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Paint and Glass

A Review: 1998 – 2001

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INTRODUCTION

This report covers significant advances in scientific methods applied to the examination of paints and glass reported since the 12th Interpol Forensic Science Symposium in October 1998. Colleagues from around the world were asked to provide information on published articles, internal research, reports and presentations given at trace evidence meetings and special conferences in this area. A literature review was also conducted covering articles published in the principal forensic journals and abstract publications. This was supplemented by an extensive search of "Chemical Abstracts" and the internet web sites for articles related to paint and glass investigation. Since electronic access to the literature and efficient search engines are readily available, extensive listing of all contributions followed by terse summaries of their content does not seem appropriate. The intent of this review is to highlight the most important contributions. The final report is therefore a selective review of references and information obtained from the various sources.

PAINT

Since the last Interpol Forensic Science Symposium in 1998, a number of advances have been made in the forensic examination of paint.
These have involved improvements in analytical techniques and in the building of databases to aid case interpretation and identification of the make, model and year of hit-and-run vehicles.

As several forensic science laboratories have to assist in the identification of art forgeries, reports centered on the examination of material of historical interest are also included. Finally the literature concerning new raw materials (binder, pigments & extender, additives) to improve coating systems and reports dealing with new products and techniques for coating of automotive bodies and OEM parts like bumpers or fenders is summarised below.

Paint formulations

The coating industry is continuing to improve coating systems in terms of their environmental compatibility. Most of the new developments by raw materials producers were thus in the field of aqueous, powder and UV-curing coating systems. A brief review of some of the new raw materials presented at the ECS'99 (European Coatings Show) has been given by Gehrenkemper (i).

Functional additives are ingredients of practically any formulation of conventional, waterborne, high-solids, or powder paints. A new series of exclusive articles covering separate groups of additives providing theoretical background information and referring to practical aspects of the use of commercial materials available on the market has been published by Verkholantsev (ii).

Pigments based on thin mica platelets coated with metal oxides are important types of pearlescent pigments today. Two new synthetic materials can now be used, beside mica, as substrates for effect pigments. New colouristic effects can be realized by coating the silica or aluminium flakes with highly refractive metal oxides such as titanium dioxide or iron oxide. In a new paper by Sharrock and Schuel (iii) the results of technical work on the incorporation, application and colour formulation of the new effect pigments have been presented.

Other new multilayer effect pigments with combinations of low refraction and strongly reflecting films exhibit a strongly angle-dependent kaleidoscope of colours with red, violet, blue, golden and green flakes. Schmid et al. (iv) reported on the development of these new lustre pigments with optically variable properties.

Heinlein and Kasch (v) have described the working principle, colouristic and application properties of the new organosilicone pigment class Helicone. Helicone pigments consist of an organic polymer network comprising a so–called cholesteric liquid crystalline phase. These new pigments have been successfully applied on various products, like automotive special editions, top range mobile phones, sports items and nail polish.

Seubert and Fetz (vi) have discussed the manufacturing process, the typical properties and main applications of the cornflake-like and silver-dollar-like aluminium pigments. Their article offers a detailed description of the methods for producing fine mirror-like pigments in a physical vapour deposition (PVD) process.

Lavallee and Beale (vii) have reviewed the history of bismuth oxychloride as a pearlescent pigment. They also describe future research directions of this important material and its current uses.

Aviles (viii) has described a new process developed by GLAZtec that transforms recycled glass products like mirrors and bottles and also shells into low-cost, environmentally friendly additives for automotive paints with unique properties. These products have attracted the attention of major automobile companies. Four of the carmakers have already displayed their glass-based conceptual paints at international auto shows. People where impressed with the appearance of these concept cars painted with the new glass flake additives which tend to enhance perception of depth in the coating and give different colour travel.

Starger (ix) has reported on a new coating technology called Spek-Trum PCS | (particle colour systems). This process is a non-pigmented colour coating that can be applied to any vehicle type. The company "Respect Innovations" has been able to retain colour and other special effects inert within a particle through micro and nanoparticalisation of organic and inorganic materials. By doing so, they capture a new level of optics for colour special effects as well as reflectability and luminosity. Spek-Trum's reflective coatings have the ability to produce spectacular colour effects when the coating is hit by light. The coating can hold light up to seven hours or more when headlight hit it at night.

Aluminium pigments are mainly used in metallic decorative topcoats and to some extent in anticorrosion paints. Zinc pigments are used as anticorrosive pigments especially in primers. A severe problem of water-borne paint systems with aluminium or zinc pigments is the hydrogen evolution in aqueous alkaline paint media. Müller and Schubert (x) have reported that one certain epoxy ester resin is an excellent corrosion inhibitor both for aluminium and zinc pigments.

Micro-titaniumdioxide pigments were not only used as UV-absorbers in coatings but also as a bluelight-scatterer in metallic base-coats to build up the so-called "frost effect". Winkler and Proft (xi) have described the most important physical and chemical characteristics of titanium dioxide pigments.

Automotive paints

Automotive coatings involve the use of various primer surfacer and top coat systems in different regions of the world. Meier-Westhues and Bock (xii) have given a general overview which coating systems are currently being used world-wide and have pointed out recognisable trends.

Increasing numbers of plastic parts are being used in the automotive industry, for reasons of weight saving and cost reduction as well as design considerations. Nowadays the surface of these plastic body parts are expected to meet the same high demands as the vehicle bodies themselves. Colour matching must be perfect, which has led some automotive manufacturers to successfully integrate the coating of plastic body parts into the series coating process. Große-Ophoff (xiii) has reviewed the most important developments currently taking place in the coating of plastic parts in the automotive industry.

No less than three new environmentally friendly clear coat systems have been introduced in recent years. In an article (xiv) a closer look has been taken at one of these three alternatives to conventional solvent-borne clear coats – powder clear coat – and a report has been given on the special features of this coating process and on experience with it in practice.

At BMW Dingolfing (Germany) more than 1,000 3-, 5- and 7-series bodies are coated daily using powder clearcoat technology in a 100% - automated process. Domitrz and Nowack (xv) have discussed the status of achievements on the Dingolfing lines, described from the view of the paint supplier.

Reducing the number of coating layers is a major objective for process simplification and cost reduction in the automotive industry. One paint manufacturer has now succeeded in developing a new 2-pack waterborne base coat which also takes on the function of the primer surfacer coat. The new coating system has already been tested in OEM application by various car manufacturers, and the results are extremely promising. Minko (xvi) has reviewed the process and application technology in different plants.

Several vehicle manufacturers around the globe introduced aluminium into car body construction many years ago. The amount of aluminium predicted for future vehicles ranges from about 10 % for an aluminium closure sheet, i.e. hood, to 30-50 % for skin panels and even 100 % in several cases. The overall concept for the pretreating of aluminium chassis parts before painting consists of passivation and the application of lubricant to the coil as well as paint pretreatment of the entire chassis. Gehmecker (xvii) have described the surface pretreatment of multi-metal and all-aluminium car bodies.

Laubner (xviii) has reported on the first in-line plasma pretreatment system for vehicle components in Europe that has now been installed at Audi in Ingolstadt. The new plasma pretreatment process is one of the things which allows the paint shop for painting components in the colour of the car body to be integrated into the chassis painting line.

Thin film organic coatings can significantly increase corrosion protection of metallic coatings in flanges and seams, even though the coating thickness is only 1-4 µm. Newly developed chromate-free pre-paint systems for metallic coated steel sheets have the potential to substitute ED coating. Androsch et al. (xix) have reviewed the types of coil coated steel sheets for the automotive industry and described further development goals.

Audi's plant in Ingolstadt has not only one but actually four paint shops, as the paint shop area has been sub-divided into four identical segments. Each segment is used for painting a different vehicle type. In his article Blume (xx) has demonstrated the benefits of this arrangement and described some further features of the new paint shop.

The New Beetle (Volkswagen AG) is produced in Puebla/Mexico. Around 600 cars a day are currently being turned out. The car has a large number of plastic parts which have to be painted in the body colour: the wings, bumpers, grille, tank lid cover, door handles and mirror covers. Sonnenberg (xxi) has studied how the high demands placed on colour matching the plastic add-on parts of the New Beetle to the body car are met by "inline" and "in house" finishing processes.

General Paint Investigation

General

A Forensic Paint Analysis and Comparison Guideline was published in May 2000 (xxii). The document is intended to be a revision of the original ASTM E 1610-94 Guide. This revision is a product of the Paint Subgroup of the Scientific Working Group of Materials Analysis (SWGMAT). The Guideline is an introduction for the forensic examination of paints and coatings. It is intended to assist personal who conduct forensic paint analysis in the evaluation, selection, and application of tests that may be of value to the investigation.

A brief discussion on the identification of paints and surface coatings has been presented by Tsubouchi (xxiii).

The possibilities for the discrimination of paint batches have been examined by Stoecklein and Palanik (xxiv). This problem of paramount importance for forensic paint analysis can only be solved if an arsenal of analytical methods like FT-IR, pyrolysis gaschromatography/mass spectrometry (PyGC/MS) and energy dispersive X-ray spectrometry (SEM-EDS) together with microspectrophotometry in transmittance and reflectance are applied.

Grünberger et al. (xxv) have described the limits and weaknesses of some methods (microspectrophotometry, Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDS) used in forensic paint analysis.

A comprehensive examination of car paints originating from 45 new and repainted cars was carried out by Nieznanska et al. (xxvi). It was found that application of microscopical techniques, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDS), enabled the authors to identify car paints, and, in the case of comparative analysis, to establish the degree of similarity within evidence material.

Zieba-Palus (xxvii) has described a similar examination. An attempt was made to discriminate between different automobile paints and the comparative material.

A study has been reported by Geyer-Lippmann and Walter (xxviii) on the analysis of protective coatings on headlamp plastic lenses being used for automobiles since 1995. Fourier transform infrared spectroscopy (FT-IR) in combination with pyrolysis gaschromatography/mass spectrometry (PyGC/MS) proved to be the best tools for discriminating the special clearcoats.

In addition to conventional "one dimensional" organic and inorganic pigments which interact with light by absorption and/or scattering an increasing number of "two – and three dimensional" plate-like pigments are finding their way onto the market. Stoecklein (xxix) has given a general overview of these new plate-like pigments in automotive paints. The same author (xxx) has developed a systematic approach for the analysis of new plate-like pigments in automotive coatings. Exact identification of these pigments in coatings can only be achieved by applying microscopical techniques in combination with SEM-EDS, microspectrophotometry and X-ray diffraction (XRD).

Egli and Massonnet (xxxi) have presented a survey of paint traces left at burglary scenes. Results from a previously study including paints from 49 crowbars analysed by FT-IR were compared with those obtained from 37 blue paint traces found at burglary scenes using the same technique (FT-IR). This study has shown that the colour as well as the IR spectral distribution are very similar for these two populations (tool paints and traces). These results are a great help in interpreting tool paint cases.

Collection of Samples and Sample Pre-Treatment

Search and recovery of trace evidence is a fundamental part of almost all forensic science examinations. As a process it can therefore consume considerable resources. Maximising the efficiency and effectiveness of this process is of considerable importance.

The successful investigation of crimes involving paints depends on the correct and best suited collection of the evidential material. The Handbook of Forensic Services (xxxii) has been published by the Federal Bureau of Investigation to provide guidance and procedures for safe and efficient methods of collecting and preserving evidence including paint.

For guidance on how to collect suitable samples see also section 7 in the Forensic Paint Analysis and Comparison Guidelines (22).

The collection and preservation of paint microtraces with the aid of an adhesive tape has been described by Bernhard (xxxiii).

Reproducible and correct measurements can only be achieved if the sample material is optimally prepared. How to prepare samples best suited for the different microscopical and analytical methods used in paint examination has also been compiled in reference (22).

Colour Measurement, Microspectrophotometry and Chromatography

Colour is one of the most important as well as the most eye-catching characteristics of microscopically opaque objects such as paint. The determination and comparison of colours is therefore usually the first step in a paint examination. Colour measurements are carried out today in a single beam technique using microspectrophotometers which are fitted with image – side monochromators with a measuring geometry of 45°/0°. Clarke et al. (xxxiv) have developed methods for the determination of colourimetric uncertainties in the spectrophotometric measurement of colour in order to meet the requirements for accreditation by the United Kingdom accreditation service (UKS), which include a statement of uncertainty for all certified quantities. The components of uncertainty which have been analysed are 100% level (diffuse reflectance), photometric non-linearity, dark level and wavelength error.

A report of available standards for the measurement of diffuse reflectance and measurement laboratories has been given by Springsteen (xxxv).

Springsteen (xxxvi) has also presented an overview of the general principles associated with measuring fluorescent colour. The chemistry and physics of what causes fluorescent pigments to work are addressed and some examples of applications for the pigments are given. Considerations as to why standard spectrophotometers and colourimeters fail to give completely accurate results in measuring such materials are discussed.

Since 1978 paint manufacturers have been using light stabilizers (UV-absorbers and radical scavengers) in 2-coat systems for automotive paints (OEM and repair). This protects the paint against gloss reduction, cracking, delamination, yellowing and blistering. Stoecklein and Fujiwara (xxxvii) have shown that microspectrophotometry in the UV-range (240-400 nm) is a non-destructive method of tracing UV-absorbers down to the nanogram range. This has resulted in the possibility to distinguish between vehicles which were originally painted in an identical manner but are indistinguishable by methods like infrared spectrometry (IR), pyrolysis GC-MS, and SEM/EDS.

Gennaro et al. (xxxviii) have presented a chromatographic method that can be easily applied in industrial laboratories for the separation and determination of three hydroxybenzotriazoles, commercially known as Tinuvin 900, Tinuvin 328, and Tinuvin 1130, widely used as UV-absorbers. The method, that involves the extraction process from the polymeric matrix and reversed phase high performance liquid chromatography (RP-HPLC) determination has been applied to commercial samples of known and unknown composition.

Light (xxxix) has studied the migration of additives (UV-absorbers and hindered amin light stabilizers (HALS)) from coating into substrate (e.g. plastic bumpers) and vice versa. Microtome cuttings (3 µm) were prepared to register the interfaces between several layers. The cuttings were placed into test tubes and extracted with a suitable solvent. The extracted additives were analyzed by HPLC (UV-absorbers) and gaschromatography (HALS).

Shon et al. (xl) have described a study on the identification of trace evidence by UV-visible microspectrophotometry. In this study, transmittance/reflectance profiles at UV-visible region (240-780 nm) were investigated by UV-visible microspectrophotometry and used to analyse the spectral characteristics of different types of 14 microfibers, 12 inks of four colours and 44 automotive paints of two colours. Good results for discrimination are presented from spectra of these samples due to the characteristic bands in the UV-visible region.

Massonnet and Stoecklein (xli) have developed a procedure for chromatography of light-fast polycyclic pigments (phthalocyanines, quinacridones, perylenes, perinones, dioxazines, indanthrones, isoindolinones, benzimidazolones). The pigments were 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 were separated by thin layer chromatography and identified by means of their respective R_f values. The visible spectrum of each pigment was recorded directly on the TLC plate (TLC spot) by microspectrophotometry. A computerised database including the R_f values and the visible spectrum of each pigment was created in order to support their identification.

Microscopic Examination

Optical Microscopy

Stereo and optical research microscopes are the most important aids in forensic analysis of paint. Palenik (xlii) has described some of the types of microscopes and microscopical techniques used to prepare coatings and coating materials for study. The range of techniques and methods is illustrated through the discussion of various case examples.

McCrone (xliii) has demonstrated the practical use of polarized light microscopy as a microanalytical approach for the authentication of art and archaeological objects. Paint media, pigments, and supports, with known data of first use, can all be identified and used to establish authenticity. McCrone asserts that only the microscopist can differentiate composition and that other information from pure elemental analysis, X-ray diffraction, and infrared absorption often fails to differentiate polymorphs.

Scanning Electron Microscopy

Ward (xliv) has produced a very useful standard guide for forensic paint examination utilising scanning electron microscopy (SEM). The term SEM encompasses the entire analytical system, including an energy dispersive X-ray spectrometer (EDS) and/or a wavelength dispersive X-ray spectrometer (WDS). This publication is the first document from a series of special guidelines intended for use by forensic paint examiner. It is a product of the Paint Subgroup of the Scientific Working Group for Materials Analysis (SWGMAT).

Toledo (xlv) has presented a paper on forensic applications of SEM. Vehicle topcoats were studied from the point of view of frequency distribution and significance of many particular artifacts formed in non-industrial coating, in which SEM proved to be very efficient.

The polychrome fragments from a terracotta Buddha statue were studied by Cam et al. (xlvi) using optical microscopy and SEM-EDS: The multilayered structure revealed an interesting long history and traditional Chinese painting techniques. The Buddha statue had been built during the Song Dynasty (960-1279), had undergone a restoration in the Ming Dynasty (1368-1661) in order to cover the degradation of red lead colour (minium and hematite), and a more recent retouching up later in the XIX century.

Currently, the only suitable method for trace evidence analysis in most forensic laboratories is SEM equipped with an energy dispersive X-ray spectrometer (EDS). Bayard and Stoney (xlvii) have designed and constructed prototypes of an electron microprobe instrument that is intended to improve the efficiency, reduce costs and extend the capability of the forensic examination of trace evidence. They have coupled a polarized light microscope (PLM) with an electron microprobe, allowing the determination of elemental composition along with direct observation of the sample's optical properties and visible cathodoluminescence. Data observed on paint chips and mineral grains from soil are shown.

The layer sequence of multi-layered white and off-white paint chips usually encountered by the forensic scientist in cases involving structural and/or maintenance paint are sometimes difficult to discern when utilising commonly employed methods. This layer sequence information becomes vitally important when comparing a questional paint sample to a paint sample of known origin. Cathodoluminescence microscopy (CLM) has demonstrated to provide the needed layer sequence information and discrimination. Cathodoluminescence is sensitive to phase differences, trace amounts of foreign atoms, and other lattice imperfections. Comparison of layer information obtained by CLM, darkfield reflected light microscopy, fluorescence microscopy and SEM-EDS of several cross-sections of architectural paint samples has been presented by Hopen et al. (xlviii).

Gas Chromatography and Mass Spectrometry

Pyrolysis gas chromatography (PyGC), particularly when combined with mass spectrometry (PyGC-MS) has shown to be a powerful, fast and elegant analytical method for the characterisation of polymers. In addition to qualitative and quantitative detection of monomer units and the identification of comonomers additional information about additives and impurities is also provided.

Burns and Doolan (xlix) have shown that by using PyGC-MS the discrimination between members within a series of modified alkyd resins which were indistinguishable by Fourier transform infrared spectroscopy is possible.

A preliminary investigation based on PyGC-MS analysis of 100 automobile paint samples of five different colors has been presented by Kochanowski and Morgan (l). Designed experiments were employed to select pyrolysis conditions for adequate discrimination. Pattern recognition techniques including principal component analysis and canonical variate analysis were used to visualise clustering of pyrograms to validate comparisons between different automotive paints. These procedures potentially ease the interpretation of data sets which involve many comparisons.

The examination of 73 automotive paint samples using PyGC has been reportet by Shon et al. (li). Four colours of each domestic automotive make that is popular in Korea were analysed. The researchers concluded that their method can be used not only to compare paint trace with their suspected sources, but also to identify the type, make and model of the car.

Lee et al. (lii) have reported on a series of experiments that were carried out to test the applicability of time-of-flight secondary ion mass spectrometry (TOF-SIMS) in forensic paint analysis and the specifity of mass spectra in paint analysis.

Static secondary ion mass spectrometry (SIMS) is a sensitive and nearly nondestructive approach to the characterisation of small samples of paint and other coating materials. A variety of automotive paints, spray paints and fingernail polish samples, which were visually similar, but had different chemical composition and formulations were analysed by Gresham et al. (liii) using quadrupole static secondary ion mass spectrometry (SIMS). Coating distinction was easily achieved in many cases because of the presence of dominant ions derived from the components of the coating, which could be observed in the SIMS spectra. In other instances, coating distinction was difficult within a product line because of spectral complexity. For this reason and because of the large number of spectra generated in this study, multivariate statistical techniques were employed, which allowed the meaningful classification and comparison of spectra. Principal component analysis (PCA) showed distinct spectral differences between most spectral groups, and also emphasised the reproducibility of the SIMS spectra. When using parcial least squares (PLS) analysis, reasonably accurate coating identification was achieved with the data.

Geyer-Lippmann (liv) has studied low temperature PyGC-MS of paints and polymers. By running a CDS pyroliser at 450°C mainly additives could be identified. The paint binder was analysed in a second run at 800 °C. It is demonstrated that the paint pyrograms of second runs show only minor differences compared to the pyrograms taken directly at 800°C. The discrimination power for paint analysis is greatly enhanced by this two step procedure. A MS-library for paint additives has been created with about 100 entries.

Chiavari et al. (lv) have reported on the characterisation of standard tempera painting layers containing proteinaceous binders by PyGC-MS. Thirty standard painting layers were analysed by PyGC-MS and by PyGC-MS in the presence of tetramethylammonium hydroxide (simultaneous pyrolysis methylation). Painting layers were prepared according to Renaissance recipes for tempera, proteinaceous binders (egg, glue and casein) and six different pigments. Thermal degradation products of proteins, carbohydrates and lipids were selected for semiquantitive analysis based on single/summed ion monitoring (SIM) mode. The relative distribution of these products was used to characterise binding media for the purpose of their identification in painting layers.

Significant results have been published by Chiavari and Mazzeo (lvi) for the characterisation of polychrome Chinese archaeological objects of art. PyGC-MS was used to detect the presence of cinnabar (HgS) and organic materials such as Chinese laquer and natural waxes.

Studies have been conducted by van den Berg et al. (lvii) on the identification of an original non-terpenoid varnish from an early 20th century oil painting. Different mass spectrometric approaches were used. Direct temperature-resolved mass spectrometry and PyGC-MS mainly showed the phenolic components, whereas thermally assisted (trans)methylation with tetramethylammonium hydroxide (TMAH) strongly enhanced the evidence for tung oil as part of the varnish. The degree of hydrolysis of the oil network was found to be low. No evidence was found for a direct link between the drying oil and phenolic resin.

Van den Berg et al. (lviii) have reported on a mass spectrometric methodology for the analysis of highly oxidised diterpenoid acids in old master paintings. Diterpenoid resins from larch and pine trees and the corresponding fractions in a more than 100 years old wax-resin adhesive and varnish and a 200-year-old resin/oil paint sample were analysed by gas chromatography-mass spectrometry (GC-MS) using several off-line and on-line derivatisation methods. The study has indicated that Py-TMAH-GC-MS and direct temperature-resolved mass spectrometry are reliable, valuable and fast techniques for the assessment of the presence and degree of oxidation of diterpenoid resins.

Spectroscopic Methods

Infrared Spectroscopy

Infrared spectroscopy (IR) remains an extremely popular analytical method for the examination of paints. The use of infrared microscopes has become an essential tool for routine application of Fourier transform infrared spectroscopy (FTIR) in forensic analysis.

During the 1990s there were improvements in the development of micro-sampling accessories. Although the attenuated total reflectance (ATR) technique is not necessarily appropriate for all sample types, and the appearance of spectra may not always compare exactly with pre-recorded data from traditional sampling techniques the user has been provided with one of the most reproducible methods available. The use of ATR accessories has been reviewed by Coates and Sanders (lix).

Urban (lx) has reported on modern methods in coating analysis. Powerful FTIR-techniques which offer surface sensitivity and selectivity without vacuum limitations and broader range of applications are: ATR, reflectance-absorbance (R-A) as well as continuous-scan and step-scan photoacoustic (SS PAS), two-dimensional (2-D), and rheo-photoacoustic (RPA) measurements.

A survey of U.S. automobile original topcoats (1974-1989) for the identification of organic pigments has been conducted using infrared spectroscopy (54-56). Data were obtained from panels of the Reference Collection of Automotive Paints for single layer topcoats, excluding base coat/clear coat finishes. Suzuki and Marshall (lxi) demonstrated the feasibility of identifying organic pigments in situ based on their absorption in infrared spectra. The technique of subtracting spectra of closely matched topcoats lacking pigment features from the spectra of topcoats containing the pigment of interest was employed to identify quinacridone pigments used in red and brown non-metallic and metallic monocoats. Four quinacridons were identified: Quinacridone Red Y (PR 209), Quinacridon Violet (PV 19), Quinacridon Magenta (PR 122) and Quinacridon Magenta B (PR 202). The same techniques were further extended by Suzuki (lxii) to identify one red pigment of the diketopyrrolo-pyrrole family (DPP Red BO, PR 254) and Thioindigo Bordeaux (PR 188) in red non-metallic and brown non-metallic and metallic monocoats. The identification, analysis, and occurrence of yellow organic pigments: Isoindolinone Yellow 3R (PY 110), Isoindoline Yellow (PY 139), and Anthrapyrimidine Yellow (PY 108) in yellow, orange, brown, and green non metallic monocoats was also reported by Suzuki (lxiii).

Infrared spectroscopy was also used by Massonnet and Stoecklein (lxiv) for the in situ identification of pigments in 27 light red, 27 dark red non metallic and five red 2-coat metallic automotive topcoats. By using an automated comparison in a pigment database with a 1st derivative correlation search algorithm a positive identification of 13 different organic pigments was possible. The discrimination power (DP) of IR was found to be very high for paints of similar colour: 0.95 for the 27 light red automotive paints and 0.96 for the dark red automotive paints.

Considering the pronounced changes in binders that can now be found in automotive paints and their potential use in a wide variety of finishes worldwide, the Paint Subgroup of the Scientific Working Group for Materials Analysis (SWGMAT) initiated a validation study to investigate the ability of commonly accepted methods of forensic paint examination to differentiate between these newer types of paints. Nine automotive paint systems typical of original equipment applications were acquired from General Motors Corporation in 1992. The results reported by Ryland et al. (lxv) demonstrated that IR spectroscopy is an effective tool for discriminating between major automotive paint manufacturers formulation types which are currently used in original finishes. Furthermore, and equally important, the results illustrate that the mid-infrared spectra of the finishes are generally quite reproducible even when comparing data from different laboratories.

Zieba-Palus (lxvi) has conducted a study to examine paint fragments originating from different easel paintings dated from the 15th and 16th century. Combining the results obtained from FTIR and SEM-EDS analyses allowed the identification of most of the painting components, i.e. of the kinds of binders, pigments, and fillers present in each layer of the studied samples (except for some kinds of oils and resins)

Raman Spectroscopy

Raman spectroscopy is a rapidly developing field. Raman microscopy has demonstrated to be an important tool because it is reproducible, of high sensitivity, non-destructive, essentially immune to interference from adjacent materials and can be obtained in situ in paint analysis. A handbook of FT-Raman and infrared spectra of polymers have been published by Kuptsov and Zhizhin (lxvii).

Some unique possibilities of Raman spectroscopy using a FT-Raman instrument have been shown by Kuptsov (lxviii) in the field of examination of paints and other materials in forensic sciences.

A computerised database comprising 98 organic pigments used in automotive coatings has been created by Massonnet and Stoecklein (lxix). Light and dark red automotive paints have also been examined using near IR (NIR) FT-Raman spectroscopy.

Confocal Raman microscopy has been used by Dupuie et al. (lxx) to characterise the chemical composition of clearcoats in three paint systems: weathered and unweathered samples of isolated acrylic/melamine and acrylic/urethane clearcoats, polyester urethane clearcoats in weathered and unweathered samples of a complete paint system on plastic, and ultraviolet - light –cured acrylic clearcoats on polycarbonate substrates. The increase in the carbonyl peak intensity was found to be an excellent means to follow the progress of photo-oxidation in isolated clearcoats as well as in a clearcoat in a complete paint system.

In situ identification and analysis of automotive paint pigments using line segment excitation Raman spectroscopy have been described by Suzuki and Carrabba (lxxi). Raman spectra were acquired using a spectrometer equipped with a 785 nm solid state diode laser. Most of the paints analysed were U.S. automotive original finishes (1974-1989) from the Reference Collection of Automotive Paints, and the inorganic pigments examined were those which had been identified previously by IR spectroscopy.

The advantages of using in situ surface enhanced resonance Raman scattering (SERRS) spectroscopy have been highlighted by White et al. (lxxii). The studies confirmed the very high sensitivity that can be achieved with the SERRS technique and the molecular information obtained from spectra were used to compare dyes and pigments used to colour a wide variety of items encountered in everyday life.

A number of examples have been given by White (lxxiii) that the spectral information of in situ SERRS analyses can also be used to identify colourants in samples and to identify colourants, without their prior separation, if a sample contains a mixture of dyes and pigments.

Brissaud (lxxiv) has presented some applications of Raman microscopy for the identification of organic and inorganic pigments used in various paints. Pigment spectra for the development of a spectral library were recorded using an argon ion laser (457,9 nm, 488,0 nm or 514,5 nm excitation wavelength) and a helium-neon laser (excitation wavelength 632,8 nm).

A Raman spectroscopic library of natural and synthetic pigments known to have been in use before 1850 AD has been compiled by Bell et al. (lxxv).

High quality Raman spectra of fifty-six pigments can be downloaded in SPC-format from the internet (lxxvi). The Raman spectra of 21 azo pigments have been analysed by Vandenabeele et al. (lxxvii) and a protocol has been established for their identification.

A new method for discriminating between fluorescence and Raman signals in luminescent samples has been described by Bell et al. (lxxviii). This technique, called substracted shifted Raman spectroscopy (SSRS), operates by taking several Raman spectra at different but closely spaced spectrometer positions. This results in the removal of the fixed pattern irregularities found in spectra taken with a CCD camera.

Analysis of archaeological objects by Raman spectroscopy has become a rapidly growing field. Characteristic Raman bands are used to identify various materials and to detect degradation products of pigments and dyes. Coupry (lxxix) has reported on the advantages and limitations of Raman microscopy and the specific experimental procedures for the study of art objects. Concerning pigments a few fields of application have been chosen in order to illustrate the wide potentiality of this technique.

A review with 64 references has been presented by Cariati and Bruni (lxxx) regarding the applications of Raman spectroscopy in art and archaeology. Topics discussed include an overview of the Raman effect, Raman instrumentation and techniques, Fourier transform near – IR Raman spectroscopy, resonance Raman spectroscopy, Raman spectroscopy as support for restoration and conservation, and application of Raman spectroscopy to the study of pigments in artistic works.

Vandenabeele et al. (lxxxi) have reported on the analysis of natural organic binding media and varnishes used in art by micro-Raman spectroscopy. Spectra were recorded of different types of proteinaceous, polyaccharide, fatty acid, and resinous media. The Raman spectra can be used as a reference for fingerprinting unknown binders and varnishes.

X-ray Spectrometry

Although many forensic institutes have integrated new X-ray spectrometry equipment in their laboratories during the last four years, e.g. capillary optics for microfluorescence analysis, total reflection X-ray fluorescence (TXRF) etc. no articles appeared in the field of forensic paint analysis during the reported period. On the other hand some interesting papers for the application of X-ray spectrometry to cultural and heritage samples have been published.

Examples of analyses by X-ray fluorescence (XRF) spectrometry in art and archaeology, including pigments in paint layers and illuminated manuscripts have been presented by Mantler and Schreiner (lxxxii). Theoretical aspects of information depths and shielding effects in layered materials are discussed. Elemental maps were experimentally obtained by a specially designed X-ray spectrometer and by electron excited XRF.

Studies have been conducted by Moioli and Seccaroni (lxxxiii) on the analysis of art objects using a portable X-ray fluorescence spectrometer. The authors have acquired considerable experience in XRF analysis, investigating more than 500 works of art including 350 easel and mural paintings.

Total reflection X-ray fluorescence spectroscopy (TXRF) and micro Raman spectroscopy were applied to pigment investigations of several miniatures in the late-medieval Breviarium Mayer van den Bergh by Vanenabeele et al. (lxxxiv). The pigments in the Breviarium could easily be identified. Comparing of equally coloured samples from the Breviarium confirmed the common origin of two illuminations attributed to the same illuminator.

Databases

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

Bishea et al. (lxxxv) have reported on the support and further development of the Royal Canadian Mounted Police's (RCMP) automotive paint database "Paint Data Query" (PDQ). A co-operative agreement between the Federal Bureau of Investigation (FBI) and the RCMP has been the offspring of the Paint Subgroup within the Scientific Working Group for Materials Analysis (SWGMAT). Financial support has been acquired through the National Institute of Standards and Technology (NIST) and the National Institute of Justice.

The automotive paint database has three distinct functions: a tool to assist the identification of unknown suspect vehicle(s), developing a statement of paint uniqueness which may be used to lend weight and credibility to court evidence, and a professional development tool for examiners so that they may maintain their expertise at a production year level since the database will reflect the yearly changes in the automotive paint industry. Tracking an original finish to make/model/year may be possible through comparison with colour of the undercoat layers, sequence of paint layers and chemistries of each individual layer to the PDQ. PDQ contains an IR library of all paint layers held in the database.

The European Collection of Automotive Paints (EUCAP) has been discussed by Piotrowski (lxxxvi). This database has been supported by the European Paint Group, a working-group of the European Network of Forensic Science Institutes (ENFSI). At the present time, 42 forensic laboratories from 21 European countries participate in the EUCAP programme by supplying analytical data, information and samples obtained through contacts with car and paint manufacturer in their countries. The Bundeskriminalamt (BKA – KT 13) has become a central co-ordinator of the project.

Hong et al. (lxxxvii) have described the compilation of a library for IR spectra of original topcoats and clear coats for Korean automobiles. The library has been constructed by taking spectra of the reference automobile paint panels of their chassis and bumpers. The paint panels of four coated layers (primer, primer surfacer, base-coat, clear coat) were kindly donated by four Korean automobile paint manufacturers, along with information on the binder types and polymerisation reactants of each coating layer. The library consists of IR spectra of chassis topcoats, bumper topcoats and chassis-/bumper clearcoats.

Park et al. (lxxxviii) have studied IR absorption characteristics of Korean automobile plastic parts and presented their database for forensic application. Collected IR spectra of the polymers were grouped according to similarities in their patterns while ignoring the additive contents and physical properties. Because paints and plastic parts were supplied by many different OEM suppliers, analysis of the plastic resins in conjunction with those of the paint binders could serve to narrow down the suspect lists of the vehicle type and the year of manufacture. Saito et al. (lxxxix) have reported on a novel identification system for automobile hit-and-run cases. They developed a digital image database comprising 4298 automotive topcoat samples provided by the National Police Agency Tokyo, Identification Section. This retrieval system is applicable to all paint traces, needs only a research microscope, is non-destructive and time-saving. As a filtering element for the retrieval process FT IR spectra were integrated into the database.

Evidential Value

A number of efforts have been made in the past to assess evidential value of paint transfer. The evidential value of paint transfer depends on many factors such as: type of paint, unusual pigments, frequency of occurrence of topcoat colour, layer sequence etc.. In traffic accident cases other factors can be of great importance, like: flow rates of traffic, 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 etc.. It was observed that responsibility of properly interpreting the meaning of paint evidence is difficult since each case is different.

In a very useful paper Evett (xc) has discussed the principles of statement writing. Although it is true that forensic science evidence is often difficult to quantify, the existence of a numerical scale as a central concept provides the forensic scientist with the basis of rational and coherent debate about the use of terminology. The Bayesian framework unifies all kinds of scientific evidence across all languages and cultures.

McDermott et al. (xci) have studied the evidential value of paint using Bayes' theorem for the first time. Over 1000 vehicles were examined and the make, colour and year recorded. In addition, the presence of foreign paint was noted and whether or not there was damage to the vehicle's paintwork that may indicate paint being transferred. The likelihood ratios for various paint transfer scenarios were calculated. These ratios were then converted to an appropriate verbal equivalent and to conclusions used by forensic paint examiners for similar scenarios.

Interesting Cases

Two cases have been described by Kuppuswamy and Ponnuswamy (xcii) where motor vehicle accidents led to fabric weave impressions and fibres being transferred to the paintwork of vehicles from the clothes of the victims.

Zieba-Palus and Trzcinska (xciii) have discussed three selected paint cases. Two of them concerned hit-and-run accidents and the third one referred to the identification of paint used for parquet painting in connection with poisoning by means of volatile paint components.

Two methods (FTIR microscopy and SEM-EDS) have been applied by Zieba-Palus (xciv) to the examination of multilayered paint fragments to provide information in two hit-and-run accidents.

The Internet

One of the dilemmas which a forensic scientist faces nowadays is caused by the fact that knowledge is subjected to a rapid shrinking of its half-life value and at the same time an enormous acceleration of its growth can be seen. To keep pace with all the developments made in paint or pigment chemistry as well as in the field of analytical methods a forensic scientist cannot afford not to use relevant databases created by various private, governmental or commercial sources.
The common platform where such databases can be found is the Internet.

Instead of using the standard WWW search engines such as Alta Vista®, Yahoo® or Google® and searching in the total WWW, it is more comfortable to start with special websites addressing forensic science, chemistry or journals.

R.P.Chamakura (xcv) provides such a compilation of web sites addressing forensic science. The paper gives a a brief overview of basic structure and essential components of the internet and presents a number of home pages that made available on the Net by forensic science societies, forensic science journals, forensic laboratories and institutions, government law enforcement agencies, colleges and universities offering forensic science programs or courses. Web sites dealing with various topics relevant for forensic scientists like trace evidence, instrumentation, scientific evidence in court or newsgroups are listed in tables. As the article was published in 1997 some sites may nowadays no longer be valid or have been moved to other locations.

A more recent review has been published by A.J.Davies and G.N.Rutty (xcvi). The paper presents a subjective analysis of information available on the Internet to those working in forensic medicine. 58 web sites have been assessed by the authors by various criteria like quality and quantity of the contents, structure and accessibility. Even if various websites are more focused on forensic medicine topics, there are also law enforcement sites or forensic science sites which are of interest for those forensic scientist dealing with trace evidence like paint.

Another short review is given by G.N.Rutty (xcvii) dealing with personal home pages listing links to websites interesting for forensic scientists.

In addition to the home pages given in the above mentionned papers a number of websites with links to journal databases have been found to be valuable sources for downloading bibliographic data, abstracts or even complete papers about relevant topics in chemistry, analytical methods or forensic science:

1. Berkeley Digital Library Sunsite
(links to more than 3000 library catalogues in 90 countries)
http://sunsite.berkeley.edu/Libweb

2. Chemconnect - Industry Journals and Magazines
(links to chemistry journals and publishers)
www.ch.cam.ac.uk/chemJournals.html

3. Jade-WWW Journal Articles Database
(free access to the bibliographic data of 10 milllion journal articles)
www.ub.uni-bilefeld.de/netahtml/jabl1.html

4. Dekker New Website
(online access to Dekker's entire journal program, books, handbooks and textbooks)
www.dekker.com

5. OPAC of the Union Cataloque of Serials (ZDB)
(The ZDB is a database for serial titles (journals, annuals, newspapers etc.) The ZDB-network is managed by the Staatsbibliothek zu Berlin; the database is held on a server of Die Deutsche Bibliothek. The ZDB contains more than 1 million bibliographic records of serials, in all languages, held in 4000 German and some foreign libraries, with holdings information.)
http://pacifix.ddb.de:7000/

6. ingenta
(gateway for the search and delivery of research articles, giving access to 20000 publications)
www.ingenta.com

7. CASELECTS™ on the web
(CA abstracts and bibligraphic information)
http://caselects.cas.org

8. Wiley InterScience Home Page
(access to the journals published by John Wiley & and Sons.Inc.)
www.interscience.wiley.com

9. JOT - Fachzeitschrift or the English version: Automotive Surface Technology
(archive with papers concerning automotive coating technology)
www.jot-oberflaeche.de

10. European Coatings Net
(this website gives information about topics relevant to coatings. In the archive a variety of papers published in the European Coatings Journal or presented at the annual European Coatings Show in Nürnberg/Germany are available in full-text)
www.coatings.de/index.cfm

11. NCJRS (National Criminal Justice Reference Service)
(the NCJRS abstracts database contains summaries of more than 160000 criminal justice publications, including Federal State, and local government reports, books, research reports, journal articles, and unpublished research. In a full-text database about 1500 full-text publications are available.)
www.ncjrs.org

12. ASTM Technical Standards for Industries Worldwide
(searching and ordering of individual ASTM standards or technical publications)
www.astm.org

13. Scientific Databases - Analytical Chemistry
(a gateway to the data collection of the National Institute of Standards and Technology including 7500 Ir spectra, 10000 mass spectra, 400 UV/Vis spectra and electroni and vibrational spectra for over 3000 compounds.)
www.nist.gov/srd or http://webbook.nist.gov/

Last but not least the Forensic Science Service (London/UK) CD ROM database FORS (Forensic Bibilographic Database) has to be mentionned. This database covers literature relevant to the examination of evidential materials, analytical methods and the presentation and interpretation of findings. The database scans a list of about 250 journals published worldwide, together with a series of abstracting and bibliographic services. Over 1900 sources are included. Updates are carried out monthly.

Books and Reviews

A number of useful and informative books and reviews have been published, which are expected to be of the greatest interest to the paint examiner. In some cases review articles have been included in earlier sections in order to maintain the continuity of the discussion.

Bieleman (xcviii) has written a book totally dedicated to additives. It provides a milestone in quality assurance covering the complete field of coatings. The following questions are answered: how do the most important groups of additives act? Which effects can be achieved by their addition?

Freitag and Stoye (xcix) have published the second edition of "Paints, Coatings and Solvents". This work serves not only as a concise practical guide but is also an authoritative reference book essential to all chemists and chemical engineers working with paints. It is an up-to-date overview of the industrial aspects of paints, coatings, and solvents including composition, production, processing, uses and methods of analysis.

Herbst and Hunger (c) have revised and updated their very wide-ranging reference work "Industrial Organic Pigments". The reader will appreciate the detailed discussion of up-to-date information on synthesis, reaction mechanisms, physical and chemical properties, test methods, and applications of all industrially produced organic pigments of the world market.

Over 40 first-class authors from leading chemical companies have created a uniform and clearly structured text covering industrial inorganic pigments. This revised and updated book edited by Buxbaum (ci) offers a concise and thorough presentation of inorganic pigments in their diversity: their manufacturing processes, their applications and markets, their testing procedures and standards, and also the health and environmental regulations relating to them.

Hugh and Smith (cii) have edited a book covering both organic and inorganic pigments as well as focusing on new technologies. With the increasing importance of high performance pigments in recent years, this text provides an up-to-date overview of scientific and technological aspects in one comprehensive volume.

Wicks et al. (ciii) have published the second edition of "Organic Coatings". The authors introduce readers to the subject with seven chapters on key properties of coatings, then proceed to cover raw materials (binders, solvents, pigments), physical concepts, formulations, and applications. Each topic has been carefully summarized and is accompanied by extensive references to sources of detailed information – particularly useful in self-study.

The second edition of "Colour Chemistry" has been published by Zollinger and Iqbal (civ). In this standard volume the properties, syntheses and industrial applications of organic dyes and pigments are described. New areas of investigation like calculation of spectra and computer modelling of colourants are included, and supramolecular aspects of interaction between colourants and between dyes and their substrates.

The first book that is devoted entirely to failure analysis of paints and coatings has been published by Weldon (cv). It deals with field and laboratory methods (both analytical and physical) involved in determining the causes of premature paint and coating failures in the commercial and industrial area.

Owing to its unique combination of high information content and ease of use, Raman spectroscopy has attracted much attention over the past fifteen years. Interest in Raman spectroscopy for paint analysis continues to grow. McCreery (cvi) has published a book which covers all aspects of modern Raman spectroscopy, including Raman microscopy and Raman spectroscopy of surfaces.

For all users of XRS and X-ray diffraction (XRD), a book edited by Buhrke et al. (cvii) will be of great help to make the best decision on sample treatment in order to get accurate results. The book provides detailed coverage of the X-ray theory, step-by-step sample preparation methods, and equipment suggestions and it contains useful bibliography and references.

A new volume has just appeared on microfluorescence analysis edited by Janssens et al. (cviii). While the main scope is instrumentation of laboratory – scale and synchrotron radiation equipment, various types of applications are described. Readers wishing to overcome the difficulties and pitfalls of quantitation problems related to microanalysis will find a separate chapter with ample references.

Bradbury and Bracegirdle (cix) have published an "Introduction to Light Microscopy". Introductory chapters encourage the user to think about the ultimate purpose for microscopical observations. Optics are thoroughly detailed, as are explanations on the hand lens, low-power stereomicroscopy, and the compound microscopes. All component parts receive detailed treatment; and the book ends with highly readable and sound advice on the practical use of the microscope.

Herman (cx) has published an updated and much-expanded second edition of his popular text "Fluorescence Microscopy". Intended as a broad introduction to fluorescence principles and applications, it lays out the fundamentals of fluorescence and outlines fluorescence microscopy. The new edition also provides details on optics, components, and microscope alignment, practical optimising techniques, individual applications, digitised video and photomicrography, and both single and multiphoton microscopy. Helpful educational web-sites are included.

"The Handbook of Analytical Techniques" (cxi) has been edited by Günzler and Williams. The handbook serves as a consise, one-step reference source for every professional, researcher, or student using analytical techniques. All relevant spectroscopic, chromatographic, and electrochemical techniques are described, including chemical and biochemical sensors, as well as e.g. thermal analysis, bioanalytical, nuclear or radiochemical techniques. Special articles are devoted to general topics such as chemometrics, sampling, and sample preparation. All articles are written and reviewed by acknowledged experts.

The 2nd edition of Volume I of the well known "Forensic Science Handbook" edited by Saferstein (cxii) has been published. Single chapters of this useful reference book are dedicated to special topics for the paint examiner like visible microscopical spectrophotometry in the forensic science, and forensic paint examination.

Review articles encompassing a two year period at a time devoted to technical advances and applications of instrumentation and methods covering IR-spectroscopy (cxiii)-(cxiv), Raman spectroscopy (cxv)-(cxvi), X-ray spectrometry (cxvii) and chemical microscopy (cxviii)-(cxix) as well as to coatings (cxx) and forensic science (cxxi) have also been published. They may be of interest to those engaged in the examination of forensic paint samples.

GLASS

Glass is by definition an inorganic product of fusion which has cooled to a rigid condition without crystallising (cxxii). This material is one of the major types of evidence encountered in crimes such as burglary, traffic accidents and vandalism. One of the common methods of examination is to measure the refractive index. However as narrow limits are set for the main components used in the manufacturing process of e.g. float glass, the ability to discriminate between float glass samples by refractive index may be considerably reduced.

Different ways of dealing with the pressure of increasing the evidential value of case work have been established. 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. Statistical and interpretations aspects should help to approach the case work in a more successful way. Recent advantages 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 physical property comparisons. New aspects of quality management and the establishment of new databases can be observed. The recent advantages made in these areas are summoned up below.

Frequency of occurrence

Several contributions have been dealing with the frequency of occurrence of glass. Triggered by the work of Lau (cxxiii) who has observed very low findings of glass fragments on outer garments of clothes of high school students, several groups have carried out similar studies on this topic.

Petterd et al. (cxxiv) have reported the examination of 2008 upper outer garments collected from random members of the public in three different metropolitan areas of south-eastern Australia for the presence of glass fragments. Due to the small number of recovered glasses, the study results indicate that the prevalence of glass particles on the surface of randomly selected clothing is very low.

Roux et al. (cxxv) have carried out a further study on the frequency of occurrence of glass. A total of 776 pairs of shoes collected from random members of the public in south-eastern Australia were examined for the presence of glass fragments. This study has shown that the prevalence of glass fragments in footwear is dependent upon the area of the shoe from which the fragments were recovered. A much higher percentage of shoes were found to have fragments embedded in the sole (5.9 %) than in the upper area of the shoe (1.9 %). These shoes were also more likely to have multiple fragments from multiple sources of glass. Only a very small percentage of shoes contained fragments in both the upper and the sole (0.3 %).

The outer clothing and footwear of 122 people attending a university gymnasium and a private gymnasium were searched for fragments of glass as reported by Coulson et al. (cxxvi). Both the surfaces and the pockets of the clothing and the uppers and soles of the footwear were searched. No glass fragments were found on the surfaces of the clothing and only a few fragments of glass were found in the pockets of the clothing. In this work several previous studies were compared. Taking the different search strategies of the different groups into account, P values were calculated for comparison. Also, an interpretation strategy based on statistical calculations has been presented. Furthermore New Zealand forensic glass cases have been reviewed in order to determine the amount of nonmatching glass present on the clothing of people who are suspected of breaking crimes.

Transfer of glass

Several studies have been carried out in order to investigate numerous aspects of the transfer of glass fragments.

Allen & Scranage (cxxvii) have investigated the number of glass fragments transferred to the clothing of a person in the vicinity of a breaking window. Clothed tailor' s dummies were subjected to flying debris from window breaking. It was found that most of the fragments were found on the jumper and substantial numbers were found on the socks, whereas very few fragments were found on the trousers. The number of fragments transferred decreases rapidly with distance from the breaking window.

In a further study Allen et al. (cxxviii) have investigated the effects of wet and dry clothing, contacting the window, smashing out most of the window with multiple blows and stepping through the broken window on the transfer of glass. The results have been presented in terms of the number of fragments found on the upper bodywear and legwear and on the debris sheets. Fragment size, distributions and the distribution of fragments with original surfaces have been included. The type of clothing had some effect on the number of fragments transferred to and recovered from the person breaking the window. Similar results were obtained from persons smashing out the remaining glass or walking through the broken window. It was figured out that wet clothes may contain more fragments compared to dry clothes.

Moreover, the possible transfer of glass between a person who has broken a window and another person has been investigated by Allen et al. (cxxix). Experiments have been designed so that the breaker was in close contact with a second person during a car ride. Out of a total of 15 experimental runs only one fragment of glass was recovered from the garments of the second person, although occasional fragments were recovered from the car seat after an individual journey. It has been shown that it is possible for glass to be transferred from a person with glass on them to a person with no glass on them, but it appeared very unlikely that large numbers of glass fragments will be transferred. Only a single glass fragment may have been transferred in this study.

The transfer of glass from the outer surface of a cardboard box to the clothing of a person carrying the box have also been investigated by Allen et al. (cxxx). In these experiments the box was placed 1 m behind a window which was subsequently broken. Glass was found on the box after all breakings, with more than 200 fragments on the surface in 7 out of 12 experiments. Between 1 and 22 fragments were recovered from the clothing (upper bodywear and legwear) of the person carrying the box. The distribution of fragment size and shape was similar to those described in previous studies.

In a following study by Allen et al. (cxxxi) the distribution of glass fragments on the ground in front of and to the sides of a car when a windscreen was crazed or shattered from the outside of the vehicle has been examined. Both toughened and laminated screens were examined. The number of fragments in front of the window decreased with increasing distance. Very few fragments were found by the sides of the car. An average of over 1400 fragments in the range 0.25-1.0 mm was found in the car when the window was crazed. As would be expected, more fragments were produced by shattering, rather than by crazing toughened glass. There was no significant difference in the number of fragments produced between crazing toughened and laminated glass. When toughened or laminated screens were crazed, the fragments recovered inside the car were from the inner surface. Fragments outside the car came from the outer surface. When the screen was shattered, glass fragments from the outer surface of the screen were found inside the car and vice versa.

A summary concerning the transfer and persistence studies has been given in chapter 5 of the recently published book on glass interpretation by Curran et al. (cxxxii). Different aspects of glass transfer (transfer to ground, transfer to garments, transfer to individuals standing nearby, transfer of vehicle glass, secondary and tertiary transfer) have been reviewed. Moreover the persistence of glass on different materials such as clothes, shoes, and hair was reviewed. A graphical model for assessing transfer probabilities has been developed.

Sampling

Sandercock (cxxxiii) has investigated the variation in the refractive index of control glass samples submitted from scenes of crime. Refractive index data were compiled for four types of flat glass: toughened float glass, non-toughened float glass, non-float glass, and wired glass. From the case data, additional control glass samples for each type of glass were simulated. This was done by standardising and pooling the data for each type of glass and then drawing a predetermined number of measurements from a given data pool. The author suggests that, as a guideline, a minimum of 17 refractive index measurements has to be made when sampling a toughened float glass control, and a minimum of nine refractive index measurements be made when sampling a non-toughened float glass control.

Faber et al. (cxxxiv) have addressed the question of the number of recovered microtraces (hairs, fibres, glass, paint, etc.) to be measured in forensic casework. If the measurement method allows for identification with absolute certainty, the appropriate probability model was identified as sampling without replacement from an urn containing balls of two colours, associated with a hypergeometric probability distribution. For the general situation, where certainty is less than 100 %, an adaptation of the classical urn model was proposed and solved. The paper was focused on fibres to illustrate the practical implementation of theoretical ideas, but the concept can also be applied to other microtraces.

Distribution of refractive index

Koons & Buscaglia (cxxxv) have investigated the variation of the distribution of RI values using the FBI database. They compared the distribution of the RI values among flat glass from 1964 through 1979 with the distribution from 1980 through 1997. They observed that the distribution of samples around the most frequently observed values are much narrower in the post-1980 samples than for those received prior to 1980. The observed narrowing of the spread among RI values has supported the necessity of using more discriminating methods that can be used to compare fragments of the glass having indistinguishable RI values.

Becker et al. (cxxxvi) have presented a database that has been designed for scene of crime and suspect glass material. The database includes information on refractive index, standard deviation, number of measurements, annealing, origin, colour, thickness, glass type, type of crime, date of measurement. The aim of this centralised database was to enhance the evidential value of a given case regarding the frequency of occurrence and further relevant questions. For data interpretation purposes statistical calculations (t-test) and several grouping algorithms (EL1, ELM1, SKM2) have also been integrated into this software.

Elemental analysis

Based on the limited evidential value of RI measurements several analytical techniques for elemental analysis have been employed. A general overview on the chemical analysis of glasses has been given in a previously published book by Bach et al. (cxxxvii). The fields of sample preparation and elemental analysis have been covered. All main instrumental techniques used in the field of glass analysis such as electron probe microanalysis (EMPA), X-ray-fluorescence (XRF), atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation (LA) ICP-MS have been presented in a brief manner.

ICP-MS

Duckworth et al. (cxxxviii) have investigated the sources of variability in ICP-MS of glass analysis to determine possible sources of variation. The sources of variation examined include errors due to sample preparation, instrument accuracy, precision, and interlaboratory reproducibility. Analysis of variance has been applied to their ICP-MS analysis of NIST standards and to the interlaboratory comparisons of float glass samples collected across a sheet in a production facility. The results of these experiments allow a more accurate interpretation of forensic glass data and a better understanding of the discriminating power (absolute and practical) of ICP-MS.

Duckworth et al. (cxxxix), (cxl) have been carried out further work on the analysis of variance into components of time (day-to-day), dissolution (sample-to-sample), calibration and instrumental (internal) variance. Elements were classified into four categories defined by the combination of precision and accuracy. Those not falling into the classification of both good precision and accuracy were critically examined before inclusion in a list of potentially discriminating elements to be used for the development of an elemental concentration database for float glasses. The final list consisted of 59 isotopes, representing 46 elements.

Stoecklein et al. (cxli) have presented the characterisation of float glasses from international sources by their elemental compositions using inductively coupled plasma mass spectrometry (ICP-MS) and wavelength dispersive X-ray fluorescence spectroscopy (WDRF). Minute fragments (300 µg – 1 mg) of 61 colourless, brown and green glasses from 43 plants were analysed after acid digestion. Using ICP-MS, the concentrations of major, minor and trace elements were measured with a precision ranging from 1.5 to about 15 %. A check on the accuracy of part of the results was followed through determination of the concentration of 8 major and minor elements using WDXRF with a precision between 0.05 and 25 %. By quantitative analysis of 30 elements a classification of float glass and a complete discrimination of all samples was possible. In addition, using ICP-MS results the discrimination of glass samples made at different times in the same float glass plant was also possible.

Becker et al. (cxlii) have applied chemometric calculations such as principle component analysis (PCA), cluster analysis, and linear discriminant analysis to the 30 concentrations of the 61 float glasses from Europe, Japan and the United States. PCA was applied to detect the most discriminating elements. Only by the application of linear discriminant analysis was it possible to fully discriminate all glasses with respect to their origin (Europe, Japan and United States).

Almirall et al. (cxliii) have determined refractive index and elemental concentrations (Al, Ba, Ca, Fe, Mg, Mn, Sr, Ti and Zr) for four product-use categories: headlamp glass, container glass, non-vehicle window float glass, and vehicle float glass. Fisher's linear discriminant modelling using these data have allowed the differentiation of the four glass types but further discrimination was not possible within a product-use category. For this specific set of glasses, the concentrations of a number of metal ions were found to be correlated in some cases using the Spearmans Rank Correlation Coefficient. This precluded the use of traditional probability calculations in using elemental composition data for interpretation of glass evidence. The authors have stated that the opportunity to classify glass to product-use categories offers new developments in glass interpretation. The information of the fragment type could now be included into databases which count the number and distribution of glasses on clothes to result in a higher evidential value.

Koons and Buscaglia (cxliv) have evaluated the frequency distributions of refractive index and the concentrations of ten elements in 204 glass specimens received as evidence in casework. For all of the 20.706 pairwise comparisons of the 204 specimens in this study, each pair were analytically distinguishable. The authors have stated that the use of highly discriminating analytical methods for the comparison of trace evidence and the corresponding low probability of two unrelated glass specimens being indistinguishable, eliminates the need to collect extensive databases for the purpose of making exact probability calculations.

This paper has triggered a vivid discussion. Curran et al. (cxlv) have stated that despite the good power of discrimination of the combined elemental composition and refractive index measurements, it is particularly important that statistics, especially Bayesian statistics, have to be applied to the data to give an indication of the probability of two samples of glass matching "by chance". In response, the authors of the original paper (cxlvi) argued that statistics are important in the interpretation of any type of trace evidence analysis, but that it is more important to develop analytical methods capable of providing accurate, precise analytical data with the best possible powers of discrimination instead using poorer analytical methods or data reduction in order that statistics can be calculated and having to rely on statistics for data interpretation.

Suzuki (cxlvii) et al. have investigated the discrimination of bottle glass of the Japanese market by RI measurements and analysis of trace elements with ICP-MS. Thirteen elements (Co, Cu, Zn, Rb, Sr, Zr, Ag, Sn, Sb, Ba, La, Ce and Pb) were found to be useful for the discrimination of bottle glasses. Of 120 pairs among 16 domestic bottle samples, 13 pairs were indistinguishable by RI measurements only. The combination of trace element analysis by ICP-MS and refractive index measurement made it possible to distinguish all the pairs.

LA-ICP-MS

Laser ablation (LA) as a sample introduction system for ICP-MS has been applied more widely to the field of forensic science. The rapid characterisation of small glass fragments by LA-ICP-MS into glass types such as bottle glass, float glass, headlamp glass and borosilicate glass has been presented by Becker et al. (cxlviii). Ten elements (Mg, Si, Al, Ca, Fe, Rb, Zr, Ba, La and Ce) were measured for characterisation.

Norman et al. (cxlix) have compared LA-ICP-MS measurements with several other techniques such as solution ICP-MS, electron microprobe analysis and proton microprobe analysis. Results obtained by the various microbeam and solution methods agree well for concentrations ranging over several orders of magnitude. Replicate analyses of the glass standard BCR-2G demonstrated an analytical precision of 2-8 % relative (1$\hat{u}$) for all elements by laser ablation ICP-MS and <3% by solution ICP-MS, except for Li (5 %). These results emphasised the utility of laser ablation ICP-MS as a quantitative microbeam technique capable of rapid, precise determinations of sub-ppm trace element abundance in a variety of targets.

Günther (cl) et al. have reviewed recent trends in LA-ICP-MS. This article has highlighted some of the systems applied successfully in LA-ICP-MS. The current fields of applications were explained on selected examples using 266 nm and 193 nm laser ablation systems. A key issue in direct sampling is the need for solid calibration standards in the desired concentration range and a high degree of homogeneity.

Rocholl et al. (cli) have presented new concentration data for 24 lithophile trace elements in NIST certified reference material glasses SRM 610-SRM 611 in support of their use in microanalytical techniques. The data were obtained by solution ICP-MS and isotope dilution TIMS analysis of two different sample wafers. An overall assessment of these new results, also taking into account ion probe studies that have been published in the literature, showed that these wafers can be considered to be homogeneous. Therefore, individually analysed wafers were believed to be representative of the entire batch of the SRM 610-611 glasses. Possible exceptions are the alkali metals (and a few volatile or non-lithophile trace elements).

SEM-EDX/WDX

Several groups have used scanning electron microscopy (SEM) for the analysis of glass.

Kuisma-Kursula (clii) has reported a study on accuracy, precision and detection limits of SEM-WDS, SEM-EDS and proton induced x-ray emission (PIXE) spectroscopy in the multi-elemental analysis of medieval glass. The SEM-WDS and SEM-EDS methods were suitable for analysing major and minor components of glass samples. Trace element (< 1 wt.) analysis has been possible using the WDS or the PIXE method. The PIXE method proved to be the most sensitive.

Further work has been carried out by Zadora (cliii) to apply statistical and chemometric methods in the interpretation of analytical data obtained during examinations of glass fragments by refractive index measurements and elemental analysis. Results of refractive index measurements with the use of a GRIM system were analysed using the "3 sigma" rule and Student's t-test. The elemental composition of the studied glass samples was determined by SEM-EDX. An attempt was made to utilise selected statistical and chemometric methods both in order to classify an unknown glass sample into a use-type group of glass objects, and to discriminate between an evidential glass sample and a comparative glass sample. Cluster analysis has been utilised as a method for the discrimination of glass types such as colourless container glass, green container glass, brown container glass, car headlamp glass, and car window glass.

In addition Zadora (cliv) has also proposed a scheme of glass classification based on results of quantitative analysis of 153 glass objects. Car window glass, car headlamps, external glass of car light bulbs, internal glass of car light bulbs, external glass of ordinary light bulbs, internal glass of ordinary light bulbs, and sheet glass have been investigated by SEM-EDX. Concentrations of aluminium, barium, calcium, iron, lead, magnesium, potassium, sodium and zinc were determined. A non statistical method and the use of cluster analysis lead to the correct classification for most of the studied glass samples.

Zadora (clv) has tried to differentiate glass microtraces (vehicle window glass and ordinary windows sheets) with the same qualitative composition of the main components using multivariable statistics.

Becker et al. (clvi) have presented a proficiency test that was carried out in 1999-2000 in order to evaluate differences between the results of elemental analysis of float glass and the different strategies of glass analysis based on refractive index measurements and elemental analysis. Three pairs of glass samples with similar refractive indices had to be examined using refractive index measurements and elemental analysis. SEM/EDX, μ-XRF, and ICP-MS were used for the elemental analysis. Based solely on the refractive index measurements a complete differentiation of the glasses was not possible. Annealing of the glass enabled further differentiation. After the use of the elemental techniques a full differentiation of the six glasses was possible. The strategies used by different laboratories in order to discriminate between the samples and the merits of the various techniques applied have been discussed.

Interesting Cases

Webb and Buscaglia (clvii) have presented a case, in which side windows from two adjacent automobiles were broken in the commission of a pair of burglaries. Five fragments of glass, each weighing less than 20 µg, were recovered from a burglary suspect's shoes. The two control glasses, one blue and one green, were not differentiable by refractive index. Elemental analysis was necessary to discriminate between these sources. Milligram-sized samples of the two control glasses were analysed by inductively coupled plasma mass spectrometry (ICP-MS), which verified that the two sources were compositionally distinguishable, in particular by concentrations of rubidium, aluminium, and potassium. A non-destructive method of analysis was preferred for the recovered fragments because of their limited size. Therefore, a method was developed and validated for the comparison of very small glass samples by TXRF. The recovered and control fragments of comparable size were then analysed by TXRF. Finally, scanning electron microscopy energy dispersive X-ray (SEM-EDX) spectroscopy was performed to measure light element concentrations. The relative merits of each technique for the discrimination of very small glass fragments and the significance of the resulting associations in this case have been discussed.

Brozek-Mucha et al. (clviii) have reported a comparative study of small glass fragments taken from the clothes of two suspected people as evidence as well as samples collected from a broken car side window as comparative material. The study included the quantitative elemental analysis by means of a scanning electron microscope with an energy dispersive X-ray spectrometer as well as a statistical interpretation of the obtained results using cluster analysis. The sets of evidence and the comparative material revealed a similarity in the chemical contents and so, the conclusion was drawn that they might have been fragments from the same glass object.

Quality management

The American Society for Testing and Materials have published a 'Standard Test Method for the Automated Determination of Refractive Index of Glass Samples Using the Oil Immersion Method and a Phase Contrast Microscope' (ASTM E 1967-98) (clix). Important features of the ASTM E 1967-98 are the calibration of GRIM with a minimum of 3 glasses/oil, the selection of an interference filter at sodium D line (589 ± 5 nm) and control measurements with an external standard differing from the calibration standards (control charts). Also the precision/standard deviation of reference material (0,00002 n_d during a period of 5 h, 0,00003 n_d during a period of 5 days) has been outlined.

Becker et al. (clx) have presented a study of the German project group GRIM aimed at the harmonisation of refractive index measurements. This group outlined minimum criteria for case working ("eleven laws" of refractive index measurements), taking into account existing documents like ASTM E 1967-98. In co-operation with the glass manufacturer SCHOTT a glass standard with a controlled refractive index homogeneity of ± $7*10^{-7}$ was obtained. This BKA-K5 standard glass was distributed to all German forensic state laboratories to be used as an external standard in order to ensure comparability of refractive index measurements. This external standard is used for quality control charts on a daily basis.

Lovelock and Wright (clxi) have presented a new approach in dealing with glass cases with a focus on the scene of crime activities (sampling). They have presented a 'Critical Success Factors in Offences involving Broken Glass' form. This form is being distributed to all police forces for completion for every case involving glass. The critical success factors like contamination avoidance procedures, time of sampling, packing of sample, hair combings have been outlined and a questionnaire for the scene of crime officer was presented. The information gained by this questionnaire should help the forensic expert to be able to draw further conclusions in case interpretation.

Glass Technology

Hayden et al. (clxii) has presented an overview on recent applications on the production of several types of glasses.

Extensive research has been carried out on tin in float glass by Frischat et al. (clxiii). In this interdisciplinary work the depth dependent distribution of tin in its various oxidation states in float glass was investigated. Methods used were Rutherford backscattering spectrometry (RBS), electron microprobe analysis (ESMA), electron spectroscopy for chemical analysis with X-ray photoelectron spectroscopy (ESCA-XPS) secondary neutral mass spectrometry (SNMS) conversion electron Mössbauer spectroscopy (CEMS) and atomic force microscopy (AFM). It was found that directly at the surface (nm-depths) the tin concentration is 3 to 4 times higher than in µm depth. The so called tin peak showed an asymmetric function, it increased up to 1 µm depth and reduced with further depth. Sn(IV) is only appearing at µm depths whereas Sn(II) showed a constant decrease by depth.

These findings were in good agreement with a study by Stoecklein (clxiv). Cathodoluminescence (CL) of glasses have been observed by SEM. A wide band with a maximum at 495 nm was characteristic for the tin (II) luminescence of float sides of soda-lime glasses. A high tin count in soda-lime glass leads to a depression of the CL signal. Apparently with a higher tin concentration tin(II) ions were oxidised to tin(IV) ions that don't contribute to CL.

Geotti-Bianchini et al. (clxv) have used conversion electron Mössbauer spectroscopy (CEMS) to determine the oxidation state of tin coatings on bottle glass. The work showed that tin is tetravalent in crystalline form with a preferential grain orientation, which is reduced on annealing. The presence of tin in other oxidation states and dissolved in the matrix was excluded.

Thin films on glass

A good overview in the field of glass coating have been given by Danielzik et al. (clxvi). Coating materials and the different thin-film forming processes have been described, properties of thin films have been listed. Fabrication issues and further trends have been discussed.

Fachet et al. (clxvii) have reported the use of cuprous halides for the preparation of thin photochromic films. Using the sol-gel technique silicon alkoxide based coating solutions with continuously distributed photoactive components were prepared. From these sols single or multilayer coatings were produced by dipping. Thus it was possible for the first time to produce photochromic coatings with a pronounced darkening and with complete reversibility of the photochromic reactions at rooms temperature.

Glass surfaces including those of automotive glazing show insufficient scratch resistance. In order to improve this Hauk et al. (clxviii) developed a sol-gel process by means of which scratch-resistant and transparent corundum coatings (ζ-Al_2O_3) may be deposited on glass surfaces. Coatings which were produced by using commercial boehmite (AlOOH) dispersions could also be completely transformed into ζ-Al_2O_3, but they were not dense enough at about 500 nm thickness. Coatings produced by an alkoxide-gel process from aluminium butoxide were dense at a thickness of maximal 100 nm and adhered very well to the glass surface which had been slightly roughened by HF etching. A scratch test with a quartz grain showed that the damage of the glass surfaces coated in this way was less than 2 % compared to that of uncoated surfaces. Transmission of these coated glasses was about 90 % in the visible wavelength range.

Wittwer et al. (clxix) have briefly described the manufacturing technology of periodically structured surfaces on glass. Periodic structures on glass surfaces with dimensions much smaller than a micron can be used in very different applications such as antireflective surfaces.

Bayes

Cook et al. (clxx), (clxxi) have described a new approach to decision-making in an operational forensic science organisation based on a model, embodying the principles of Bayesian inference, which has been developed through workshops run within the Forensic Science Service for forensic science practitioners. This model is based on three aspects, the customer requirement, case pre-assessment and the service delivery including the evaluation of the likelihood ratio. Issues which arise from the idea of preassessment of cases were explored by means of a case example involving glass fragments.

Taroni and Aitken (clxxii) have investigated problems associated with the interpretation of scientific evidence (fibres and glass) in forensic science. The investigation includes the use of probabilistic arguments associated with expert scientific testimony in the courts. The authors described the principle of the Bayesian approach, including the calculation of the likelihood ratio for the value of the evidence in a given case. The authors believe that the education of scientists and jurists in a Bayesian framework for representing the value of scientific evidence at trial could lessen considerably the current imperfections.

Curran et al. (clxxiii) have presented the robustness of the Bayesian approach to deviations from the statistically convenient notion of normality of the measurements. Taking into account that a large portion of recovered glasses originate from surfaces or near to one and that these fragments tend to have a higher refractive index than fragments from the bulk glass, no normality distribution of refractive index can be assumed. The effect of departures from normality on the likelihood ratio have been investigated in this work. It is has been concluded that using the t-distribution (with Welch's modification) will provide a robust approximation to the true difference in the means of the control and recovered samples.

Books and reviews

A very comprehensive guide of the global glass market have been published by DMG Business Media (clxxiv). Analysis of over 40 national glass markets and more than 20 company profiles have been described in this work.

Brettell et al. (clxxv) have reviewed publications dealing with forensic science covering 13 citations for the period 1997-1999 connected to glass. In a recent review by Brettell et al. (clxxvi) 5 citations connected to glass can be found.

Bach and Krause (clxxvii) have edited a book on the analysis of the composition and structure of glass and glass ceramics. As already stated above, the fields of sample preparation and elemental analysis have been covered. All main instrumental techniques used in the field of glass analysis such as electron probe microanalysis (EMPA), X-Ray-Fluorescence (XRF), atomic absorption spectrometry (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and laser ablation (LA) ICP-MS were presented in a brief manner.

Bach and Krause (clxxviii) have also presented a book on thin films on glass. Covering six chapters coating materials were described, properties of thin films were listed, the different thin-film forming processes are described. Fabrication issues and further trends were discussed.

In addition Bach and Krause (clxxix) have presented another book on the properties of optical glass. It comprises of eight chapters from different authors covering all kinds of aspect of optical glass (historical, considerations, refractive index, chemical composition, mechanical and thermal properties, optical quality and selected applications).

Curran et al. (clxxx) have published a book on the forensic interpretation of glass evidence. In six chapters a wide range of topics of glass investigation have been presented. Starting with the examination of glass, the conventional approach to evidence interpretation was presented.The Bayesian approach to evidence interpretation was presented for improvement. After discussing frequency of occurrence studies and transfer and persistence studies followed by a chapter on statistics, the book ends with the reporting of glass evidence with a focus on the verbalisation of a likelihood answer.

CONCLUSIONS

This review of the literature published over the last three years, covering all aspects relevant to examination of paint and glass, has highlighted the following:

- 4# **The coating industry is continuing to improve coating systems in terms of their environmental compatibility. Most of the new developments by raw materials producers have been obtained in the fields of aqueous, powder and UV-curing coating systems.**

- 4# **Analytical studies have been started with the aim to identify forensically useful special features of new binder types. If the results are validated these features will become a powerful new tool for tracking down questioned paint samples to a specific vehicle in hit-and-run fatalities and other associated investigations involving automotive paints.**

- 4# **The new generation of effect pigments, based on synthetic silica and alumina flakes coated with highly refractive metal oxides have expanded the range of possibilities for stylists and designers in areas such as automotive coatings and coloured plastics.**

- 4# **The coating of plate-like, reflecting pigments like aluminium or micaceous iron oxide with weakly refracting, non-absorbing layers and semi-transparent iron oxide films has led to optically variable pigments with colour flops in the red, golden, and green colour space. In combination with absorption pigments new vivid colours with exciting, angle dependant hues have been developed especially for automotive coatings.**

- 4# **Dramatic colour flops in automotive paints have also been created by the application of Helicone pigments. These newly developed pigments consist of an organic polymer network comprising a so-called cholesteric liquid crystalline phase.**

- 4# **Studies have been conducted in order to classify and identify these newly developed plate-like and optical variable pigments. It has been shown that only by applying microscopical techniques in combination with SEM/EDS, MSP and XRD can exact results be obtained.**

- 4# **Some schemes have also been presented for the identification of one dimensional organic pigments. By applying the protonation technique using trifluoroacetic acid many organic pigments can be solubilised. Afterwards they can be separated by thin layer chromatography and identified by microspectrophotometry.**

- 4# **Infrared spectroscopy remains an extremely popular analytical tool for paint examiners. Several studies have been published with emphasis on the identification of organic and inorganic pigments.**

- 4# **It has been documented that Raman microscopy is a powerful technique for in situ analysis of forensic and archaeological paint samples. Characteristic Raman bands have been used to identify and detect inorganic and organic pigments.**

- 4# **Pyrolysis GC-MS – especially in the presence of tetramethylammonium hydroxide – has been shown to be a more powerful discriminatory method than FT-IR spectroscopy in the characterisation of automotive paints and binding media of old master paintings.**

- 4# **It has also been demonstrated that the discrimination power in paint analysis can be greatly enhanced by applying low temperature pyrolysis in combination with high temperature pyrolysis.**

- 4# **Pattern recognition techniques including principal component analysis and canonical variates analysis have been used to visualise clustering of pyrograms to validate comparisons between different automobile paints.**

To increase the evidential value of glass examinations several trends could be observed:

- 4# **Various kinds of statistics including the Bayesian approach have been applied to glass case work.**

- 4# **A more frequent application of elemental analysis techniques such as ICP-MS, LA-ICP-MS, SEM/EDS, μ-XRF, TXRF to increase the discriminating power of the investigations.**

- 4# **Ongoing developments on quality management systems including new reference materials and the development of new databases as a tool for case interpretation.**

- 4# **To improve interpretation, several investigations have been carried out on the frequency of occurrence of glass.**

- 4# **After the establishment of quality management systems in many laboratories a focus is set on the improvement of the first step of the chain of custody – the sampling of glass fragments at the scene of crime.**

- 4# **A number of articles concerning databases have been published or presented and discussed in scientific meetings. These databases can greatly assist the forensic chemist with the interpretation of evidence.**

- 4# **Validated methods and protocols of paint and glass analysis in the USA/Canada and in Europe, and traceability of standards used for examinations have greatly enhanced the possibility of sharing databases internationally.**

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