procedure to achieve the sublimation and crystallisation of pigments, and the manner of observing the characteristics of the crystals have been discussed. It is suggested that the procedure should always be applied to the known paint first to determine if the techniqe provides useful additional information in a specific situation. The crystals may be identified further by IR microspectroscopy.

Evidential Value

A number of efforts have been made in the past to assess evidential value of automobile paint transfer in traffic accident cases. The evidential value of paint transfer depends on many factors; such as type of paint, unusual pigments, probability of another vehicle of the same colour/model being at the scene at the same time as the suspect vehicle, distribution of vehicle model of a particular colour, flow rates of traffic, layer sequence of paint, frequency of occurrence of topcoat colours etc. It was observed that responsibility of properly interpreting the meaning of paint evidence is difficult since each case is different.

McDermott and Willis (30) surveyed paint examiners on a series of eight hypothetical paint transfer scenarios ranging from 'one layer paint transfer in one direction' to 'multilayer non-manufacturer finish transferred in each direction'. The respondents were asked to use a given scale of conclusions from 'slight support' to 'conclusive' to express their opinion. A total of 124 replies were received from various geographic locations in about a dozen of countries. The exchange of multilayer non-manufacturer's finish paint was considered to be very strong evidence. The majority of respondents assigned it either 'very strong support' or 'conclusive'.

This study based on hypothetical scenarios may not be of much statistical significance so far as the statement of evidential value of paint transfer is concerned. But, it does highlight many of the problems associated with paint evidence. However, this effort provides some guidelines to examiners of paint to use a scale of conclusions while evaluating their findings.

Stoecklein (31) discussed the evidential value of automotive paints, and observed that if two multilayered paint fragments with the original layer sequence (the suspect and the control material) are indistinguishable after using state of the art examination techniques, it cannot be concluded with certainty that these samples came from the same source. The chips must not necessarily originate from one and the same vehicle. However, the probability is very low that a second automobile with identical morphological and chemical characteristics in its paint layer structure was in the vicinity of the crime scene at the time of the accident. Thus, the evidential value of such results is nevertheless very significant.

The performance of laboratories, which took part in a proficiency testing programme, has been evaluated by Peterson and Markham (32). The evidence type paint and glass fall in the category where 10% or more of the results disagree with manufacturers regarding the source of samples.

Databases

A number of databases on automotive paints have been developed in various countries over a long period of time (33-38). The structure and utility of some of the databases were published or presented and discussed at scientific meetings held during the period under review. These are mentioned below.

The history and technology behind the development of the Royal Canadian Mounted Police Forensic Laboratory automotive paint database has been described by Buckle et al.(33). The database has been generated over more than 20 years: to be able to classify individual paint layers by identifying major organic and inorganic components; to provide spectral data of sufficient detail and quality for comparison to unknowns; and to provide a universal database that could be up-dated and searched at remote locations by qualified examiners. The PDQ system contains the colour, chemical composition and layer sequence of the complete paint systems (topcoats and primers) applied to most of the foreign and domestic vehicles marketed in North America since 1970. It is not a population database but a representative database. Data entry and data retrieval methods have been discussed in detail.

An IR spectral database of US automotive paints was developed at the Georgia Bureau of Investigation Forensic Laboratory (34), to assist law enforcement officers in the investigations of crimes involving vehicles. The objective of this work was to evaluate the effectiveness of matching spectra of paint specimens using a computerised library search. It was observed that when high quality spectra are obtained, the likelihood of obtaining the correct result is significant.

A brief overview of the capabilities, and future directions, of the F.B.I. Laboratory in the identification of vehicles involved in violent criminal acts was discussed by Bishea et al.(35). Tracking an original finish to make/model/year may be possible through comparison with colour, layer structure, and chemistries, to the National Automotive Paint File. This collection represents approximately 20,000 original finishes submitted to the laboratory from the automotive manufacturing plants since the 1930's domestically, and foreign facilities from the 1960's. An international collaboration is being pursued through the Technical working Group on Material Examination(TWGMAT) to include domestic and foreign paint databases with the assistance from the National Institute of Standards and Technology.

The BKA's central automotive paint collection was discussed by Stoecklein (36). It consists of about 50,000 original paint samples, product information, and results of various methods of analysis (4,800 FT-IR spectra, 600 clear coats, 1,400 base coats from two-coat metallics, 1,400 solid measurements, 700 primer-surfacer, 700 primer, 30 undercoats, 1,000 XRD measurements, and several thousand colour measurement results) concerning the coating material for the production years 1975 through 1993 for 23 different European and Japanese automobile companies. The database is updated annually with 500 new paint systems.

Massonnet (37) analysed about a hundred samples of grey metallic paint chips by fourier transform infrared spectroscopy between 4000 and 650 cm^{-1}. The results enabled the creation of four databases of the four types of layers that were measured primer, primer surface, top coat including the basecoat of two coat metallic paints, and the clear coat. A preliminary computerised search for each spectrum, according to its layer type, was then carried out in corresponding database (Search algorithm: Metric, Euclidean distance). The thirty best matches given by the computerised search were then visually compared and the non-differentiated pairs were stored for each sample and for all layers. The primer surface is the most characteristic layer while the clear coat is the least. The more layers there are, the greater the chances are of

identifying the make of a vehicle after a research in different databases. As a unique layer, the primer surfacer is nevertheless the layer that gives the best information.

The morphological profile data on approximately 4500 specimens of effect topcoat were collected as microscopic photo images by Fujiwara (38). A database for application to screening suspect cars in hit-and-run cases was compiled on the basis of microscopic photo profiles, kinds of pigments, colour images and so forth as identification factors. The searching simulations using above database gave good results.

Books and Reviews

A number of useful and informative reviews and books have also been published during the period under review (39-44), which may interest those engaged in the examination of forensic paint samples.

Smith (39) has described the major generic types of coatings used to protect industrial structures. The list is in no way complete but was selected to represent the most commonly used generic types. The generic types are classified by resin, curing mechanism, and general description, including strengths and limits of generic classification.

LeSota (40) published an Encyclopaedia of coatings, which contains over 6000 definitions including state-of-the art technology.

Automotive coatings formulation, manufacture, application, and sale has been compiled by Fettis (41). Following an introduction there are chapters on each stage of the coating operation starting with pre-treatment, through undercoats, surfacers and topcoats. There then follow two chapters covering paints for non-metallics and specialities. Chapters on technology licensing and technical service/market support have also been included.

The forensic analysis of paint, including sample preparation, microscopy, chromatography, spectroscopy, and other techniques has been reviewed by Stoecklein (42).

Gower (43) has prepared an international guide to 11,000 products by trade name, chemical, function, and manufacturer, which is available in 3.5" disks, CD-ROM, or as a two volume set of books.

A guide for forensic paint analysis and comparison has been published by the American Society for Testing and Materials. The guide is intended for application to the analysis of industrial and commercially prepared paints and related coatings (44). It is a guide to a reasonable order for testing; and to the strengths, limitations, and possible pitfalls of each of a variety of potentially useful analytical methods.

Interesting Cases

The forensic evidence surrounding a case of hit-and-run on the water, and its use in developing investigative lead information has been described by Horton and Jergovich (45). A ski boat was hit and run over by a speeding vessel which fled the scene leaving two dead and six injured.

The forensic examination of the ski boat revealed transferred paint and fibreglass gelcoat which indicated that the striking boat was blue and white in colour. Analysis of the blue paint by fourier transform infrared microspectroscopy revealed it to be a polyurethane modified acrylic-alkyd enamel which is typical of an automotive refinish. Investigators were informed that they should look for a white fibreglass boat with a blue accent colour that had been applied or refinished with an automotive refinish paint. This was somewhat of an oddity as most two-

colour fibreglass boats are manufactured by adding the colour to the gelcoat rather than painting it on.

During a hunt, the officials located a blue and white cabin cruiser moored at a covered dock. Forensic examinations revealed it to be constructed of white and blue fiberglass which had been partially refinished with a blue polyurethane modified acrylic-alkyd enamel paint. These examinations also revealed trace smears of black alkyd enamel paint and multicoloured polyvinyl chloride plastic which were consistent with having been transferred from one boat to another. Comparison of these materials included the following techniques: stereomicroscopy, brightfield and polarised light microscopy, microchemical tests, FTIR, dual column pyrolysis gas chromatography, microspectrophotometry and elemental analysis by scanning electron microscopy/energy dispersive X-ray analysis. Because this cross transfer of trace materials presented such a strong indication of contact between the boats, the suspects were each charged with and pled guilty to three counts of misdemeanour offences.

Cortner (46) has described a case in which the forensic identification and examination of spray paint led to the fourth conviction of a man. This evidence had not been discovered in the routine evidence processing in 1962 as the techniques and instrumentation needed to find and analyse this ever-so-small paint evidence was not available at that time. The re-examination of the evidence involved reprocessing over 300 items of evidence and examining some 6,000 pages of trial transcripts. After the original evidence had been reanalysed, some new evidence surfaced. Paint spheres found in the defendant's vehicle were also present in the victim's bedroom.

The unique shaped spheres were analysed by using a scanning electron microscope that was attached to an ion microprobe. Both, questioned and reference samples were found to contain titanium as a major inorganic element, as well as lead, aluminium, and silicon in lesser amounts. The fourier transform infrared spectroscopy performed on all samples indicate the paint is based on an alkyed. The colour of the paint was due to the pigment ferric ferrocyanide as indicated by the inorganic cyanide absorption at 4.79 micrometers. Armed with this new evidence, for the first time in 24 years the defendant was actually placed in the victim's bedroom.

Glass

Glass as a physical clue is frequently encountered in crimes such as burglary, road accidents, and vandalism. The examination of glass evidence has depended, traditionally, on comparing the physical and chemical characteristic of a questioned fragment with a known fragment. The physical measurement include the observation of colour, thickness, density, and optical properties. Recent advances in analytical capabilities for the trace element characterisation of glass fragments have provided a high degree of discrimination between glass fragments that was previously not available with the physical property comparisons. There has been considerable interest in the probability of transfer of glass fragments and their retention on the clothing of a suspect of glass breaking. The recent advances made in these areas are summed up below.

Transfer of Glass Fragments

If a glass pane is broken in the commission of a crime, the fragments of glass transferred to and retained by the offender could be evidence that he broke the glass. Thus, transfer and persistence of glass fragments, on clothing of suspect of window breaking, are important and crucial points in the interpretation of glass evidence. There has been several studies of these phenomena in the past. However, considering the complexity of the transfer and persistence of glass fragments, new experiments were performed by Hicks et al. (47) to answer various questions related to these phenomena. Panes of float glass were broken using several breaking devices (hammer, stone, and pendulum). The experiments, including two persons (the breaker and the accomplice), consisted in breaking a pane and wearing the clothing for variable periods of time. One pane was broken for each experiment. The results of the study confirm that the number of fragments transferred on the clothing, depends not so much on breaking device, as on the number of strikes and the distance between the pane and the person standing near by. Even eight hours after breaking a glass pane, it is possible to find as many as seven glass fragments on clothing, although most fragments are lost within thirty minutes. The small fragments are retained longer. The number and size of recovered fragments depend on the time elapsed between widow breaking and search, and on the weave/composition of the garment. It has also been noticed that activity could be an important factor.

Underhill (48) has reported the results of a set of experiments conducted to test the idea that an examiner can distinguish glass acquired by the backward fragmentation from that acquired by contact with already broken glass. The variability of results from these investigations reaffirms the inconstancy in the process of acquisition of glass fragments by a person breaking a window. However, it was observed that not finding glass on the clothing, and in hair combing is not evidence that the suspect did not break a window; the shapes of glass fragments do not show whether they are acquired by breaking a window or by contact with already broken glass; finding of glass fragments having original outer surface is a good indication that the glass was acquired by backward fragmentation; and hair combing is a good source of glass evidence since contamination of hair from other older origins is less likely. It may be mentioned here that hair combing of the suspect for collection of samples of trace evidence like glass, fibres etc. is facilitated by combs loaded with cotton wool. Griffin and Crawford (49) have developed a 'comb-loader' which reduces significantly, the time taken to load the cotton wool on to the combs. Using this method it is easier to prepare loaded combs of a consistently better quality.

The distribution of glass fragments recovered from the clothing of over five hundred individuals suspected of criminal involvement with breaking or broken glass was studied by Lambert et al. (50). An earlier survey of such population was mainly concerned with the RI distribution, rather than considering the significance of the numbers of matching and non-matching glass fragments on the clothing of an individual. Hence, a more comprehensive survey was conducted to find out the significance of the numbers of matching and non-matching glass fragments recovered from clothing. The refractive indices of over four thousand recovered glass fragments were measured. A grouping method was applied to the data, providing information on the number of types of matching and non-matching glass present on the clothing. Comparisons of the proportions of matching and non-matching glass were made on the different types of clothing and for the different locations on the clothing. Group sizes were also studied, and comparisons of refractive index distributions were made. It was observed that it is not unusual to find a large number of non-matching glass fragments on the clothing of an individual suspected of criminal activity, although these were almost invariably from a number of different sources. It

was further observed that it is unusual to find more than three fragments of non-matching glass from a single source on the clothing of an individual. The refractive index distribution of non-matching glass on clothing is found to be different from that of control glass encountered in case work, and there has been a marked change in the RI distribution of control glass in the recent past.

The frequency of occurrence of paint and glass on the clothing of high school students was examined in detail by Lau et al. (51) to find out how common is it to find such trace material on outer clothing/footwear of persons, who are not connected with crime; and to provide a baseline, for their service area (city of Vancouver). The frequency occurrence of paint chips and glass fragments on the outer clothing and footwear of 213 high school students from different area of the city were determined. Students are generally not involved in crime but have a active lifestyle. It was observed that the presence of paint chips and glass fragments on the surface of the clothing and footwear, in the area surveyed, were relatively uncommon. Hence, mere presence of paint and glass on clothing and footwear can be assigned some level of significance, and if such fragments match a known source by standard forensic tests, then their significance is enhanced by the number and location of the particles found.

A prior knowledge of the number of groups of glass fragments, recovered from clothing of a suspect of window breaking, is required in the statistical analysis. A divisive method for dealing with the grouping problem has been proposed by Triggs et al. (52). This method of detecting groups within the recovered samples of glass fragments is efficient as compared with the agglomerative methods in vogue.

Evett et al. (53) used a Bayesian perspective to explore issues of glass evidence interpretation. Data from two surveys of glass on clothing, conducted earlier(50,54), were used to discuss various aspects of the Bayesian approach to glass evidence. The probabilities of transfer/persistence of glass fragments were also taken into consideration and the sensitivity of the likelihood ratio to various factors were discussed. A method of analysis has also been suggested for dealing with the explanations which may be put forward, by the defence counsel, for the presence of glass on suspect's clothing. Triggs et al. (55) also advocated the Bayesian approach to interpreting forensic evidence. Curran et al. (56) have proposed the use of simple modelling techniques as a method for consistent and objective evaluation of the transfer probabilities and have recommended the graphical modelling technique for assessing probability of transfer.

If a large number of glass fragments are recovered from the suspect then it may be more efficient to examine a subset of these fragments. However, such sampling incurs information loss. Curran et al. (57) have derived an expression that allows a partial quantification of this loss. A system to assess the effects of the grouping in Bayesian interpretation of forensic glass evidence and to quantify the loss that occurs during the normal casework activities of sample selection and glass fragments groupings has been discussed further (58), and the use of a grouping algorithm in the interpretation of forensic glass has been recommended.

Glass Fracture

Fracture surfaces of different commercial glasses have been studied with an atomic force microscope by Wünsche et al. (59).The atomic force microscope enables direct imaging of the surface of a non-conducting material with high lateral and vertical resolution. The surface roughness could be measured all over the fracture surface, and it was found to increase with growing distance from the origin of fracture. The detection of nanometer steps in the fracture

origin and in the mist and hackle zones showed that the breaking of glass occurs in shear mode even on the nanometer scale.

Elemental Analysis

The comparison of questioned and known glass samples on the basis of the physical properties only does not yield definitive results about their source correspondence. The elemental analysis of glass fragments as a complementary technique to achieve discrimination of glass samples has been explored for some time in the past. There has been considerable interest in this area during the period under review also.

Parouchais et al. (60,61) investigated the use of inductively coupled plasma mass spectrometry for the elemental analysis and discrimination between glass fragments. An important step in the analysis of glass by ICP technique is the digestion procedure to produce suitable working solution. A three acid digestion procedure (HF, HNO_3, HCl 2:1:1) was developed for glass to minimise interference, and loss of elements in the form of volatile salts, and to permit use of a quartz sample introduction system. With this digestion procedure, the application of ICP-MS to forensic analysis of glass was investigated for its ability to discriminate glasses with matching refractive indices. Up to sixty two elements were determined in a range of glass samples. Glasses that could not be distinguished on the basis of refractive index measurements could also be discriminated. A procedure of measuring a range of elemental ratios, which eliminated the need for weighing, was used to compare small samples typical of case work. The elements that provided discriminatory information varied widely between the different sample pairs. The most common elements used, however, were Mn, Zn, Rb, Sr, Zr, Ba, Pb, Th and the rare earth elements. The utility of this technique for analysing small fragments of glass (<1mg) and the minimum volume that could be used for sample nebulization have also been explored.

The ICP-MS requires dissolution of the glass samples with acids to make working solutions, which is a time consuming procedure. The laser ablation inductively coupled plasma mass spectrometry is a technology which is capable of analysis of solid glass samples. The use of this technique was investigated by Watling et al. (62) for its potential to provide data on relative trace elemental compositions to uniquely characterise and compare physical evidence from crime scenes. Glass and steel samples were examined as they frequently occur as physical evidence and represent two distinctly dissimilar sample types. A fine focus Nd:YAG laser was used enabling specimens of approx. 50 μm in diameter to be examined. Ablation protocols and optimum compromise sets of laser parameters were established for the analysis of both sample types using both free running and Q-switched mode of laser operation. Mass spectra acquired under these conditions were reproducible and were generated in a fraction of the time required for the conventional solution analyses. Sixty-two glass samples were examined of which thirty-one were float glasses, four were sheet glasses, and twenty-seven were container glasses. The LA-ICP-MS method is at present an essentially qualitative technique and relies on comparison of trace element assemblages or ratios. Samples can be conveniently compared by direct overlay of spectra or interpretive software can be used. Software facilitating the inter-comparison of three elements simultaneously (ternary plots) in large groups of samples was used to establish both the reproducibility of the 'fingerprint' and the uniqueness of the inter-element associations. Stoecklein et al. (63) have also investigated the use of laser ablation inductively coupled plasma mass spectrometry for determining trace impurities in glass in addition to major and minor elements.

Buscaglia et al. (64) analysed 62 window panes by Energy Dispersive X-ray Fluorescence. The samples were obtained from a single residential dwelling, and high precision RI measurements had been previously obtained for each sample. Multiple EDXRF spectra on each glass sample were obtained such that intra-sample and intra-element variability could be determined. Qualitative and semi-quantitative analyses offered additional discrimination between samples which were indistinguishable by RI alone. Quantitative data were collected as X-ray net intensities and elemental ratios were employed in evaluating the discrimination available amongst glass samples by applying a Bayesian approach. The discrimination available amongst window panes from measurements of the following seven elemental ratios was studied: Ca/Fe, Ca/As, Ca/Sr. Ca/Zr, Ca/Mg, Ca/Si and Ca/K. Five window panes were selected for study to evaluate the discrimination potential of the 7 elemental ratios. Five measurements of each of the 7 elemental ratios were available from each of these 5 selected window panes. Comparison was made using likelihood ratios. The most discriminating elemental ratios were found to be Ca/Fe, Ca/As, and Ca/Si.

Micro-beam X-ray Fluorescence and other techniques for the comparison and discrimination of glass fragments have been evaluated and reviewed by several other workers as well (65-70).

Classification: Product-Use Type

The classification of glass samples into their product-use type is important, at times, in corroborating or disproving an alibi, product tampering, and in the studies related to population of different types of glass. Almirall et al. (71,72) determined refractive index and elemental concentrations for four product-use categories: headlamp glass, container glass, non-vehicle window float glass, and vehicle float glass. For this specific set of glasses, the concentrations of a number of elements were found to be correlated in some cases. This precluded the use of traditional probability calculations in using elemental composition data for interpretation of glass evidence. In order to predict the type of glass to which a particular glass belonged, Fisher's linear discriminant analysis was applied to the data. It was possible to differentiate between the four glass types using elements, Al, Ba, Ca, Fe, Mg, and Sr in conjunction with RI. The same analysis was carried out within the product-use category also but further discrimination was not possible within a group. It was not possible to discriminate between manufacturers or suppliers of glass.

The small fragments of beer bottle left at the scene of crime, frequently become an important evidence. Furukawa (73) carried out elemental analyses of beer bottles using Electron Probe Microanalyser (EPMA), which could analyse very small specimen and many elements at the same time. Hence, the possibility of discrimination, by statistical analysis of the concentration of each elements determined using EPMA, was examined. The elements Si, Al, Mg, Na, K, Ca, Fe, and O were detected qualitatively from small fragments of beer bottles. A quantitative analysis revealed that contents of SiO_2 and CaO were nearly constant (about 73% and 10 %) in all the samples. However, the concentrations of other elements had a wide range. Statistical analysis by Mahalanobis' generalised distance was carried out for contents of Al_2O_3, MgO, Na_2O and K_2O, and it was found that the discrimination of small fragments of beer bottles was possible in many cases.

Thin-film coatings on architectural glasses are a complex technology utilising a host of materials deposited as single or multiple layers with individual layer thickness down to a few nanometers. The sequence, composition, and thickness of the layers are the main diagnostic features that are applicable for forensic comparisons of architectural glass. Hopen et al.(74) used

transmission electron microscope to examine these diagnostic features and to characterise architectural glass. Several methods are available to characterise coated glasses, however, none provide the detailed knowledge that can be achieved by preparing cross sections of the coated glass for analysis in the transmission electron microscope. Cross sections are prepared by gluing two coated surfaces together, cutting a thin plate perpendicular to the coated surfaces with a diamond saw, and grinding the plate to a uniform thickness of ~50 to 80 µm. The plate is cut into 3mm diameter disc and then dimpled so that the crater is ~10-20 µm thick. The final thinning is performed using an ion mill to make the disc electron transparent. The TEM analysis allows the number and thickness of layers to be imaged, the composition of layers can be obtained using energy-dispersive X-ray spectrometry or electron energy loss spectroscopy, and the crystallinity of the layers can be determined using electron diffraction or high- resolution imaging.

Evidential Value

A statistical approach to the significance of glass evidence using independent physicochemical measurements and chemometrics was suggested by Almirall (75). Traditional interpretation of the significance of trace evidence matches or exclusions relies on qualitative descriptors such as "indistinguishable from", "consistent with", "similar to" etc. By performing physical and chemical measurements which are independent of one another, the significance of object exclusions or matches can be evaluated statistically. Chemometrics can be employed to group similar objects using clustering algorithms and provide statistical significance in a quantitative manner. This approach is enhanced when population databases exist. Since the selection of the variables used and their pre-processing can greatly influence the outcome, several different methods should be employed to obtain a more complete picture of the information contained in the data. The analysis of glass samples using refractive index measurements and the quantitative analysis of the concentrations of the metals: Mg, Al, Ca, Fe, Mn, Ba, Sr, Ti, and Zr has been reported. It has been suggested that, this statistical approach should not replace the current interpretative approaches to trace evidence matches or exclusions but rather yields an additional quantitative measure. The lack of sufficient general population databases containing the needed physicochemical measurements and the potential for confusion arising from statistical analysis currently hamper this approach.

Curran et al. (76) have also proposed statistical analysis of elemental composition for comparison and characterisation between glass fragments. The elements in minor and trace concentration viz. Aluminium (Al), Iron (Fe), Magnesium (Mg), Manganese (Mn), Strontium (Sr), Zirconium (Zr), Calcium (Ca), Barium (Ba) and Titanium (Ti) were considered. The elemental concentration data for glass fragments from a brown bottle and those from a colourless bottle were used to demonstrate advantages of Hotelling's T^2 test, a multivariate analogue of Student's t-test, over the '3 sigma rule' approach, which has two problems; it does not take into account any correlation between the elements, and there is some probability of false rejection. While Hotelling's T^2 test is a better approach, it has the weaknesses inherent in hypothesis testing. The authors have further suggested to adopt a Bayesian approach to overcome these weaknesses (77).

Combining forensic resources through independent distributive computing has been advocated by Mitchell et al. (78). It is possible now to access distributive database by using computers. A Java application combines information from separate databases that are written in different operating systems. The concept has been demonstrated by finding the frequency of occurrence of a glass sample, given its composition and refractive index.

Interesting Cases

Suzuki et al. (79) have described an interesting case of hit-and-run in which characterisation of mirror fragments played a very important role. A victim (45 years old man) was hit by a car and died. After the incident, 12 small fragments were collected by the investigators, 5 were found at the crime scene, and 7 on the clothing of victim. These appeared to have been broken from a mirror. They were compared with the control samples taken from a mirror of the suspected car, in order to examine the possibility of contact between the suspected car and the victim. Examination of the control sample under a stereomicroscope revealed that it had three layered structure, a thin aluminium layer between a paint layer and a glass layer. It was found that some of the suspected samples also had similar structure, while the other suspected ones were composed of only one or two layers, which indicated the possibility that these were chipped off portions of the mirror. The control samples offered two RI values, 1.5170 or 1.5160. The suspected samples also, except one, had similar RI values. Analysis of trace elements using ICP-MS was performed on some of the suspected samples and the control ones. The glass fragments were thoroughly cleaned before they were analysed. It was found that the elements Rb, Sr, Zr, Ba, La, Ce and Pb were contained in the glass fragments. Determination and comparison of the trace elements was carried out. The concentrations of the trace elements showed a good agreement between the suspected and control samples.

Another practical example of glass evidence interpretation has been discussed by Walsh et al. (80). In this case, the float glass window at the front of a druggist's shop was smashed. The offenders took drugs and prescription medicines worth thousands of dollars. Two suspects were apprehended an hour and half later. A number of glass fragments were recovered from the clothing of the suspects. The refractive index results were compared using the Student's t-test and were deemed not to match at the 99% significance level, although the refractive indices were quite close. It may be because of the fact that often a very small control is submitted which may not be a representative sample. The Bayesian approach to interpreting the glass evidence was applied in this case to determine the likelihood ratio, which supported the suggestion that the clothing of the suspect had been in contact with the glass from the window. The authors have advocated a move to continuous model of this type for all cases involving glass evidence.

Prompted by an unusually large change in refractive index after re-annealing of a windshield glass in a case work, Edmondstone (81) examined and studied changes in refractive indices of windshield glass, manufactured by different processes e.g. tempered, non-tempered, press bending, and gravity bending; and concluded that laboratory re-annealing allows discrimination between the two different manufacturing processes used to shape automotive windshields. DRI values intermediate between those expected for tempered and non-tempered glass for windshields indicate that the press bend process was likely used. An effort has been made to generate re-annealing database for windshield glass manufactured in or after 1984 model years. Such databases would be useful and should be generated and shared.

Conclusion

Infrared spectroscopy continued to be the popular method of investigating paint samples to identify organic/inorganic pigments and binders. An extensive survey of U.S. automobile original topcoats for binder and pigment composition has been carried out using FT-IR technique. Chromatographic techniques and UV/Visible spectroscopy have also been used to study the composition of paint samples. The use of image analysis to evaluate colour and texture

of paint samples has been explored. This appears to be a promising technique and should be evaluated further. The X-ray techniques, XRF and XRD, hold the promise of significant contribution in enhancing evidential   value of paint. A number of databases on paint were published or presented and discussed in the scientific meetings held during the period under review.

The earlier interest in the study of the phenomena of occurrence, transfer, retention and recovery of glass fragments continued after the 11th Forensic Science Symposium also. A number of experiments were carried out at different forensic science laboratories. These studies have reaffirmed earlier observations and added informative findings to the knowledge base. There has been special interest in the statistical interpretation of these phenomena for appreciating the value of glass fragments recovered from the suspect as an evidence of his guilt. A number of efforts have been made to evaluate the capabilities of various analytical techniques, such as ICP-MS, LA-ICP-MS, and ED-XRF, for trace element analysis of glass fragments and it has been observed that trace element profiling of glass fragments offered additional discrimination between the fragments that were indistinguishable on the basis of refractive index.

The forensic examination of paint and glass normally involves a comparative analysis. Two or more samples are compared to determine if they could have originated from one source. Commonly used physicochemical methods do not take us far in this direction. The availability of sophisticated and sensitive techniques of analysing trace composition of these evidences may be of help and prove better. There has been a trend to look for sensitive techniques that help to analyse minute quantities of samples. However, the sensitivity is achieved at the cost of precision. Also, if we settle with minute sample size for analysis, the question of qualitative and quantitative uniformity of the parent material should be interrogated and settled. In case samples of these evidence types are not reasonably uniform with respect to their qualitative and quantitative trace composition, it would be dangerous to rely on the results of the analysis of a speck of these evidences. It means that at least two sets of methods of analysis should be developed; one for minute (microscopic) samples and other for not so minute samples, which would naturally have different precision levels of determination. Instead of doing qualitative or semi quantitative analysis of a large number of elements it may be worthwhile to choose a smaller number of elements suitable for quantitative analysis so that meaningful databases could be generated for assessing evidential value.

Methods of appreciating evidential value of comparative studies, for establishing source correspondence, should be developed. Statistical treatment of data generated on the samples, and making use of the databases for the attributes studied, yield quantitative estimate of the significance of the scientific findings. The selection of suitable statistical procedure for treatment of the evidence data to estimate its strength, would also depend on the judicial requirements for the decision making. The basic question is whether the evidence should be evaluated for the probability of guilt or for the probability of innocence of the suspect, that is, whether we should determine the discrimination potential or the association potential of a given attribute of a physical evidence. The discriminative approach presumes the suspect to be innocent while the associative approach presumes him to be guilty of the crime. Taking ratio of the probability of guilt and that of innocence is another way to look at the evidential value. How to treat the data statistically, may be explored if the intent is clear. It may be worthwhile to debate and decide on these issues; and adopt, internationally, suitable statistical methods for evaluating physical evidences.

The importance of databases for the evaluation of evidences can not be over emphasised, and it is nice to be able to access distributive databases using computers. Nevertheless, the

databases should not only be searchable but should also be shareable internationally. It would require validated methods and protocols of analyses, and traceability of standards used for determinations. It would also be desirable to standardise vocabulary used for expressing the value of the evidence, in the laboratory reports.

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