CHEMICAL CRIMINALISTICS

THE FORENSIC EXAMINATION OF FIBRES

– A Review: 2004 to 2007 –

Ray Palmer
Consultant Forensic Scientist
The Forensic Science Service Ltd
Hinchingbrooke Park, Huntingdon
Cambridgeshire PE296NU, UK

Email: ray.palmer@fss.pnn.police.uk

Contents

Introduction

This report catalogues the research and advances in scientific methodology relating to the forensic examination of fibres since the 14th INTERPOL Forensic Science Symposium held in October 2004. This report primarily consists of a literature review of published articles in forensic science journals and the proceedings of various working groups between May 2004 and August 2007. It also contains references from other sources such as periodicals, text books and the internet.

General

The scientific working groups in Europe and North America continue to be active in training and collaborative research - not only in developing laboratory methodology but also in the production of data useful for more robust interpretation of this evidence type. The European Fibre Group (EFG) of the European Network of Forensic Science Institutes (ENFSI) [41] and the Fibre subgroup of the Scientific Working Group for Materials Analysis (SWGMAT) led by the FBI, continue to be the main organisations promoting and developing this evidence type. Many of the citations in this document originate from the activities of these groups and/ or their members.

The EFG has remained committed to disseminating best practice and over the last 3 years has introduced a program of themed ‘development’ workshops, aimed at court reporting practitioners with less than 3 years experience. The workshop planned for this year is in Krakow, Poland and the theme is ‘intelligence’. In addition production of a document outlining the best use of fibre evidence in terrorist cases is underway. Once complete, the intention is to disseminate this to all law enforcement agencies in Europe (and abroad).

The EFG continues to collaborate with colleagues in SWGMAT and Australia and this remains extremely productive.

Likewise, the fibre sub-group of SWGMAT continues to be active. A review of the revisions to the Fibre Examination Guidelines document (originally published in 1998) is ongoing. Collaboration with colleagues in the EFG and SMANZFL continues, with work underway on a MSP project as well as the assessment of backpack fabric damage due to explosions.

Representatives from SWGMAT continue to attend the annual meeting of the EFG and *vice versa*.

Fibre Recovery

The recovery and preservation of fibres (whether at the crime scene or in the laboratory) is arguably the most crucial step in the examination process since in the majority of instances there will be little if any opportunity to re-perform this process. The ‘GIFT’ (‘get it first time’) principle remains the paramount objective.

Over the last few years there has been increased interest in the process of fibre recovery involving the 1:1 taping method whereby a detailed distribution map of transferred fibres can be made which may assist in elucidating the nature of contact between victim and assailant - either for intelligence or corroborative purposes in an investigation. Whilst many law enforcement agencies have seen the potential value of this technique, uptake has been poor due to the immense resources required at the scene and laboratory to achieve the end result.

Palmer [3] argued that whilst there is no doubt that true 1:1 taping at scenes can produce highly detailed maps of fibre distribution (such as reported by Nehse [40]), there is a question over whether this level of detail and the resources required are completely necessary. He reported on an alternative method which The Forensic Science Service has adopted, referred to as ‘Zonal’ taping. Although this method produces a map of fibre distribution which is less detailed than 1:1 taping, it has been demonstrated to be a more pragmatic ‘fit for purpose’ approach and much less resource intensive at the scene and in the laboratory. This technique essentially involves recovering fibres from predetermined zones on a body rather than using a single strip of tape to equate to an equal area of surface. This method is now beginning to find favour amongst police forces in the UK.

The subsequent searching of fibre tape lifts (regardless of whether 1:1, zonal or the ‘standard’ method is employed) remains the most time consuming part of the examination process. Various instruments attempting to automate this process have become available over the last decade, however, none have been shown to reliably compete with human searching. The most recent evaluations of such instruments have shown that these still suffer from the problems identified in previous instruments. Monard-Sermier et al [26] compared automatic fibre searching (using the Maxcan fibre finder) with manual searching, in terms of efficiency. The effect of several parameters (including colour, thickness, and background) on the efficacy of the fibre search was investigated. In the laboratory, 18 experimental tapes containing different target fibres and different background populations were prepared. Operators from four European laboratories carried out fibre searches, either manually or automatically with the Maxcan instrument. The results obtained suggest that automated searching with this particular instrument was as efficient as manual searching, *except* (as with previous instruments) when very pale or very dark fibres are involved. However, it was noted that the laboratory-prepared tapes may not have been representative of tapes submitted in actual casework situations.

The performance of a different instrument, the Q550fifi (Leica) was assessed by Campioli et al [2] who found that its performance was marred by a large number of false positives.

A consistently reliable automated fibre searching system therefore remains to be developed.

Coyle [1] highlighted the usefulness of fluorescence stereomicroscopy for the searching of tape lifts for fibre evidence. This approach exploits the fluorescent properties of fibres in order to enhance the contrast between the target fibre and background fibres. This is particularly useful when the target fibre and the background fibres are similar in terms of shade and/or structure. The process of discriminating between colourless fibres can also be enhanced by fluorescence stereomicroscopy. This method therefore provides the potential to speed up the searching process without the use of automation.

The subsequent recovery and preservation of fibre evidence from tape lifts onto the microscope slide in preparation for examination, requires the use of a suitable mountant, which needs to conform to specific criteria. Since established sources of such material can become unavailable (due to economic factors or health and safety concerns) the identification of suitable alternatives becomes extremely important.

Wiggins and Drummond [32] investigated possible replacements for the XAM Neutral Medium Improved White mounting medium which has now become unavailable. The replacement media tested were Clarion, Entellan, Eukitt, Euparal, home-made Phytohistol, and Practamount. The performance of each mounting medium was assessed in terms of colour, refractive index, setting, fluorescence, ease of handling, bubbling, crystal formation, shrinkage, yellowing, cracking, microspectrophotometry (visible and UV/visible) Fourier Transform Infrared (FTIR) spectroscopy, and thin-layer chromatography (TLC). Of the mounting media tested, Entellan and Eukitt performed consistently well, resulting in the recommendation of Entellan for forensic fibre examinations.

The robustness of fibre evidence not only depends on its correct recovery and preservation, but on the quality management systems in place within a laboratory to ensure subsequent contamination does not occur. Whilst anti-contamination issues relating to DNA evidence are often in place in a laboratory, it is disappointing that in some instances this is not applied to trace evidence.

Akrap [3] conducted a survey of laboratory anti-contamination procedures at various laboratories throughout Europe. From the survey returns, it was concluded that in general terms, the standard of anti-contamination procedures employed by most forensic laboratories and police forces are very good. However, it became apparent that a number of scientists need to spend some time educating the police officers that they work with in order to improve the submissions to the laboratory. Disappointingly, there was also evidence that some laboratories need to considerably improve their working practices with regards to contamination.

Analytical Methods

As in previous years, publications report attempts to improve existing techniques in terms of efficiency, sensitivity or a combination of both. The current methodologies used in fibre examinations are by and large tried and tested in this respect and therefore improvements in time and/ or increased discrimination afforded by new instrumentation and/ or methodologies have to be demonstrated before uptake is justified in terms of cost.

Research into the application of RAMAN spectroscopy to the forensic examination of textile fibres has continued since the last review, with members of the European Fibre Group being the most active in this area [1, 2, 3]. Work by other researchers in this field [18] has complimented the efforts of the EFG. Despite this research, adoption of this technique into mainstream operational laboratories is still poor, primarily because it has yet to demonstrate any substantial improvement in discrimination afforded by the combination of existing analytical protocols against the cost of the instrumentation. Nevertheless, research in this area is active and it is possible that the problems associated with its application in this area may be resolved.

The cross-sectional shape of fibres is an important comparative feature and a number of methods have been described for the preparation. Kolar [3] described the cork method, the metal plate method, microtome methods with various embedding media and polyethylene plastic tube method etc., which could be used for cross section preparation. A new simple method for preparation of fibre cross sections has been tested in the ICP. Shirt buttons, power glue, a glass microscopic slide and abrasive paper have been used for the fibre cross sections preparation. The section fixed on a glass microscopic slide has been prepared by ablating and polishing the surface of the button to a very thin layer. This method is easy and fast.

Infra Red Spectroscopy still remains an important part of the standard protocol of fibre analysis and comparison and several workers have carried out projects to extend the scope of this technique;

Causin et al [15] used Infrared (IR) microspectroscopy to obtain absorbance peaks of nitrile, carbonyl and C-H groups for 48 colourless acrylic fibres. The carbonyl signal, related to the co-monomers most often used in acrylic fibres, was ratioed against the nitrile and C-H bands, pertaining to the polymer chain backbones. Ratios representing a relative measure of the co-monomer content of the fibre were used for sample differentiation. There was a decrease in the crystallinity of fibres with increasing co-monomer content. Analysis of different fibres from the same sample generated results which were reproducible to within 6%. The ability to discriminate between colourless acrylic fibres enhances their evidential value.

Flynn et al [20] analysed bicomponent fibres using infrared chemical imaging. The fibres were examined either side-on or in cross-section. In six samples, infrared chemical imaging could spatially resolve two spectroscopically distinct regions when the samples were examined side-on. This technique yielded characteristic IR spectra for each component whilst providing images that clearly showed the side-by-side configuration of the components in the fibre. Preparing cross-sections of the fibres proved difficult for all but one of the samples. In five samples, the IR spectra could be used to identify the overall chemical composition of the fibres, in accordance with a published classification scheme, although the components of the fibres could not be spatially resolved. The analyses were also hampered by problems such as interference fringeing and sloping baselines, especially when acrylic-type fibres were examined.

Whilst microspectrophotometry is still used routinely to compare fibre colour in an objective manner, there is still an inherent subjective component to this method – particularly where very pale or opaque samples are involved and the resultant spectra are broad and featureless. The use of first derivative calculations is well documented in many areas of science but until recently there has been little (if any) literature relating to the potential of this technique to improve resolution and discrimination in forensic fibre examinations.

Wiggins et al [31] measured a range of fibre samples across the visible and UV/visible wavelength ranges, respectively. The first derivative of the absorbance spectra was then calculated and studied. For many of the samples, calculating the first derivative did not add any extra value because of the high number of points of comparison in the absorbance spectra. When the absorbance spectra produced for some samples were broad and featureless, the first derivative spectra provided more points of comparison, which facilitated the interpretation of the results. However, for some samples which had a high level of variation in absorbance spectra, the associated first derivative spectra showed differences between fibres which could have suggested that they did not match. Because of this, considerable care needs to be taken when using first derivative calculations as a tool in forensic fibre analysis, in order to avoid false exclusions.

One area of concern to the fibre examiner is the potential to falsely exclude a suspect fibre as having come from a particular source. It is known this potential can be increased if inadequate sampling of a garment is carried out where high intra-garment variability in colour exists.

A collaborative study between the EFG and SWGMAT reported by Wiggins [2] found no evidence of MSP spectral variation across a garment.

Methods of dye analysis (other than RAMAN) remain a fertile area of research.
The use of reactive dyes to colour fibres has increased over the last 10-15 years and these are often seen in casework. Before the introduction of techniques that allowed reactively-dyed fibres to be compared using TLC, only comparison microscopy and microspectrophotometry were routinely carried out. Since many microspectrophotometer equipped laboratories possess only visible range instruments, it is therefore important to see which techniques could potentially provide additional information in terms of a direct examination of the dye itself.

Wiggins et al [12] obtained samples of reactively dyed wool and cotton from a range of dye manufacturers, dye distributors and the Forensic Science Service (FSS) Fibre Data Collection. Red, blue and black fibres were selected as they are often encountered in casework. The results demonstrated that TLC and UV-MSP both provide important information over and above that obtained from comparison microscopy and visible range MSP.

Whilst the use of Thin Layer Chromatography (TLC) is firmly established as a method for classification and comparison of dye stuff, relatively large amounts of dye are required for this technique to be effective. Work has continued to identify methods which may increase the sensitivity of dye analysis to allow the analysis of material presently precluded by the use of TLC.

Petrick et al [19] assessed the usefulness of high-performance liquid chromatography-electrospray ionisation mass spectrometry (LC-MS), in the analysis of fibre dyes in forensic casework. A multi-stage chromatographic method using acidified water and acidified acetonitrile was developed to separate and identify a mixture consisting of 15 basic and 13 disperse dye standards. LC-MS was also applied to the detection and analysis of dyes extracted from individual 0.5 cm acrylic and polyester fibres which demonstrated its usefulness for this type of analysis. The advantage of LC-MS compared with other analytical methods of textile dye analysis was demonstrated by the differentiation of three black acrylic fibres that could not be fully differentiated on the basis of their UV-Vis spectra and/or chromatograms.

Roux et al [30] assessed the usefulness of ultra performance liquid chromatography (UPLC) for the analysis of fibre dyes. The results obtained confirmed the potential of this technique for trace evidence analysis, although further research is needed. It appears that UPLC can successfully analyse dyes extracted from single, black, polyester fibres with sufficient sensitivity and selectivity.

Huang et al [17] successfully used liquid chromatography-mass spectrometry (LC-MS) for the discrimination of textile dyes that could not easily be distinguished based on their UV/visible absorption profiles. LC-MS was used to identify seven pairs of commercially available dyes with almost identical UV/visible absorption profiles and absorption maxima within 5 nm. LC-MS was also capable of discriminating between two pairs of cotton fibres which were indistinguishable by microspectrophotometry. Dye elution from the column was monitored by a single-wavelength UV/visible detector.

The uptake of these techniques as a standard means of dye analysis will require further work to demonstrate their efficiency with a broad spectrum of fibre type/ dye combinations, against the cost of the instrumentation.

Whilst colour remains the critical component of fibres in terms of their instrumental analysis, attempts have been made to increase the discrimination of non-coloured fibres which presently are generally perceived to have little or no evidential value.

Causin et al [21] studied the application of pyrolysis gas chromatography mass spectrometry in the differentiation of colourless polyacrylonitrile-based fibres with similar structure. Fibres differ slightly in terms of the concentration and distribution of head-to-head arrangements of their monomers. Such structural variation can significantly affect the composition of the mixture of the pyrolysis products, allowing the fibres to be differentiated. It was found that hydrocyanic acid, acetonitrile, acetic acid, acrylonitrile, 1,3-dicyanopropene, 1,3-dicyanobutene, 2,4-dicyanobutene and 1,3,5-tricyanohexane were the most suitable degradation products for discriminating between samples studied. Principal component analysis was used evaluate the results.

Interpretation

Whilst many workers strive to improve the efficacy of the various methods of identification and comparison, the main emphasis on research over the last few years has been on the interpretation of fibre evidence. In many ways this is not surprising, since it is more often the case that fibre ‘matches’ are in themselves not contested, but that the significance of their presence is. For those employing the Bayesian approach to interpretation, it is vital that empirical data is gathered and that this process is ongoing. Since many studies have consistently shown that the chances of finding two fibres matching by chance are extremely low, it is important to demonstrate that in an ever changing textile environment these findings continue to hold true.

Was-Gubala [5] assessed the frequency of occurrence of different fibres in Poland, the Czech Republic and Germany. To this end, fibres were collected from seats of public transport in Krakow, Prague, and Stuttgart. The results of this study were broadly similar to those obtained in previous studies carried out in the UK, Germany, Switzerland, and Austria and therefore the establishment of pan-European fibre frequency databases may be feasible.

A similar study by Leung [4] was carried out using clothing from casework to determine whether the probability of chance matches was increased in a small geographical area with a large population density (Hong-Kong). The results obtained were in accordance with previous studies performed in Europe.

For many fibre examiners the discrimination of clothing comprising of ubiquitous fibres (such as indigo dyed denim jeans) has remained problematical – particularly in cases where these are the only garments potentially available for comparison.

Biermann et al [22] investigated the use of microspectrophotometry for the discrimination of fibres dyed with indigo and seven derivative dyes. Normally, indigo-dyed fibres are excluded from fibre-transfer examinations because they are so widespread and, therefore, lack evidential value. However, indigo substitutes are used as dyes in the fashion industry and if the use of such dyes is widespread, it may be necessary to revise the assumption that all denim material is dyed with Vat Blue 1 dye. This work presented the results of a microspectrophotometric study of fibres from 160 samples of denim articles which showed that the use of derivatives is still comparatively rare and therefore if found in casework, are likely to be of high evidential value.

Palmer [1, 2] reported casework examples where jeans dyed with indigo- blue were discriminated on the basis of fibre content and fluorescence.

In many instances, there is an assumption that some fibre type / colour combinations are of low evidential value, usually because of the perception of their commonality at the *generic* level (e.g. 'blue' cotton, 'blue' polyester', 'blue' wool). Since the combination of comparative tests available to the fibre examiner is highly discriminatory, this perception has been shown to be erroneous by a number of current studies.

Target fibre studies, population studies and research into 'blocks of colour' by Biermann et al [2] have confirmed the polymorphism of textile fibres - especially man-made fibres - and have demonstrated that when a questioned fibre is believed to have a specific putative source, the chance that it came from another source by coincidence is very small. A more recent study by Biermann et al [8] goes further, using blue polyester fibres to show that even within a narrow segment of the entire general fibre population, many examples of a specific colour/type of man-made fibre obtained from random sources can be compared and the chance of any two being identical is remote.

Another similar study by Biermann [3] showed that the very high discriminating power obtained using a combination of light microscopy, fluorescence microscopy and uv/ vis microspectrophotometry means that even blue and red cotton fibres can provide excellent evidence when involved in fibre transfer cases.

The discriminating power of microscopy alone was highlighted by Oein [1] who in a casework situation demonstrated that none of the 49 textiles containing black wool could be associated to the black wool fibre recovered from the evidence. Of these, comparison microscopy alone was able to distinguish 46 of the textiles, while microspectrophotometry was necessary to discriminate the final three samples. Based on these results, it seems that the evidential value of black cotton and black wool is higher than originally expected.

Similar data was obtained by Wiggins and Drummond [9] who searched 58 garments for extraneous mid- to dark-blue wool fibres. The 2,740 blue wool fibres identified were subjected to microspectrophotometric analysis. Three hundred independent blue wool populations were identified on 56 of the 58 garments searched. Although blue wool is considered to be a common fibre type, 300 unique spectral shapes were identified by the use of microspectrophotometry alone. This demonstrated that the dyes used in the colouring of blue wool are highly variable.

Fibre population studies seek to assess the frequency of fibre type/ colour combinations at the generic level. Since these frequency figures are produced in the absence of instrumental analysis, the data is extremely conservative but nevertheless useful, particularly when the Bayesian approach is employed. Since the frequency of certain fibre types and/ or fibre type/ colour combinations may change due to fashion, season and geography, it is important that such data is kept current and any changes monitored.

Marname et al [24] studied the total foreign fibre population on a small number of items of clothing. The number of coloured foreign fibres present on six white T-shirts after each garment had been worn for one day was determined, revealing that the T-shirts contained between 9,108 and 13,925 coloured foreign fibres. Microscopic examination of the coloured fibres was carried out in order to determine their colour, width and length, and classification (cotton, wool, synthetic, silk, or miscellaneous). Pair-wise comparisons of similar fibres were subsequently carried out in order to determine the number and size of the groups of foreign fibres present on the garments. These findings supplemented the information currently available on background foreign fibre populations on clothing and other items.

Watt et al [7] investigated the coloured fibre population in domestic washing machines during spring in Sydney, Australia. This work involved the washing of white cotton T-shirts, individually and mixed with a normal load of washing, and the subsequent taping of the washed T-shirts for extraneous fibres transferred during the wash cycle. In total, 12,178 fibres recovered were classified according to length, colour and generic class. The most frequently encountered fibres were cotton (69.4%) and man-made fibres (24.2%). The most frequently encountered colour/generic class combinations were black/grey cotton (27%), blue cotton (20%), and red cotton (15.6%). Other combinations accounted for less than 2% of the total fibres recovered. Most (65.9%) of the recovered fibres were less than 2 mm long.

An important aspect in the interpretation of fibre evidence is the consideration of dye batch variation. Very few papers have been published on studies of this effect, the most recent being Wiggins and Holness [13]. They studied four sets of acrylic fibre samples which were obtained from a company that dyes fabrics for the fashion industry. Between seven and ten different batches of fibres constituted each set. Comparison microscopy, visible and UV range microspectrophotometry and thin layer chromatography (TLC) were used to compare the dyes on each batch of fibres within the sets. Only one of the four sets exhibited variation when both microscopical and analytical techniques were used. In addition, two further sets of samples had been obtained from a company that produces carpets for the car industry. The first set consisted of 26 batches of acid-dyed orange nylon fibres. The second consisted of 21 batches of acid-dyed, mustard-coloured nylon and direct-dyed brown viscose fibres blended together. When the first set was viewed under UV light, one batch had more pale orange fibres present, which fluoresced more brightly than the other fibres. When tested using visible and UV range microspectrophotometry and TLC, further dye batch variation was not detected. The second set was examined after separating the nylon and viscose fibres from each other. The nylon fibres were indistinguishable when a range of microscopical and analytical techniques were employed; however, the viscose fibres showed dye batch variation when TLC was used.

In the commission of crimes where the perpetrator conceals his identity using a mask/ balaclava (e.g. robbery, terrorism etc) fibres may be transferred from the item in question to their hair. The value of the recovery of fibres from head hair was the subject of a paper by Palmer [4]. The persistence dynamics of these fibres have been the subject of a number of studies and can be used as a ‘time frame for wear’ (up to 7 days). However, when a suspect is apprehended outside this ‘window of persistence’ any value in attempting to recover fibres from their hair is usually lost. In these situations, anecdotal information suggests that consideration of potential secondary transfers may provide a useful alternative. This was the subject of a study by Palmer and Banks [10] who considered the effects of fibre type, hair style, time, and fibre persistence on the secondary transfer of mask fibres to pillowcases, via head hair. Volunteers with a range of hair styles and masks consisting of different fibre compositions were used in the study. Fibres from the masks were found to transfer from donor subjects to the pillowcases up to 14 nights after the mask had been worn. On average, the number of secondarily transferred fibres found decreased with time; however, this decrease appeared to be more 'linear' in nature rather than an exponential decay. The greatest degree of secondary transfer occurred with cotton, followed by acrylic, then wool. In a primary transfer/persistence experiment with a 50% acrylic/50% wool mask, wool was found to persist in the hair more readily than acrylic. The results also showed that the greatest degree of secondary transfer occurred via short, straight and long, straight hair, with no clear pattern emerging between medium-length hair (both straight and curly) and with long, curly hair.

In a similar study involving the persistence of transferred fibres to bare hands and gloves, Marshall [2] reported a half life of persistence of around 5 minutes.

Textile/ Fibre Damage

A number of studies into the effects of environmental challenges to textile fibres have been carried out since the last review.

Was-Gubala and Krauss [23] investigated the damage to textiles and single textile fibres caused by direct contact with a heating plate as well as exposure to an open flame. Tests were carried out using textiles of different colours, fibre composition and textile construction. Optical and scanning electron microscopy (SEM) were used to examine the specific types of changes occurring in thermally degraded textiles and fibres.

Hirschler et al [25] analysed 16 commercially available items of clothing in terms of their fabric composition which were then subjected to fire testing. The three fire exposures used were: (1) a simile of 16CFR1610, (2) a small vertical candle on a small swatch of fabric, and (3) a candle applied to a complete garment on a mannequin. Examination of the test results revealed a general correlation between increased fabric areal density (weight/unit fabric area) and improved fire performance. Where outliers to this generalisation were found, the improved fire retardation performance was because of the inherently superior performance of specific types of fabric such as silk. In general, the quantitative behaviour regarding the rate of flame spread after the ignition of cellulosic, thermoplastic and blended fabrics depended more on fabric areal density than on chemical composition. Very lightweight fabrics were found to pose a potential risk, with the regulatory value of 2.6 ounces per yard squared representing an arbitrary cut-off in this regard.

Rosengarten [2] reported on the analysis of damage that occurred in Nylon straps used at a military airport which were originally thought to have been caused by wolves. Visual inspection, low power microscopy and SEM were used and revealed a pattern similar to that of a hacksaw, thus the straps were found to be damaged as a result of sabotage and not by wolves.

A similar case involving such methodology was also reported by Vasconcellos [1] in determining whether a parachutist’s straps had been deliberately cut.

Calzetta et al [2] presented a case study of an assault which involved the use of a corrosive liquid against the victim. These authors attempted to determine the causes of the faded stains on items of clothing. Based on macroscopic and microscopic observations, and chemical tests involving questioned liquids, it was concluded that the damage to the clothing was caused by contact with hydrochloric acid.

Causin et al [14] described a novel method, based on the integration of infrared (IR) absorption bands, for the differentiation of single poly(ethylene terephthalate) (PET) fibres. This technique used involved IR microscopy in transmission mode, differential scanning colorimetry and optical microscopy. Particular attention was paid to fibres which had been immersed in water and exposed to solar irradiation for a three-month period. It was found that this exposure to the elements had no effect on the morphology of the PET fibres, therefore the significance of fibre comparison results appeared unaffected by weathering.

W_s-Guba_a [3] investigated the kinetics of colour change in textiles and fibres treated with detergent solutions using a 14-day experiment involving blue, red and grey/black cotton, wool, acrylic and polyester textiles. The kinetics of the changes in the colour of the textiles were tracked in UV as well as visible lights, using fluorescence microscopy and MSP.

Textile Technology

The textile industry worldwide is in a permanent state of flux and it is essential that forensic fibre examiners keep up to date with technological developments, fashion trends, the emergence of new fibre types and dyes, optical brighteners and finishing agents.

Grover et al [16] described the increasing interest in the use of eco-friendly natural dyes for the colouring of fibres and investigated the extraction of dyes from different parts of plants and the optimisation of dyeing variables of the natural dyes for the dyeing of silk. The use of metallic mordants to give a wide range of dye colours was also discussed.

Greaves and Bainsford [11] looked at fibre samples between 1970 and 2005 in order to determine why there has been a steady increase in the production of Peru's coarser alpaca fibre at the expense of its finer, more commercial properties. Microscopical analyses and comparisons with older data (where available) were also carried out using llama, vicuna and guanaco fibres.

Wiggins and Cornelius [29] performed a study to determine which processes used during fibre production have a significant effect on the spectral and chromatographic results seen in casework. Theoretically, any information obtained from spectra in the visible region is likely to be due to colouration whereas that in the UV region could be due to the dye or from other compounds used throughout the manufacturing process. This paper demonstrated that many of the processes used prior to dyeing have little or no effect on the finished item when examined using spectral or chromatographic techniques. The only exception was a colourless viscose sample which gave spectral information in the UV region, inferring that this may be due to optical brighteners and/or UV absorbers being used in production.

Koch [28] produced statistics which showed that the production of cellulosic fibres is increasing. Such fibres are usually specialty-type fibres often found in underwear and active wear, with examples being Soy silk, Bamboo, Viloft, and Sea Cell. This article outlines some of the important characteristics of these fibres for the benefit of forensic microscopists who may encounter them during casework.

Likewise Lunt [6] reported on Dow Cargill's Ingeo, which represents the first of a new class of manufactured fibres produced from annually renewable resources. This new fibre, which is a polylactic acid (PLA) polymer derived from the fermentation of natural plant sugars, possesses the full range of textile properties but has very little environmental impact.

Other useful resources in this category include a number of recently published books [33 to 39].

A number of internet web sites cited in the previous report [42 to 56] also remain useful sources of information.

Miscellaneous

Oien [1] reported that during the analysis of evidence recovered from an improvised explosive device, a question arose as to whether the superglue process for latent fingerprint immobilization should be conducted in the field in order to preserve potential latent fingerprints. Since the items subjected to this process could potentially be examined for other types of evidence, this study was undertaken to determine if there were any detrimental effects from latent fingerprint processes on fibre examinations. The effect of the superglue treatment was found to have no adverse effect on the fibre examinations. This was an important finding as it dispelled any concern about the pre-treatment of evidence using superglue prior to fibre examinations being conducted.

Roux [3] reported a study in which natural and man-made fibres were exposed to increasing doses of radiation intended to simulate some degree of exposure to a typical category two industrial radiography source (e.g. Cobalt-60, Cesium-137, Iridium -192). At each juncture, the fibres were evaluated using a range of forensic techniques to ascertain if any radiation damage had been manifested. Changes were noted in the colour and resultant MSP spectra at high radiation doses.

Bull et al [27] carried out a study into the transfer and persistence of trace particulates such as pollen using different clothing fabrics. The results of this were in accordance with previous studies involving fibres.

The Future

With the increased threat of terrorism, law enforcement agencies are continually looking to forensic science for the provision of intelligence in these (often) complex investigations - not only to identify the perpetrators of a specific attack, but also in preventing future incidents.

Biermann [1] presented an overview of fibre and textile examinations carried out by laboratories dealing with general terrorist attacks, especially in relation to firearms, bomb and arson attacks (including letters), hidden depots, hiding places, kidnapping, letters claiming responsibility and letter bombs. Image comparison, size determinations of clothing found in hiding places, label evaluation (intelligence work by determination of manufacturers), country of production, time of sale, country of sale, region of sale, number of sold textiles, determination of garment age, fibre analysis, research & development, construction analysis, industrial enquiries and development of case databases, were all cited as probative methods and lines of investigation.

Oien [2, 3] reported on the role of the Terrorist Explosive Device Analytical Centre (TEDAC) and gave an update on fibre examinations relating to improvised explosive devices (IED’s) collected from Iraq and Afghanistan, which continue to be a major initiative for the FBI Laboratory. He reported that over 3000 devices had been examined in the Trace Evidence Unit, with an additional 2000 devices awaiting examinations. Numerous associations between different devices have been made based on the fibre examinations alone, with additional associations being made with latent fingerprints, mitochondrial DNA examinations, and examinations of the IED's themselves. The large number of fibres being identified on these devices have necessitated the development of a database of fibres, and future research projects are being contemplated on developing a useful, searchable database of fibre properties, including microspectrophotometry data, to facilitate the examinations in these cases.

Collaboration between the EFG and SWGMAT into the research on the effects of explosions on textiles and also in a survey of fibres used in the manufacture of backpacks is on going and progress was reported by Was-Gubala [3].

Over the last few years fibre examinations have demonstrated the value as a powerful intelligence tool in large complex enquiries, providing invaluable investigative steers. As already mentioned, forensic science is being increasingly asked to provide answers in these enquiries and trace evidence examinations are becoming increasingly important – particularly as many criminals are 'DNA' aware.

De Wael [1] described the use of fibres as an intelligence tool in a case where no donor source was found. Palmer [2, 40] reported on the use of fibres as a powerful intelligence tool with reference to major complex enquiries.

Advances in label technology, in particular the use of transponder technology in this area have been highlighted by Dillinger [2]. The potential value of these items particularly in intelligence led enquiries is potentially enormous due to the amount and nature of the information they contain.

There is a general consensus that a 'fibre database' would be an invaluable tool not only in general casework, but also in terms of delivering intelligence in major enquiries. Drotz [3] outlined the ways in which such a database can assist in casework by allowing more robust interpretations and conclusions to be made. Whilst virtually all practitioners see the benefits of such a system, to date no significant progress has been made in this area.

Summary

The work of the ENFSI European Fibre Group and the fibre sub group of SWGMAT has continued to be pivotal in steering research and identifying ways in which fibre examiners can rise to the increasing challenges presented to them by law enforcement agencies.

The considerable research carried out in this field over the last three years, particularly in the area of interpretation, reflects a willingness by practitioners to address the cogent issues facing them. The challenges facing forensic science and the ever changing nature of technology and the textile industry will ensure that this impetus will continue.

References

1. Proceedings of the 12th European Fibres Group meeting, Prague, Czech Republic, 2004

2. Proceedings of the 13th European Fibres Group meeting, Bled, Slovenia, 2005

3. Proceedings of the 14th European Fibres Group meeting, Rome, Italy, 2006

4. Proceedings of the 17th International Association of Forensic Sciences, Hong Kong, China, 2005

5. Was-Gubala J. Comparative Population Studies of Fibres Secured in Poland, Czech Republic and Germany, Zagadnien-Nauk-Sadowych, 2004, 60, 58-77

6. Lunt J. Ingeo PLA Fibres: Chemistry, Manufacture and Application, TEXTILES, 2004, 31 (3), 15-16.

7. Watt R, Roux C, Robertson J. The population of textile fibres in domestic washing machines, Science & Justice 2005, 45(2); 75-83

8. Grieve M, Biermann T, Schaub K. The individuality of fibres used to provide forensic evidence – not all blue polyesters are the same, Science & Justice 2005, 45(1), 13-28

9. Wiggins K, Drummond P. The analysis and comparison of blue wool fibre populations found at random on clothing, Science & Justice, 2005, 45(3), 157-162

10. Palmer R, Banks M. The secondary transfer of fibres from head hair, Science & Justice, 2005, 45(3), 123-128

11. Greaves P, Bainsford F. Camelid fibres compared and contrasted, Textiles, 2005, 32(3/4), 46-48

12. Wiggins K, Holness J-A, March B. The importance of thin layer chromatography and UV microspectrophotometry in the analysis of reactive dyes released from cotton and wool fibres, Journal of Forensic Sciences, 2005, 50(2), 364-368
13. Holness J-A, Wiggins K. A further study of dye batch variation in textile and carpet fibres, Science & Justice, 2005, 45(2), 93-96

14. Causin V, Marega C, Guzzini G, Marigo A. The effect of exposure to the elements on the forensic characterisation by infra-red spectroscopy of PET fibres, Journal of Forensic Sciences, 2005, 50 (4) 887-893

15. Causin V, Marega C, Schiavone S, Marigo A. A quantative differentiation method for acrylic fibres by infra-red spectroscopy, Forensic Science International, 2005, 151(2/3), 125-131

16. Grover E, Sharma A, Rawat B, Paul S, Jahan S. Dyeing of silk with natural dyes, International Dyer, 2005,190(10), 9-16

17. Huang M, Russo R, Fookes G, Sigma E. Analysis of Fibre Dyes by Liquid Chromatography Mass Spectrometry (LC-MS) with Electrospray Ionisation: Discriminating Between Dyes with Indistinguishable UV-Visible Absorption Spectra, Journal of Forensic Science, 2005, 50 (3), 526-534.

18. Thomas J, Buzzini P, Massonnet G, Reedy B, Roux-C. Evaluation of Raman Spectroscopy for the Analysis of Coloured Fibres: A Collaborative Study, Forensic Science International, 2005, 152 (2-3), September, 189-197.

19. Petrick L, Wilson T, Fawcet W. HPLC UV-Visible spectroscopy-electrospray ionisation mass spectrometry method for acrylic and polyester fibre dye analysis, Journal of Forensic Sciences, 2006, 51(4), 771-779

20. Flynn K, O'Leary R, Roux C, Reedy B. The Forensic analysis of bicomponent fibres using infra-red chemical imaging, Journal of Forensic Sciences, 2006, 51(3), 586-596

21. Causin V, Marega C, Schiavone S, Della- Guardia V, Marigo A. The forensic analysis of acrylic fibres by pyrolysis gas chromatography/ mass spectrometry, Analytical Applications of Pyrolysis, 2006, 75, 43-48

22. Grieve M, Biermann T, Schaub K. The use of indigo derivatives to dye denim material, Science & Justice, 2006, 46(1), 15-24

23. Was-Gubala Y, Krauss W. Damage caused by the action of two types of heat, Forensic Science International, 2006, 159(2/3), 119-126

24. Marname R, Elliot D, Coulson S. A pilot study to determine the background population of foreign fibre groups on a cotton/ polyester T-shirt, Science & Justice, 2006, 46(4), 215-220

25. Hirschler M, Umino P, Zicherman J. Forensic evaluations of fabric flammability, Proceedings of the 17th Annual Conference on Flame Retardancy, 2006, 335-357

26. Monard – Sermier F, Massonnet G, Buzzini P, Fortini A, Gason F, De-Wael K, Rovas P. A comparison of efficiency of manual and automatic fibres each with the Maxcan fibre finder, Forensic Science International, 2006, 160 (2-2), 102-108

27. Bull P, Morgan M, Sagovsky A, Hughes G. The transfer and persistence of trace particulates: experimental studies using clothing fabrics, Science & Justice, 2006, 46(3), 185-195

28. Koch S. Beyond cotton, nylon and polyester. The emergence of new fibres and yarns, Global Forensic Science Today, 2007, 1

29. Wiggins K, Cornelius J-A. A study in relation to the effect of processes used in the dyeing industry on the finished article, Global Forensic Science Today, 2007, 1

30. Roux C, Austin C, Bennett S, Beavis A, Dawson M, Doble P, Lennard C, Robertson J. Ultra performance liquid chromatography – an emerging technique for the forensic analysis of trace evidence, Global Forensic Science Today, 2007, 1

31. Wiggins K, Palmer R, Hutchinson W, Drummond P. An investigation into the use of calculating the first derivative of absorbance spectra as a tool for forensic fibre analysis, Science & Justice, 2007, 47, 9-18

32. Wiggins K, Drummond P. Identifying a suitable mounting medium for use in forensic fibre examination, Science and Justice, 2007, 47, 2-8

33. FIBRES & TEXTILES in Eastern Europe, Instytut Biopolimerów i W_ókien Chemicznych (Institute of Biopolymers and Chemical Fibres), Poland, 2007, Volume 15, 2(61)

34. Kadolph S, Langford A. Textiles, Prentice Hall, 10th Edition, 2006, ISBN: 9780131187696

35. Xin J. Total Colour Management in Textiles, CRC Press, 2006, ISBN: 9780849392078

36. Shishoo R. Textiles in Sport, CRC Press, 2005, ISBN: 9780849334863

37. Scott R. Textiles for Protection, CRC Press, 2005, ISBN: 9780849334887

38. Hu J. Structure and Mechanisms of Woven Fabrics, CRC Press, 2004, ISBN: 9780849328268

39. Shindler W, Haur P. The Chemical Finishing of Textiles, CRC Press, 2004, ISBN: 0849328256

40. Trace Evidence Analysis, Edited by Houck, Elsevier Academic Press, 2004, ISBN: 0123567610

41. http://www.enfsi.org/

42. http://www.eurotexx.com/

43. http://www.fashion-links.de/

44. http://www.fashionseek.net/

45. http://www.ita.rwth-aachen.de/

46. http://www.techexchange.com/

47. http://www.texdata.com/

48. http://www.texi.org/

49. http://www.textile.fr/

50. http://www.textileweb.com/

51. http://www.textileworld.it/

52. http://www.textilexpert.com/

53. http://www.textilserver.de/

54. http://www.texweb.de/

55. http://www.ivc-ev.de/HTDOCS/index.html

56. http://www.trevira.de/

Thanks go to Martin McIvoy for the assistance in carrying out the literature search.

FIREARMS

– A Review: 2004 to 2007 –

Prepared by:
Sébastien Charles, PhD
Jan De Ceuster, PhD
Patrick De Smet, PhD
Desiré Laza, PhD
Bart Nys, PhD

Approved by :
Jan De Kinder, PhD, Director

INCC - NICC
Chaussée de Vilvorde 100
1120 Brussels
Belgium
http://incc.fgov.be/

Contents

Introduction

This review paper covers advances in scientific methods applied to firearms (mainly ballistics and chemistry) reported since the 14th Interpol Forensic Science Symposium in October 2004.

A literature review was conducted covering articles published in the principal forensic journals since 2004. Major forensic laboratories around the world were also asked to provide information.

Firearms – Ballistics

Firearms and toolmarks identification

Criteria for identification

Establishing criteria for identification is an ongoing matter of discussion. And it should be. Miller already published two articles on this subject in 1998 and 2000 (1,2). More recently in a third paper with similar title and subject, he addresses the consistency of determining what constitutes a matching line (3). Furthermore the scientific reliability of using the Consecutive Matching Striae (CMS) theory as a criterion for identification of striated toolmarks is examined. The trainees that performed the test were first introduced to the history of firearms and toolmarks identification. They were explained what constitutes an identification and how known match/known non match comparisons are necessary for the development of the CMS concept. Then the trainees had to perform comparisons between striated toolmarks produced in 35 mm photographic film emulsion using 60 grit sand paper. They were asked to count the lines and perform identifications using CMS, determine the highest total of matching lines as well as the highest percent of matching lines. The author found that counting the highest total matching lines and the highest percent of matching lines leads to false inclusions and false exclusions. By consequence, it should not be used as an identification criterion. Although variations in counting striae and consecutive groups of striae were noted, this had no effect on the conclusions reached by the examiner using the CMS criterion. A few missed identifications occurred only when the pattern area was limited. Miller used the data obtained by the trainees to perform a statistical study of the uniqueness of toolmark patterns.

Nichols is also very active in this domain. In his literature overview, he discusses the criteria for identification through a study of ten consecutively manufactured extractors (4). It was observed that subclass characteristics were present and persisted on two surfaces of the extractor hooks. However, as no carry-over was observed on the cartridge cases, the study demonstrated that it was of great importance to assess how the tool and the surface interact with each other. Apparently the corners adjacent to the two surfaces that bear the subclass characteristics have ridges that protrude away from the surfaces. These ridges have a significant impact on the toolmarks produced by the extractor so much that the issue of subclass characteristics is negated.

Having discussed this, Nichols enters into detail about the AFTE Theory of identification and the necessity of understanding the tool manufacturing processes. A great deal of attention goes also to the persistence of the individual characteristics and the issue of subclass characteristics. Nichols cites and discusses the relevant literature. In the framework of the AFTE Theory of Identification and the definition and measurement of the Best Known Non Match, he explains the concept of Consecutive Matching Striae for the description of pattern matching. He concludes that the underlying premises of the AFTE Theory of Identification and the conservative numerical criteria of CMS are scientifically valid and reliable.

Besides establishing criteria for identification of striated tool marks, some first attempts were also made for impressed tool marks. In 2003 Stone published a theoretical statistical study on the uniqueness of impressed toolmarks from hypothetical hammer faces (5). Although this article is about toolmarks, the results can, to some extent, be translated to firearms identification since the firing pin impression and breechface signature are also impressed toolmarks. Stone considers five variables in the analysis of toolmarks being: Origin, Resolution, Configuration, Orientation and Position. Furthermore he describes standardised individual characteristics: Point, Line, Curve, Enclosure and Three-dimensional Characteristics. He considers a hypothetical hammer face and determines the number of positions where a toolmark could be positioned, taking into account the conventional resolution and magnification factor of a comparison microscope. He then calculates the probability of finding a certain characteristic in a specific orientation and position. When the number of characteristics is increased, extremely low probabilities of obtaining these toolmarks by chance alone are very rapidly obtained. In other words, the probability of finding more and more individual toolmarks in a specific position, specific orientation and specific shape approaches zero.

This theoretical model was subjected to an empirical study performed by Collins in 2005 (6). The author was able to detect the standardised individual characteristics as proposed by Stone on the faces of 20 worn hammers. With slight modifications to the original theory of Stone and using relatively conservative criteria, Collins was able to demonstrate that the probability of random occurrence of these features can indeed become extremely low as more and more characteristics are combined in the analysis. Collins furthermore applies his model to the firing pin of a firearm and demonstrates that the theory is also applicable in these situations.

There are a few different approaches that a firearm examiner can follow when he evaluates a pattern of matching markings. Either he uses basic pattern matching looking at the amount of matching striae or the percentage of matching striae, or he can apply the conservative numerical criteria of the consecutive matching striae (CMS) method. In any case, he evaluates the pattern while comparing it with the best known non match that he has seen through his experience or that is published in literature, and he compares the match with what he would expect to see from a known matching pattern before reaching his conclusion. This weighing is in fact a Bayesian way of analysing. In the late nineties and the beginning of the years 2000 some papers were published that assessed the possibility of applying a true Bayesian likelihood calculation for a pattern match (see e.g. (7)). Buckleton et al.

published a paper in which they set up an exploratory Bayesian model for the interpretation of Bayesian toolmarks (8). The model is based on the CMS approach, while Bunch criticised this in 2000 (9). The data that was used to test the model was obtained through two previous CMS studies of the consecutively manufactured bullets and ten consecutively manufactured extractors. The probability of obtaining different runs of CMS was calculated. Whenever there was no data available for a certain CMS run, the authors simulated these values using conservative Deinet factors (i.e. taking a defined percentage of a neighbouring value). The likelihood ratios were then calculated by comparing the probabilities for known matches to the probabilities of known non matches. To express the results, the authors used a Bayesian reporting scale in which the likelihood ratio is translated to a verbal wording. Buckleton et al. found that CMS and the Bayesian approach are not inherently incompatible but do stress that the model should be further developed further using more data. The overall conclusion is that the higher the CMS count the larger the likelihood ratio. It is up to the examiner to determine his threshold for an identification based on the likelihood ratio reporting scale.

A paper by Deinet et al. comments on the application of Bayes' rule in the field of firearms and toolmarks comparison (10). First it is explained how the formula of Bayes' rule is created. The formulation in which it is mostly used in forensic science is: posterior odds = likelihood ratio x prior odds where the likelihood ratio is defined as the ratio of p(E|H) and p(E|-H). However, the authors feel that the likelihood ratio is not what the court wants you to tell them. Further, the authors discuss the CMS model and the Renewal Theory Model, the latter being mostly used by these authors. Besides, they comment on the subjectivity of the determination of striae in patterns. Which striae are random? Which lines match, which don't? Background statistics are required to be able to distinguish between the actual pattern and noise. The background statistics for p(E|H) are estimated from several comparison patterns of the questioned mark generator by testing the reproducibility of the pattern production. For p(E|-H) the background statistics are derived for accidental matches of striae. For this purpose, the authors have developed computer programs. The authors conclude that all theoretical probability models have pros and cons, so that they could perhaps complement one another. They propose the parallel use of different models in critical cases.

After all the work that has been done to define criteria for identification, the discipline of firearms and toolmark examiners received a lot of criticism, especially in the amicus brief by Schwartz in 2005 (11). She criticises the reliability and admissibility of firearms and toolmark identification and states that because of systemic scientific problems, this field of expertise should be inadmissible across-the-board. Schwartz comments on the absence of a sound statistical basis that helps to decide if a toolmark was made by a particular tool. According to the author, the courts have not yet understood the scientific issues concerning firearms and toolmark identification. Schwartz goes on and explains the pitfalls in firearms and toolmark identification: 1) the individual characteristics of toolmarks are comprised of non-unique marks, 2) subclass characteristics shared by more than one tool may be confused with individual characteristics unique to one and only one tool, and 3) the individual characteristics of the marks made by a particular tool change over time. No statistics have been developed on the rate at which subclass characteristics are produced by various types of tools. Schwartz often refers to fingerprint and DNA comparisons. Fingerprint and DNA only consists of unique markings and do not change over time whereas the opposite is very much true for firearms and tools. The similarities between toolmarks made by different tools and the differences between toolmarks made by the same tool imply that a statistical question must be answered to determine whether a particular tool was the source of a toolmark on an object recovered from a crime scene. Schwartz discusses the more objective CMS approach and highlights its drawbacks: it deals with striated toolmarks only and not with impressed toolmarks. Additionally, the danger of misidentifying on subclass characteristics when not recognised by the examiner still exists. To date firearms and toolmark examiners have not established databases of tools able to support their conclusions with a certain statistical significance. The error rate of the firearm and toolmark examiners could be derived from proficiency tests but the examiners are extra observant when the test is declared rather than blind. Computerised firearms identification does not always solve the issue of misidentifications and missed identifications. At present, the current systems are not yet ready to be used in large databases and certainly not for reference ballistic imaging databases. Using three-dimensional images rather than two-dimensional images could yield more accurate results (see below).

After the Daubert case, firearm and toolmark examiners were gravely concerned that increased judicial scrutiny might result in the exclusion of their testimony. However, both before and after Daubert, firearms and toolmark identification has largely been admitted as a matter of course. No court has recognised the systemic scientific problems with the field. Schwartz concludes by saying that all firearms and toolmark identifications should be excluded until the development of firm statistical empirical foundations for identifications and a rigorous regime of blind proficiency testing has been completed.

In response to the critique that was uttered by Schwartz, Nichols published two publications to defend the scientific foundations of firearms and toolmark identification (12,13). First of all he comments that while Schwartz was apparently aware of the large number of articles available that can be used to address many of the issues, there was no mention of them made in her argument. Nichols states that firearms and toolmark identification is rooted in scientific methods. He refers to the AFTE Theory of Identification and to the many studies on known non-matches from consecutively manufactured tools to support the criterion for identification. He furthermore says that Schwartz has misinterpreted the information that she quotes or that she does not cite all of the available literature on the subject. In regard to subclass characteristics, Nichols says that knowledge and study of manufacturing processes of tools, in combination with the many studies addressing the issue of subclass characteristics, assist a trained and qualified examiner in easily discerning their potential for interference in comparative casework. He then discusses the studies on this issue and explains the rules that exist to distinguish between subclass and individual characteristics. Nichols admits that the surface of a tool will change over time. But, in contrast to Schwartz, he says that this does not make identification unreliable. Again he refers to a vast amount of literature, which proves that use of a firearm does not necessarily render identification impossible. In contrast to DNA identification, which is entirely based on subclass characteristics, firearms and tool mark identification is based on individual characteristics. Furthermore, by saying that the likelihood that another tool could have made the mark is so remote that it can be considered a practical impossibility, the AFTE Theory of Identification does not support claims of absolute individualisation. Nichols says that the implied need for representative statistical databases for each and every tool one might encounter is not founded because the science of firearm and tool mark identification is based on manufacturing methods and on the ability to assess and distinguish among the class, subclass and individual characteristics produced by the tool manufacturing process. Nichols comments on the application of statistics in firearm and toolmark examination. In regard to a Bayesian approach he says that the likelihood ratio does not answer the question as discretely as the judicial system may like. It is true that numbers representing the likelihood ratio are generated but, the explanation for what those numbers mean in a real sense leaves the judicial system no closer to a real answer that has much more meaning than what is being offered now. Nichols waves away the comments of Schwartz on the proficiency tests by stating that they offer an assessment of laboratory practice, quality assurance and quality control procedures. As it comes to the critique on computerised systems such as IBIS^{TM}, Nichols negates the opinion of Schwartz. The systems are developed to serve as a computerised database of data and images from bullets and cartridge cases for rapid searching of these images in an attempt to link cases that might have otherwise not been linked. As such it is an investigative aid only. Nichols concludes by reviewing the court decisions offered by Schwartz for which it appears that the courts do have adequate and sufficient knowledge regarding the intricacies of firearms and toolmark identification.

A good attempt to statistically support the significance of consecutive matching striae is done by Howitt et al. (14). The conservative numerical CMS criterion is defined as a cut-off value above which a matching line pattern constitutes a match and below a non-match. Howitt understands that the idea of an absolute cut-off is unrealistic, but the statistical likelihood that a particular correspondence of the lines will occur by chance has never been properly assessed. Howitt et al. made a derivation of the probability of finding line correspondence and matching sets of consecutive striae on the surface of a bullet. They developed a statistical model for the calculation of the probability of occurrence of line sequences. They took into account the available, discernable line positions, sequence of lines and number of lines present. The probability of finding three or more consecutive lines rapidly drops. The theory further demonstrates that if the criterion of consecutiveness is not taken into consideration, the probability of finding multiple lines matching is a lot higher. Thus, the concept of consecutiveness adds to the probability.

The ENFSI Expert Working Group Firearms organised their first proficiency test for firearms identification in 2005 (FAID 2005). The test consisted of 15 sub-sets of castings of bullets and cartridge cases. This set-up ensured that all sixty participants were looking at the exact same markings. Each sub-set consisted of 2 known references (controls) and one unknown that had to be compared with the controls. The question for each sub-set was: “Is the unknown item from the same firearm as the two controls”? Results (15) show that not all participants of the FAID 2005 interpret the found similarities or differences equally. This test should therefore first be regarded as a collaborative study, to find ways to reduce differences in interpretation and have more (all) examiners use the same identification methodology.

Parameters that influence identification

There are a number of parameters that can affect the identification of recovered bullets and cartridge cases from a crime scene to the firearm that fired them. This part aims to cover a few of these parameter studies that were found in the literature.

As gunshot victims are not always discovered immediately after the shooting took place, the bullets can become subject to the putrefaction of the bodies. Chow et al. performed a time dependent study of the damage to four types of bullets (16). They test fired into pig carcasses or simply put bullets obtained by test firing in a water tank into pig’s carcass at an acceptable depth. They express the time that elapsed in Accumulated Degree Days (ADD), a term also used in Forensic Entomology. After 200 ADD the two copper bullets and one of the two brass bullets from the test either were not suitable for identification or the results were inconclusive. The other brass bullet and the aluminum bullet could still be identified after more than 400 ADD.

Fired bullets and cartridge cases are not always immediately discovered as they can be regarded as fairly small objects with respect to furniture, grass, debris … Environmental exposure, depending on the medium and the length of deposition, can complicate or preclude microscopic laboratory comparisons of fired bullets and cartridge cases. Larrison evaluated the effect of the environment and time in situ (17). Bullets and cartridge cases were deposited in soil, water, open air and a dog carcass. Larrison concluded that if the cartridge cases and bullets are kept in open air or soil, they can still be restored and identified after two years. Very likely the same is true in great excess of this time period. However, items left in an aqueous or decomposing tissue environment fare much worse and may not remain identifiable past two years, if not earlier. But small areas of identification can still survive beneath the oxidative scale. Copper jackets and nickel primers are vulnerable to the soft, fatty tissue of the abdominal cavity and the copper jackets degrade almost as rapidly in an aqueous environment. Nickel primers hold up quite well in an aqueous environment, keeping their individual characteristics intact over time.

Certain brands of ammunition, such as Sellier & Bellot and Geco have a primer sealant that is applied across the entire surface of the primer. When a cartridge is discharged, pressure not only drives the bullet out of the barrel but an equivalent pressure is working on the bottom of the cartridge case. The head of the cartridge is pushed with great force against the breechface of the firearm. During this action, toolmarks from the breechface are impressed on the head of the cartridge. Hayes et al. have investigated the absorbing effect that the primer sealant can have on the transfer of toolmarks (18). Cartridges with and without primer sealant were fired and consequently compared with each other. To objectify their observations, the IBIS^{TM} system was used to scan the imprint of the breechface in the primer. The authors observed a significant reduction of the quality of the striations, certainly the medium and light intensity markings. Hayes concludes that the lacquer acts as a shock-absorbing layer. The lacquer itself does seem to pick up breechface markings. While it might be standard operating procedure to remove the lacquer, it is recommended to investigate and photograph the cartridge case before this.

Also, damage done to the firearm can affect a successful identification. Firearms that have to be researched for fingerprints are usually subjected to vaporous superglue. This means that the cyaonoacrylate glue will also set on the inside of the barrel and on the breechface of the slide. Bishop et al. have asked themselves whether or not this would hamper the identification of bullets and cartridge cases to the firearm (19). An experiment with a number of different firearms was performed. Bishop concluded that even though superglue did not hinder firearms identification, the practice of placing cotton in the barrel of a firearm when conduction latent print examination will protect the interior of the barrel and preserves any forensic evidence that might be of probative value prior to test firing the firearm.

Fire damage can also be expected to cause a lot of trouble. The idea for a thorough study came to Gerber et al. after having done a case where the suspect had put fire to the crime scene where, afterwards, valuable firearms evidence was found. The authors want to asses the effects of fire and fire damage to the reliability of firearms identification (20). They have selected two different firearms: one with a ferrous and one with a non-ferrous frame. The guns were testfired and then placed in a “home made crime scene” that was consequently put to fire under controlled conditions. The firearms were recovered, cleaned, repaired and parts were exchanged with other firearms from the reference collection whenever necessary. After this, the guns were testfired again and comparisons were made with the pre-fire test fires. The authors conclude that it is possible to identify bullets that have been fired from a gun prior to being burned in a fire to test fires taken after the firearms have been recovered. This proves also that it is feasible to clean and reassemble the damaged firearms into working order. The barrels show obvious signs of pitting and burning on the lands and grooves after the fire, which affected the amount and placement of the original individual markings. Consequently, some original individual markings disappeared while new ones appeared.

Hess and Moran discuss a method for removal of superficial rust and corrosion from the working surfaces of firearms (21). After first having given an overview of the literature, the authors tested the chemical Whink® Rust Stain Remover. They propose a protocol for the treatment of firearms that are received in a bad condition with the intent to restore any potentially surviving identifiable signature. The procedure has proven to be successful in addressing superficial to minor rusting of the working surfaces of firearms and is not intended as a method for “restoring” permanent damage to the working surfaces caused by rust/corrosion.

A few authors also came up with some ideas to help improve identification or to critically evaluate the efforts that have been done in this direction. As it was proven by two empirical studies that the idea of a Ballistic Fingerprinting Database is not working with the currently available technology, the idea of nanotagging firearms gained interest. A NanoTag™ mark consists of a numerical code and possibly a bar code that is imprinted on top of or along the side of the firing pin. Krivosta has considered this idea and looked into its feasibility (22). He wanted to asses if the markings are readily decipherable, if they resist to wear and if they are susceptible to intentional defacement. Whereas the idea of a NanoTag™ seems simple and straightforward, many test fires demonstrate that much change took place. It has been observed, by aid of the NanoTag^{TM} mark that a firing pin mark with four to five overlapping impacts as a result of one single firing does occur. The research has shown that implementing this technology will be much more complicated than burning a serial number on a few parts and dropping them into firearms being manufactured.

It is widely accepted that a firearms open case file or a ballistic fingerprint file for that matter will become less and less efficient if the amount of data that is in it grows. It is likely that in certain countries a vast amount of firearms of the same make and model is used by the criminals. These have, of course, similar class characteristics. For circular firing pin impressions, such as from the Kalashnikov assault rifle, Bati demonstrates that one can go one step further in using the width of the firing pin as a class characteristic to use as an exclusion parameter (23). A high reproducibility for the measurement of the width was obtained. This width can help to discriminate between different manufacturers of Kalashnikov rifles. Bati proposes a modified firing pin acquisition protocol for the IBIS^{TM} system that results in a much better performance of the correlation.

As it is known to be quite a task to identify bullets that were fired through the polygonal barrels produced by Glock, the company has started to develop a barrel with more identifiable markings. The improvements were examined by the Miami-Dade Police Department Crime Laboratory Bureau (24). The gross markings allow for quick indexing and the fine striations for improved identifications. These individual characteristics persisted after 3000 rounds and the bullets remained readily identifiable. One cannot, however, rely on the gross markings alone as they can be subclass carry-over. The new rifled barrel design is marketed by Glock as Enhanced Bullet Identification System (EBIS).

Equipment

This part aims to discuss the recent developments in equipment as the firearms and tool mark examiner strongly depends on it

Dutton had the opportunity to test the new generation of the LEICA comparison macroscope and made a critical comparison with the widely spread LEICA DM-C (25). He firstly assesses the optics and objectives. The new FSC makes use of a turret which allows for six different objectives. On the macroscope he tested, there were only four installed. While the DM-C has the advantage of the zoom objective, Dutton feels that a comparison macroscope should never be used at different zooms as this is distorting the pattern and this means also changing reality. Furthermore, he looked at the available magnifications. The max is 60x. Dutton concludes that the available range could best be extended (e.g. with additional objectives) so that the range is from e.g. 2x to 90x. He also looked at the central control box that is available for the FSC. This control box commands the movement of the stages as the FSC is fully automated. Although the control box is straightforward to use, Dutton comments that it did take a little getting used to. The speed of the movement of the stages is variable for different magnifications. Overall, Dutton concludes that the new instrument certainly is an asset for any lab working in the field of firearms and toolmarks examination. His only reservation is the automation of the instrument, which makes it somewhat more difficult to operate.

In a series of two papers Koch explains the technique of positive casts that was developed at the Bundeskriminalamt (26,27). With this technique one is able to make a complete replica of crime scene bullets and cartridge cases as well as any other object. The resolution of the casting is so high that even fine microscopic striation and impressed markings are duplicated. The castings can prove themselves useful in a number of situations: 1/ sending evidence around to neighbouring countries without having to send the actual exhibit with the risk of loss and 2/ organising proficiency tests such that each participating institute will receive the exact same test items.

Automation and 2D/3D imaging

Recent research on automation and imaging techniques for forensic firearms applications has been continued by both commercial and government institutions. Additionally, several results have been reported by academia and other independent researchers.

Some work reported on 2D imaging applications has been focused on the implementation of so-called “content based image retrieval” databases (28,29). CBIR databases allow objects to be searched for based on visual information such as shape, distance or relations between specific areas of interest (e.g., firearm screws), etc.

New work on the analysis and automated comparison of projectile and cartridge case images (30,31,32) has also been reported on.

Because it is very important to know how the performance of an automated system is affected, Nennstiel and Rahm discuss the parameters that have an important influence on the performance of the IBIS^{TM} correlator in (33,34). The first paper gives sort of a general background whereas the second reflects the author’s experience with the open case file database. The success rate of the IBIS^{TM} correlator is defined as the probability of finding an existing match. This success rate depends on a number of variables: type of the mark taken into consideration (e.g. breech face, firing pin …), number of evaluated mark types, mark quality, database size, number of test firings and number of signatures from the same unrecovered firearm. Logically, the further one goes down the hit list ranking of the IBIS^{TM} correlator, the higher the chance for success. The authors demonstrate that the quality of the marks determines the success rate. Some brands of ammunition have better marks than others. It is important to select the same brand of ammunition for the test fires as was used to commit the crime. Besides, it is best to put multiple cartridge cases of the same gun in the system. However, the success rate will decrease with increasing size of the database. The data is best arranged in calibre/firearm subgroups.

Based on the above parameters, the authors have tested their own system. They encourage inserting only the ammunition that is suitable for comparison as it is regarded essential for the use of any electronic preselection process. A success rate in the area of 75-95% for cartridge cases and 50-75% for bullets can be obtained under certain conditions. If these conditions are fulfilled, only the first 5 or 10 positions in the hit list should be checked, preferably regarding a combination of different marks. Insert more than one test fire and if available do the same for the specimens from the crime scene. It is furthermore advised to remove from the system any ammunition that passes a certain expiration period.

Regarding the choice of ammunition, a study was performed by Bernard (35). The goals of this study were to determine if the IBIS^{TM} correlation scores are dependent on the brand of ammunition used, and which brand produces better scores. Bernard has testfired Federal, Remington and Winchester jacketed ammunition through three different calibre guns: .38 revolver, .32 semi-automatic pistol and .45 semi-automatic pistol. The author not only compared the IBIS^{TM} scores of the cartridge cases: breechface, firing pin impression and ejector mark but also the Max LEA (land-engraved-area), Peak Phase and Max phase of the bullets. The results indicate that the calibre, ammunition brand or the two factors combined, do not significantly affect the IBIS^{TM} ejector mark scores but they do affect significantly the Max Phase Scores, Breech Face Scores and Firing Pin Scores. However, the results did not reveal one best brand of ammunition. The author did not observe a statistically significant difference on the markings as a function of firearms use.

De Kinder et al. assess the performance of a Reference ballistic imaging database (RBID) (36). 600 9 mm Sig pistols were fired and inserted into the database. Two Remington cartridges and five additional brands were fired per firearm. One of the Remingtons of all 600 firearms was put in the database. Hereafter 32 firearms were randomly selected. For those firearms, the second Remington cartridge case as well as the five additional brands were compared to the RBID. Of the 32 Remington cases, only 72% ranked in the top 10 positions. Likewise, of the five different brands, only 21% ranked in the top 10 positions. It is very likely that a realistic reference ballistic imaging database may contain more than 600 firearms of the same brand and type. The results of the study illustrate that an RBID cannot adequately and efficiently compare specimens. Such a database is unsuitable for law enforcement work.

Three-dimensional imaging methods have been studied in order to determine if 3D imaging methods can help to improve more traditional investigative work by providing 3D virtual microscopes and surface comparison tools (37,38,39). Additionally, some results concerning the performance of (2D versus) 3D methods have been published (40,41,42).

Using a comparison macroscope for the examination of pattern matching on bullets and cartridge cases will, to a certain degree, always imply some subjectivity of the examiner. And this is even before the examiner gets to the interpretation of the patterns. The illumination conditions to start with are very important; e.g., a grazing incident light allows the examiner to visualise 3-D features in the 2-D imaging plane. Any change in illumination may reveal a somewhat different pattern where striations may look broader or smaller. If the lightning for the two parts of the microscope is set differently, or equivalently, the questioned bullet or cartridge case is oriented in a different way, the examiner may potentially miss to see the matching pattern. Forensic Technology has developed and marketed over the past few years a new state of the art system that will analyse and compare the 3-D topography of the bullet or cartridge case rather than comparing 2-D images (43). This is an asset for ballistic comparisons as the third dimension contains valuable information. Using the improved MatchPoint+^{TM} software it is furthermore possible to analyse the images using a combined 3D-2D visualisation, which should increase the success rate of the system.

Forensic Technology challenged its newest 3D technology BulletTRAX-3D^{TM} with a test involving 21 pairs of bullets, among which 20 are fired from consecutively manufactured and button rifled barrels (44). After scanning the bullets, the system performs an automated comparison of the land engraved areas (LEA) and returns a MaxPhase value. This value gives an indication of which LEA matches best with another LEA and adds up for the whole bullet. After a pre-training period of the system the authors found that the highest MaxPhase score for a known non match was 570. Therefore the authors defined a MaxPhase of 650 as a decision criterion. All bullets that were in a matching position exceeded this threshold value without any problem.

In (42) Vorburger et al. examine the feasibility and utility of a national ballistics database of casing and bullet images. Such a database would be set-up by conducting test firings for every weapon sold over the counter, with the intent of identifying any such weapon and its owner if the weapon would be used in a crime. This extensive and in-depth report (42) discusses issues such as distinguishability, gun and ammunition factors, region differences (breech face, firing pin, ejector marks), and topography and current optical technology. More specifically, the authors discuss results obtained using both a 2D-IBIS and their own 3D-measuring system, for two collections of test material (NBIDE, De Kinder). Among many other interesting (statistical) results, they conclude that the 3D measuring system demonstrated more accurate behaviour, but that the required performance for building a national database still remains an open problem.

Similar studies are likely to appear in the future as 2D/3D issues may have an important impact on various aspects of currently used or developing investigative methods. In particular such studies may also extend existing and new work that discusses some performance issues of existing 2D identification database systems (32,36,42).

Shooting Incident Reconstruction

General considerations

Shooting Incident Reconstruction encompasses all techniques and knowledge that can be applied when examining a crime scene. Haag has recently combined his knowledge and expertise in a book (45) that provides the reader with a vast overview of criminalistic techniques that can be applied directly in field work. The book discusses how to recognise bullet impacts and how to prove them using chemical reagents, how to determine distance and orientation of the shot, how to reconstruct the bullet trajectory, what are the penetrating/perforating capabilities of bullets through different materials, how to recognise ricochet markings, what can be learned from trace evidence found on bullets, and many more items. Case examples and self performed shooting tests make the book easy to read and a must-have for every firearms examiner that goes out to process crime scenes.

Although his book covers a great deal of information on shots through glass, Lucien Haag adds a few useful ideas in an AFTE Journal paper (46). Haag makes notice of the velocity drop of bullets perforating tempered glass under different angles. He further makes a suggestion for the determination of direction of fire as this can be more difficult than for bullet holes produced in single strength plate glass. Tempered glass is very fragile and it is likely to fall out of the window frame after impact. One should collect as many fragments as possible, especially the ones with cone fractures. Notes of the interior and exterior side have to be made on samples of pieces of glass that are still stuck inside the frame. By use of ultraviolet light one side of the glass will strongly fluoresce.

Not covered in his book is the issue of determining the calibre of bullets in surviving gunshot victims. It is not uncommon in cases of surviving gunshot victims that the projectile is not surgically removed. Sometimes an operation would do more damage or carry more risk than if one would just leave the bullet in place. It can be, however, important for the shooting reconstruction to know by which calibre/type of bullet the victim was struck. X-ray films can provide the means to determine this as bullets are radio opaque. The bullet length to diameter aspect ratio is independent of the scale of the photograph and can always be determined if the x-ray photograph is taken in a side-view. Haag et al. provide a table with the aspect ratios of some common encountered bullet types (47). As damaged or expanded projectiles do not have the same outlook as the pristine bullets, the authors suggest putting a reference projectile plate in the picture for easy comparison. In this reference plate one can put bullets that were fired in the water tank. This way, one can more easily distinguish the characteristics of e.g. the Federal Hydra-Shok or the Winchester Black Talon.

Also Moran has written a chapter on shooting incident reconstruction in a book edited by Chisum (48).This chapter discusses general concepts in the investigation of shooting incidents with an emphasis on the reconstruction of events that occur at such scenes using a comprehensive approach that includes pre and post shooting incident considerations. Considerations for the forensic scientist are numerous in shooting incident reconstruction, but are not widely discussed in the literature. To this end, the author has attempted to organise the discussion into a chronological progression of considerations that include: 1) a philosophy of the critical thinking; 2) an introduction to various specific shooting incident / firearms related phenomenon that offer reconstructive information integrated with other forms of physical evidence; 3) practical approaches to reconstructive techniques that can be applied during the direct investigation of shooting scenes and/or resolving reconstructive issues that inevitably arise after the fact; and 4) practical considerations gleaned from a review of sources from both investigative and/or physical evidence prepared by various professionals in law enforcement and forensic science.

However, within the confines of a single chapter, detailed descriptions of specific methods and procedures associated with shooting incident reconstruction are not practical. Therefore, emphasis in this chapter is placed on introducing the reader to an overall approach to shooting incident investigation and reconstruction. The ideas set forth in this chapter will better equip the reader to approach these investigations and thereby recognise pieces of the puzzle that might otherwise remain mute and to provide the best representation of such observations with regards to the application of the scientific method. This in turn will contribute towards a more successful shooting incident reconstruction.

In (49) Klees presents a case report where the recovered fatal hollow point bullet showed no indication of expansion and only very slight deformation. Klees performed some research into what could hamper the expansion or mushrooming of hollow point bullets. Hollow point bullets rely on simple hydraulic action to initiate radial expansion. As fluid enters the bullet's nose cavity, the fluid gets compacted and will push the cavity walls aside under relatively high pressure. If a hollow point bullet impacts dry, intermediate targets first, the cavity might fill up with non-fluid material. This can prevent the cavity to expand if the bullet consequently hits a fluid-like target. The worst non-fluid like material is probably wallboard that consists of gypsum.

In a paper by Rowe, the author gives an exact calculation of the shotgun pellet pattern distribution of pellets impacting a flat surface (50). The pattern is usually visible as an elliptical mark. From the measurement of the shortest (W) and longest (L) axis of the ellipse, one can estimate the angle q of impact. This can be done using a simplified formula sin q = W/L. The author demonstrates that this simplified formula works well for most angles of impact. The error becomes larger for more grazing incident pellets.

Sims and Barksdale have performed experiments to gain information about the ejection pattern of cartridge cases (51). The ejection is dependent on a number of variables: type of firearm, stance, hand and weapon position (grip) and movement. Five firearms with different calibre were testfired from different stances (Weaver and Isosceles) and different grip: either two hands or one hand 'gangster' style. Among the five different weapons there were observable differences. The use of the original firearm and ammunition is, when possible, always the best choice. The different stances did not seem to have an important influence. The variable that made the most difference was the grip. When fired with a normal grip, the casings end up to the right and slightly to the back of the shooter. When fired using a 'gangster' grip, the casings were located to the left and slightly behind the shooter. The type of surface the cartridge cases land on is bound to have an important influence as well. The authors learned the value of research when faced with the challenge of reconstructing the events of a crime scene.

Wound ballistic simulations

As the firearms examiner is frequently asked to assess the lethality or wounding capacity of projectiles, it is important to know which human body simulants could be used for the purpose of these types of tests. In a series of papers, Jussila thoroughly examines the existing techniques that are used nowadays for wound ballistic simulations. In a first paper (52), Jussila compares the different methods of gelatine fabrication that are reported. His research looks into the variables of preparing ballistic gelatine and their effects on penetration resistance. Jussila changed water pH, water temperature at different steps in the preparation and cooling time. Besides this, he looked at different gelatine batches. Reproducibility tests resulted in an empirical derived linear formula for the penetration depth versus impact velocity of a 4,5 mm steel BB. This formula and graph should be used for verification of the gelatine. Jussila makes the following recommendations: use purified water, calibrate every gelatine batch, do not use extreme water temperatures, store gelatine in a dark, dry and formaldehyde free environment and verify penetration with two shots at different velocities. Furthermore, Jussila describes a standard method for the preparation of 10% gelatine blocks.

In a second paper, Jussila assesses the various methods that exist for the calculation of kinetic energy dissipation by a bullet into ballistic gelatine (53). The wound profile method (WPM), originally proposed by Fackler in 1985, gave the best correlation with the velocity drop as opposed to fissure surface area (FSA) and the total crack length method (TCLM). In the WPM, the lengths of the two largest cracks are added together to produce an estimate of the temporary cavity diameter. Correlation results of about 89% are obtained. Jussila suggests using an elastic shroud to hold the gelatine in place or, as an alternative, increase the size of the gelatine block.

Besides testing the ballistic gelatine as a tissue simulant, Jussila compared various alternatives for the simulation of skin (54). It is generally accepted that the skin becomes an important factor once the bullets have very low velocities and/or impact under a grazing angle. The skin simulant should have values close to the average human skin, i.e.: threshold velocity of 94±4m/s, tensile strength 18±2N/mm_ and elongation at break of 65±5%. Jussila first gives an overview of the literature where after 13 synthetic and natural alternatives are tested. A semi-finished chrome tanned upholstery “crust” cowhide of 0,9 - 1,1 mm thickness gave the best results for the natural simulants. For the synthetic materials, the 1 mm thick rubber is a reasonable good alternative although its threshold velocity is somewhat lower that required. It can be used for worst case scenario ballistic reconstructions. Jussila is confident that a synthetic material with the desired properties can be developed for wound ballistic research.

Daubert hearings

An important aspect of litigation may revolve around the scientific reliability and admissibility of investigative techniques and (resulting) evidence or testimony. This is particularly true in the U.S.A. where, at the trial of Daubert v. Merrell Dow Pharmaceuticals, Inc. the court outlined criteria which they believed could be important to establish the reliability of expert testimony. These criteria include the following:

> Has the technique or theory been *scientifically tested*?
> Does the technique or theory have a known or potential *error rate*?
> Has the technique or theory been subjected to *peer review and publication*?
> Is the technique or theory subject to *standards* governing its application?
> Is the technique or theory *generally accepted* by the relevant scientific community?

Although these criteria were not meant as a checklist, they are being applied in this way. If one of these criteria is not met, then any evidence or testimony may be found to be inadmissible.

The SWGGUN website (55) provides an overview of information on Daubert as well as reports on Daubert hearings.

The following Daubert hearings may be of interest to firearms examiners:

1. *U.S. v. Edgar Diaz et al. Criminal #CR 05-00167 WHA, February 12, 2007 U.S. District Court of Northern District of California (Judge William Alsup)*
2. *U.S. v. Jamaal A. LEWIS. Criminal # U.S. Army 217-08-8512, October 3, 2006 Office of the Chief Circuit Judge, Fort Lewis, Washington (Judge Debra L. Boudreau)*
3. *Comm. of MA v. Jason MEEKS and Michael WARNER. Criminal Action #2002-10961 and #2003-10575, Sept. 27, 2006*
   Superior Court (Judge Raymond J. Brassard)
4. *U.S. v. Darryl GREEN et al. Criminal #02-10301-NG, December 20, 2005 U.S. District Court of Massachusetts (Judge Nancy Gertner)*
5. *U.S. v. Amando MONTEIRO et al. Criminal #03-10329-PBS, November 28, 2005*
   U.S. District Court of Massachusetts (Judge Patti B. Saris)
6. *U.S. v. Michael J. O'Driscoll. Criminal No. 4:CR-01-277, February 2003*
7. *U.S. v. Aaron DeMarco Foster. Criminal No. CCB-02-0410, February 2004*

In summary, for each of these hearings, the court ruled that the firearms evidence and/or the expert’s testimony were sufficiently reliable. Nevertheless, some limitations or reservations were also formulated with respect to the scope, methodology or protocols used in some particular cases.

Firearms – Chemistry

During discharge from a firearm, primer and gunpowder residues as well as metal particles from the projectile and the cartridge case are escaping from the muzzle and other openings of the firearm. These residues are referred as primer residue, firearm discharge residue or gunshot residues (GSR).

Inorganic GSR

General considerations

Scanning electron microscopy coupled to energy dispersive X-ray microanalysis (SEM/EDX) still is the method of choice for the identification of inorganic GSR on samples.

In 2005 a group of internationally recognised GSR experts convened at an FBI-organised symposium to discuss the relevant topics related to inorganic GSR examinations using SEM/EDX (56): GSR definition, composition, sampling, contamination, case-acceptance criteria and report writing were discussed.

A general consensus was reached that a spheroid, condensed or rounded particle morphology in conjunction with the three-component lead-barium-antimony should be considered as characteristic of GSR particles.

On the topic of samples collected from suicide victims, it was concluded that the presence of GSR can not determine with a high degree of certainty whether the victim's death was the result of a homicide or suicide. Some recommendations were also stated with respect to testing of clothing. Finally most participants agreed that in order to compare GSR found on the suspect, it may well be interesting to analyse the victim's clothing and/or the expelled cartridge case of the crime scene as reference material. It is, however, noted that residue produced in a test firing of the firearm may well contain contributions from other discharges, and that therefore interpretation of comparisons should be handled with caution.

Fundamentals of GSR formation

De Forest et al. determined the velocity of gunshot particles using high speed stroboscopic photography (57). While most particles have enough energy not to be influenced by normal wind velocity and to embed themselves on certain nearby targets, they decelerate rapidly, explaining why only few particles are found beyond a certain distance (e.g. 1 m range).

Concerning the effect of revolver cylinder gap on GSR production, as expected the greater the space, the more the production of GSR to the side. This was illustrated with an example (58).

With the increasing interest of the scientific community in nanomaterials and nanostructures, an application to GSR in this domain was proposed by Yang et al. (59) who analysed the formation of nanometer-sized lead particles from the condensation of the lead vapour emitted from the barrel at the time of discharge. The authors noted a marked linear relationship between the size of the nanoparticles (50 to 200 nm diameter range) and the distance to the target (10 to 50 cm range). The nucleation process of the lead spheres was modelled using thermodynamic and diffusion principles and the resulting calculated lead particle diameter is in accordance with the general findings on samples acquired from firing a Winchester 9mm cartridge from a semiautomatic handgun.

Interpretation

Most handgun ammunition manufacturers now offer lead-free ammunition because of health concern on airborne lead produced by firearms. With lead removed, this ammunition does not produce the characteristic lead-barium-antimony particles, preventing correct identification of GSR (false-negatives). Oommen and Pierce studied eight lead-free ammunitions, in order to characterise the composition of the particles produced by these ammunitions (60). All of the eight ammunitions contain some combination of Al, Si, Cu and Zn, sometimes associated with specific elements such as Sr, Sn, K and/or Ba. With the increasing use of such ammunitions, this study points out the necessity of a case by case approach in order to prevent false-negatives. However, further studies are necessary to identify environmental sources of particles containing similar compositions.

Deposition of GSR particles in the shooting environment is an important study subject in the context of crime scene interpretation. Fojtasek and Kmjec (61) have studied the deposition time of microscopic particles in the vicinity of the shooter. Experiments with two pistols and a revolver show that the deposition of GSR particles takes place over a period of several minutes after the shot is fired. Interpretation of crime scene analysis results clearly need to take this deposition time into account as it is possible that a person entering the scene moments after the shot is fired can very well be contaminated, and the shooter who leaves the scene quickly may, on the contrary, show a less positive result as was formerly expected.

Based on an empirical study of police vehicles and facilities, Berk et al. have evaluated the potential contamination risk due to secondary transfer (62). Although the potential for secondary contamination seems to be low, some recommendations such as transporting the suspects in vehicles with vinyl seats or not reusing equipment without maintenance are stated.

These considerations have been summarised in the New Scientist by Mejia (63) in stating that due to the differences in evaluating the contamination risks by different crime labs and police forces, the credibility of the science behind GSR analysis is put to the test. Criminalists should therefore be more consistent in evaluating the test results in the light of possible contamination by police forces, particle deposition times and composition with regard to possible other sources like brake pad linings.

In the context of the interpretation of the GSR analysis results, a few interesting publications illustrating the use of Bayesian principles have appeared. Although their article is concerned with the application of Bayes’ theorem in toolmarks problems (see previous section), Deinet and Katterwe (10) show a very clear derivation of the principles behind the Bayesian approach and emphasise the need of the courts for the experts to offer not only a likelihood ratio, but also discuss prior probabilities. This is argued as the experts are the only ones able to assess these factors from their experience and scientific know-how.

One of the first applications of Bayesian principles to GSR is reported by Biedermann and Taroni (64); they take as an example the interpretation using Bayesian principles of combined results of ballistic bullet striation comparisons and shooting range evaluation obtained by chemographic methods. It is shown that in the case of experiments for which by their nature likelihood ratios are difficult to calculate, the use of Bayesian networks is still possible.

Moreover Cardinetti et al. (65) show that the application of simple statistical techniques can offer substantial insight into the interpretation of results of GSR analysis experiments. Applying a statistical framework of Poisson distributed means for the calculation of probabilities of finding a number of GSR particles on the hands of a group of shooters and non-shooters after a certain time since firing, they show that the calculated likelihood ratio reveals very reasonable results for the expected number of GSR particles. This technique can easily be applied to similar experiments.

Instrumental methods

Continuing on the subject of interpretation issues, an extended application of SEM/EDX, i.e. X-ray mapping, has been proposed by Cardinetti et al. in order to discern between true GSR particles and other non-firearm related particles with similar compositions (66). Specifically in the areas of automobile, pyrotechnics and electrical engineering a number of sources of the latter type of particles have recently been identified. X-ray mapping was applied on particles originating from brake linings of different models of cars, hand samplings of subjects with particular occupations, as well as from cartridge types of different make and calibre. The results show that all of these sources can potentially produce X-ray spectra with the characteristic lead-barium-antimony composition, making a correct GSR classification based on the spectrum alone problematic. Due to differences in the physical conditions of their formation, however, the spatial distribution of the elements in the particles differs. This effect can be visualised by X-ray mapping. The authors therefore suggest that the use of X-ray mapping is becoming an indispensable tool in discerning true GSR particles from similar environmental aggregates.

While SEM/EDX is nowadays routinely used in forensic laboratories, bulk methods such as Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) are still attractive for special applications. Roeterdink et al. (67) report the analysis by ICP-MS of GSR extracted from larvae. Significantly higher concentrations of lead, barium and antimony were detected within larvae feeding on a shot piece of beef. This method could be used in caseworks for which there are no identifying marks on decomposing corpse, in order to establish whether a firearm was or was not involved in the death.

Proficiency tests for GSR analysis by SEM/EDX

Niewoehner et al. (68) published the results of the latest proficiency test program GSR2003. The principle of this test had already been reviewed in the previous report paper (14th Interpol Forensic Science Symposium), but for the first time three-element composition lead-barium-antimony particles were prepared and distributed in four size classes (2.4 µm, 1.2 µm, 0.8 µm, 0.5 µm). As expected, the smaller the size, the lower the detection capability.

Estimation of shooting distance

General considerations

Nichols reviewed gunshot proximity testing in order to provide firearms examiners with a single comprehensive resource (69). Variables such as gun and cartridge characteristics, target material and environmental conditions are discussed. These variables have to be as far as possible controlled to achieve good interpretations of the evidence. Visual and chemical examinations were also reviewed. An additional paper (70) by the same author deals specifically with shotguns and related issues such as shot dispersion since examination and interpretation of shotgun proximity testing is substantially different from other firearms. Haag illustrates with an example (12 gauge shot shell) the necessity to use the same type of ammunition that was fired during an incident in order to estimate shooting distances (71). Another article deals with special cases where specific low-density particles, coming from plastic buffer material present in some American shotgun ammunitions, are used to determine shooting distances (72). The distribution of shotgun pellets after ricochet was studied by Rowe, using a geometric approach (50).

Colour tests

A muzzle-to-target distance determination necessitates GSR patterns visualisation. If this can be done by direct observation on light-coloured garments, chemical tests are often performed after visual examination since some residues are not visible to a macroscopic examination. This is particularly true for dark, multi-colored or bloodstained fabrics. The Modified Griess Test (for nitrites) followed by the Sodium Rhodizonate Test (for lead and barium) is still the preferred method for examining GSR patterns. The latter has to be conducted in an acidic environment in order to reveal the metals. However the acidic medium and the order of spraying seem to be major factors on colour intensity and persistency. Rawls et al. tested tartaric acid, acetic acid and sodium bitartrate media (73). They concluded that spraying 2% sodium bitartrate followed by rhodizonate solution is the best procedure to reveal lead, while still discriminating barium from lead.

Copper can be detected by using either 2-nitroso-1-naphtol or dithiooxamide. These chemical tests were recently summarised by Haag et al. (74).

The importance of colour tests was pointed out by Adeyi et al (75) who report a case for which a false conclusion could have been proposed just by observing the entrance wound. In this example the analysis of GSR dispersion using the Sodium Rhodizonate Test led to a different conclusion, illustrating that possible detailed examinations and additional tests have to be performed in order to yield correct interpretations.

The Modified Griess Test protocol for nitrites identification uses desensitised black-and-white photographic paper. However with the increasing scarcity of such papers, an alternative is the use of inkjet photographic papers (76). It saves time and money since the desensitisation step and the use of a dark room facility are avoided. The performances of several commercial inkjet papers were evaluated (77,78). Though some of the tested papers are not suitable, others give better results than traditional black-and-white photographic paper; moreover these papers do not interfere with the Sodium Rhodizonate Test (77), often used in conjunction with the Modified Griess Test.

Nevertheless, these chemical techniques usually necessitate the GSR to be transferred to a support and so are destructive to evidence. Bailey et al. (79,80) report the use of a sodium hypochlorite solution for direct visualisation on dark and multi-colored fabrics, by bleaching the dyes and eliminating the background colour.

Although the use of sodium hypochlorite does not influence the GSR pattern size, some fabrics (2 of 12 tested) cannot be bleached.

Targets

Marshall conducted experiments in order to evaluate fabric media and target pigskin on visible gunpowder particles dispersion and sodium rhodizonate patterns (81). If cotton seems to be a good simulant to pigskin, high variations between the fabrics were observed, probably due for the most part to differences in interaction with GSR. This again states the importance to use the same test material when conducting range tests, since visual and chemical examinations can lead to variations depending on the type of material being used. The issue of hair effects has also been reported (82): when trying to identify visual GSR and interpreting distance estimations, the hair can act as a filter and bad conclusions can be drawn if no (or only a few) GSR are observed.

For very close distance for which target materials are not suitable because of their fragility, craft foam seems to be suitable (83).

Non-destructive techniques

The development of non-destructive techniques for direct observation of GSR patterns has also been reported. For instance alternative light sources are widely used in forensic laboratories for questioned documents, fingerprints etc… The use of these sources was extended to GSR patterns with success (84,85,86). However further investigation and validation studies are necessary to prevent misinterpretation and artefacts (84,85).

X-ray techniques (85) may also be valuable methods for direct observation of GSR patterns. Recently, Berendes et al. reported the use of millimetre-X-ray fluorescence analysis (m-XRF) equipped with a special sample holder as a valuable technique for the investigations of GSR patterns (87). It allows XRF mapping of large surfaces (20x20 cm_) within 4 hours, with access to qualitative and semi-quantitative GSR distributions.

Organic GSR

Screening of gun propellant powder components

Smokeless powder is the primary propellant in civilian and military ammunition and is used in the fabrication of improvised explosive devices (IEDs). This powder is composed of nitrocellulose (propellant), nitroglycerin (energetic material) and additives such as diphenylamine (stabiliser), ethylcentralite or methylcentralite (stabilisers and/or gelatinisers), dinitrotoluene isomers (flash suppressor). Diphenylamine is known to decompose into N-nitrosodiphenylamine and into various nitroderivatives. Determining the additive contents presents an important forensic interest in the investigation of criminal cases for which the use of firearms or IEDs is known or alleged.

Mathis and McCord developed a gradient reversed-phase liquid chromatographic-electrospray ionisation mass spectrometric (ESIMS) method for the comparison of smokeless powders (88). The efficiency of electrospray ionisation was first studied by infusing individual standards of powder components in a methanol/aqueous ammonium acetate solution. A separation method (i.e. LC for Liquid Chromatography) was then developed using the optimised ESIMS parameters. The resulting LC-ESIMS method was applied to determine the organic additives in several smokeless powders. The authors concluded that the developed method should prove useful in the analysis of compositional variation and smokeless powder degradation. Additionally, the same authors studied the mobile phase influence on a positive electrospray ionisation for the analysis of smokeless powders with the above-mentioned method (89). In this study, several parameters were investigated. The results of the analysis showed that the electrospray ionisation of smokeless additives is affected by the acetate ammonium concentration, as well as by the pH of the solution.

West et al. investigated the use of ion mobility spectrometry (IMS) for the detection of ethylcentralite, diphenylamine and some of its nitroderivatives (90). Standards and gunpowder samples were analysed in both positive and negative ion modes. The authors report that gunpowder stabilisers can be detected using dual-detection modes: ethylcentralite, diphenylamine and N-nitrosodiphenylamine are detected in positive ion mode; while nitroderivatives of diphenylamine are screened in negative mode. This mode is usually selected to detect nitro compounds such as nitroglycerin, dinitrotoluene and trinitrotoluene.

To assess the accuracy of quantitative measurements of additive contents of propellants/explosives by the use of various analytical methods, the US National Institute of Standards and Technology (NIST) has developed a smokeless powder reference material (91), which provides reference concentrations with relative uncertainties less than 5 % for nitroglycerin, diphenylamine, N-nitrosodiphenylamine and ethylcentralite.

As smokeless powders contain also inorganic ions, Hopper and McCord used capillary zone electrophoresis methods to determine the inorganic ion contents of burned and unburned smokeless powders (92). A variety of smokeless powders and samples from deflagrated or intact pipe bombs were analysed. Notably, the authors pointed out that the concentration of inorganic ions in burned and unburned smokeless powders could yield information in the characterisation of such a material.

Instrumental methods for organic gunshot residue (OGSR) analysis

Muller et al. suggest a novel method for the analysis of discharged smokeless powder residues left on a target material (93). This method, including Modified Griess Test and gas chromatographic analysis (gas chromatography/thermal analysis and gas chromatography/mass spectrometry) of nitroglycerin, dinitrotoluene and stabilisers, is devoted to the estimation of intermediate-to-long firing distance ranges. Full metal jacketed bullets were used to perform firings with a 9 mm Luger FN semiautomatic pistol. The authors concluded that in the firing distance range of 0,75-3 m, the Modified Griess Test is not adequate to confirm the

GSR nature of the few particles found on the target because of its lack of specificity. A complementary instrumental analysis (using gas chromatography) of the organic components of the particles may confirm the nature of the GSR.

OGSR analysis is also recommended when the traditional SEM/EDX analysis of metallic particles fails to confirm the presence of GSR, particularly due to the use of lead-free ammunition or ammunition without heavy metals.

Laza et al. developed a quantitative liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) method for the analysis of common propellant powder stabilisers in gunshot residues (94). Samples were collected from hands of a shooter immediately after firings with various types of firearms and ammunition. Samples were prepared using a solid phase extraction protocol and were subsequently analyses by LC-MS/MS. The authors confirm that this method constitutes an alternative technique for OGSR analyses. However it should be optimised for an efficient detection of OGSR expelled from calibres smaller than 9mm Para.

Zeichner et al. have conducted a feasibility study of the use of Ion Mobility Spectrometry (IMS) for the analysis of gunpowder residues collected from clothing worne by shooting suspects (95). They assess the applicability of the portable sampler combined with the fibreglass and the Teflon filters, which are supplied with the commercial IMS instrument. Samples collected by vacuuming were treated by solvent extraction and were subsequently analysed by IMS, gas chromatography/thermal energy analyser (GC/TEA) and by gas chromatography/mass spectrometry (GC/MS). The authors concluded in the feasibility to use the IMS portable vacuum sampler for gunpowder residue collection from the clothing of suspects even if this clothing was previously sampled by the tape-lift method for inorganic GSR analysis with SEM/EDX. GC/TEA and IMS were found sensitive enough to detect and identify gunpowder residues in real cases.

Combining GC/TEA, IMS and SEM/EDX, Zeichner and Eldar proposed a novel method for extraction and analysis of gunpowder residues on double-sided adhesive-coated stubs which are usually used for the collection of primer residues (96) prior to SEM/EDX. The efficiency of the extraction procedure was studied using different solvent compositions and various samples which were composed of a standard working solution of nitroglycerin and 2,4-dinitrotoluene mounted on an adhesive-coated stub. An optimised extraction procedure was applied to the analysis of gunpowder residues and was tested in shooting experiments. Concluding on the feasibility of the extraction and analysis of gunpowder residues collected with adhesive coated stubs, the authors reported that the extraction may be carried out after the traditional analysis of the stub by SEM/EDX.

Bird et al. (97) discuss the first (to their knowledge) application of time-resolved fluorescence microscopy to GSR particles. In their study macroscopic partially burnt propellant GSR particles, produced from firing a Winchester .38 special cartridge at a cotton fabric target, were collected and individually mounted on microscope slides. The particles were imaged by time-resolved confocal laser scanning microscopy and the time-resolved imaging was carried out by time-correlated single photon counting. Theoretically, the major constituents of powder (nitro compounds like nitrocellulose and nitroglycerine) do not exhibit specific fluorescent behaviour, but the additives (stabilisers, oxidisers, etc.) may very well do. The authors demonstrate that a spatial distribution of the lifetimes of the emitting species allows for the identification of the GSR particles. The results indicate that the examined GSR particles do contain undetermined emitting species with different fluorophore lifetimes and that the fluorescent effect, observed when using forensic light sources on targets, originates from a light scattering effect in combination with pure fluorescence.

Mahoney et al. (98) used Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) to characterise the organic composition of unburnt propellant powders. Smokeless powders, black powders and black powder substitutes were analysed. Positive results were obtained in analysing all additives in smokeless and black powder, both organic (like ethyl centralite, dibutyl phtalate and nitrocellulose) and inorganic (like potassium nitrate, potassium perchlorate and sulfur) in nature. Using Principal Component Analysis (PCA), the samples could be clustered in the different groups they belong to, showing the applicability of the technique in this field. This is very interesting in cases where unknown samples need to be compared to reference materials. Because of the high-vacuum conditions inside the instrument, however, the technique is not very well suited for the analysis of the more volatile components such as nitroglycerine.

Use of special analysis or sampling techniques

Sampling

Hanson and Springer (99) discuss the use and applicability of the Instant Shooter Identification (Isid^{TM}) Sampling Kits produced by Law Enforcement Technologies Inc. This binary test uses a swab and indicator liquid to yield a colour reaction on the presence of nitrates, upon which the results can be confirmed with SEM/EDX analysis of the swab.

Shooters were sampled immediately after shooting or after a delay (from five minutes to three hours). It is concluded by the authors that the Isid Kit is inferior to the classic stub sampling method for several reasons such as i) the effectiveness of nitrate detection and its visual identification by the expected colour and ii) the effectiveness and the time-consuming of particle identification on the swab by SEM/EDX analysis.

Hall and Fairley propose a single approach to the recovery of DNA and GSR on garments (100): prior to analysis, GSR are collected using the conventional tape-lift method. After SEM/EDX analysis, the adhesive tapes are removed from the aluminum stubs and the DNA is extracted for identification. The usefulness of this method is illustrated with two caseworks.

Ferrotrace

The method used to visualise firearm imprints on hands is the "Ferroprint" or "Ferrotrace" test, consisting in spraying an aqueous solution of PDT (3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine) and ascorbic acid on the hands; this test reveals the presence of iron due to the formation of a magenta complex.

In order to determine why some persons develop clear marks while others do not, Almog et al. conducted quantitative studies on several factors influencing stain intensity (101,102). The authors demonstrated the relationship between stain intensity and quantity of iron present on the hands; they also pointed out palmar moisture level and gripping period as major factors influencing stain intensity. Finally the transfer process of iron was found to be a chemical dissolution rather than a mechanical dislodgement; in this process, chloride ions (present in high levels in palmar sweat) seems to have a significant effect by enhancing the dissolution.

The analysis and use of bullet lead composition

As was already known, there is a substantial bullet lead deposition inside the barrel of a firearm. This "lead memory" effect renders the association of bullet composition to the firearm – and hence the shooter – in most cases difficult. Zeichner et al. (103) have shown, using Multiple-Collector Inductively Coupled Plasma/Mass Spectrometry (MC-ICP/MS) that this memory effect is impossible to remove using mechanical and chemical means. However, in certain particular cases, where several firearms were used employing types of ammunition with bullet lead isotope ratios differing significantly between ammunition types/firearms, it may be possible to point out which bullet/firearm caused a particular gunshot entry in the target. Also, although there is a significant variation of lead isotope ratios among bullets, cartridges and primers produced by the same manufacturer, it is generally possible to distinguish specific batches of ammunition from different manufacturers.

On the subject of eliminating the lead contamination from a gun barrel, Haag and Niewoehner (104) show that even after the firing of a substantial number of lead-free cartridges through a lead fouled barrel, the "lead memory" effect of the barrel remains visible with SEM/EDX in the elemental X-ray mapping mode. The residual lead deposition seems to be concentrated predominantly in the groove/land interface area.

It is well known that bullet lead composition varies within the production lines of all manufacturers, even to the extent that the bullets in one box may show differences when analysed with the sensitive and accurate instruments of forensic science. The use of such analytical data in casework comparisons of bullet and shot samples is therefore often scrutinised. In the field of evidential value of lead trace element analysis for use in bullet matching, an article published in 2002 (105) stated that bullets with indistinguishable compositions could have come from different sources. However in a recent study Koons and Buscaglia (106) have compared a sample set of 1837 bullets and shot pellets selected from case samples received by the FBI Laboratory in the period 1989 to 2002. Analytical

Inductively Coupled Plasma - Optical Emission Spectrometry I(CP-OES) and Nuclear Activation Analysis (NAA) data of seven trace elements (Sb, As, Bi, Cd, Cu, Ag and Sn) was used in determining the uniqueness of a bullet in this set. The results of the study show that the probability of the occurrence of an exact match is of the order of 10^{-3} to 10^{-5}. It is therefore very unlikely that a bullet recovered from a crime scene having the exact same trace element composition as another bullet found on a suspect would come from a different source.

References

1. Miller J. Criteria for identification of toolmarks. AFTE Journal 1998; 30(1); 15-61
2. Miller J. Criteria for identification of toolmarks part II: single land comparisons. AFTE Journal 2000; 32(2); 116-130
3. Miller J. Criteria for identification of toolmarks part III. Supporting the conclusion. AFTE Journal 2004; 36(1); 7-38
4. Nichols RG. Firearm and toolmark identification: the scientific reliability and validity of the AFTE theory of identification discussed within the framework of a study of ten consecutively manufactured extractors. AFTE Journal 2004; 36(1); 67-88
5. Stone RS. How unique are impressed toolmarks? AFTE Journal 2003; 35(4); 376-383
6. Collins ER. How “Unique” are impressed toolmarks? – An emperical study of 20 worn hammer faces. AFTE Journal 2005; 37 (4); 252-295
7. Champod C, Baldwin D, Taroni F, Buckleton J. Firearm and tool marks identification: the bayesian approach. AFTE Journal 2003; 35(3); 307-316
8. Buckleton John, Nichols R, Triggs C, Wevers G. An exploratory Bayesian model for firearm and toolmark interpretation; AFTE Journal 2005; 37(4); 352-361
9. Bunch S. Consecutive matching striation criteria: a general critique. Journal of Forensic Sciences 2000; 45(5); 955-962
10. Deinet W, Katterwe H. Comments on the application of theoretical probability models including Bayes theorem in forensic science relating firearm and tool marks. AFTE Journal 2007; 39(1); 4-7
11. Schwartz A. A systemic challenge to the reliability and admissibility of firearms and toolmark identification. The Columbia Science and Technology Law Review 2005; 6(2); 1-42
12. Nichols R. The scientific foundations of firearms and tool mark identification – A response to recent challenges. The CACNews – 2nd quarter 2006; 8-27
13. Nichols RG. Defending the scientific foundations of the firearms and tool mark identification discipline: responding to recent challenges. Journal of Forensic Sciences 2007; 52(3); 586-594
14. Howitt D, Tulleners F, Cebra K, Chen S. A calculation of the statistical significance of the consecutive matching line criteria used for the analysis of bullets. Submitted for publication to Journal of Forensic Sciences. And additionally: The Statistical Significance of a Bullet Match. Presentation at the AFTE2007 trainings seminar. San Francisco, CA; The Statistical Significance associated with matching lines on a bullet. Presentation at the The Eighteenth Annual International Scientific Meeting on Scanning Microscopies, Monterey, CA.
15. Pauw-Vugts P. FAID 2005 – Proficiency Test or Collaborative Study of Firearms Identification, presented at the AFTE 2007 training seminar in San Francisco, CA. (http://www.afte.org)

---

16. Chow SM, Striupaitis P, Haskell N, Gaensslen RE. Time-dependent effects of the putrefaction in bodies on individualizing striation mMarks on bullets – A pig model. AFTE Journal 2003; 35(4); 388-393

17. Larrison RM. Degradation of fired bullets and cartridge cases in different environmental mediums. AFTE Journal 2006; 38(3); 223-230

18. Hayes CS, Basoa M, Freese R. Reduction of characteristic breechface marks due to primer sealants. AFTE Journal 2004; 36(2); 139-146

19. Bishop B, Rosati C, Leas R, Ennis M, Lee J, Janeksela V. Does superglue hinder traditional firearms identification? AFTE Journal 2005; 37(1); 3-7

20. Gerber K, Marsanopoli J. Effects of fire damage on the ability to make identifications part 1: bullets. AFTE Journal 2005; 37(3); 206-212

21. Hess PA, Moran B. The removal of superficial rust/corrosion from the working surfaces of firearms for the purpose of revealing their potentially identifiable signature and an application of this technique in a firearms identification. AFTE Journal 2006; 38(2); 112-132

22. Krivosta GG. NanoTag^{TM} markings from another perspective. AFTE Journal 2006; 38(1); 41-47

23. Bati C. The width of the firing pin imprint as a class characteristic in 7,62 x 39 mm Kalashnikov cartridge cases. AFTE Journal 2007; 39(1); 24-30

24. Fadul TG, Nuñez A. Glock's new "EBIS" barrel: the finale to the Miami barrel saga. AFTE Journal 2006; 38(2); 96-100

25. Dutton G. LEICA FSC comparison macroscope. AFTE Journal 2004; 36(4); 256-261

26. Koch A. Abformungen bei der Waffen- und Munitionsuntersuchnung. Der Auswerfer. Sonderausgabe Schusswaffensymposium München. 67-80

27. Koch A. Abformtechniken für komplexe 3-D Strukturen. Der Auswerfer 18; 57-83

28. Murthy SS, Mazumdar C, Rao MS, Pal AK. Digital image matching of 9mm pistols. AFTE Journal 2004; 36(2); 155-165

29. Wen CY, Yao JY. Pistol image retrieval by shape representation. Forensic Science International 2005; 155; 35-50

30. Li D. Ballistics projectile image analysis for firearm identification. IEEE Transactions on Image Processing 2006; 15(10); 2857-2865

31. Brein C. Segmentation of cartridge cases based on illumination and focus series. SPIE Conference Proceedings, Image and Video Communications and Processing 2005; 5685; 228-238

32. Leon FP. Automated comparison of firearm bullets. Forensic Science International 2006; 156; 40-50

33. Nennstiel R, Rahm J. A parameter study regarding the IBIS^{TM} correlator. Journal of Forensic Sciences 2006; 51(1); 18-23

34. Nennstiel R, Rahm J. An experience report regarding the performance of the IBIS^{TM} correlator. Journal of Forensic Sciences 2006; 51(1); 24-30

35. Bernard M. The effects of ammunition brand and firearm use on IBIS correlation scores. Canadian Society of Forensic Science Journal 2005; 38(2); 69-83

36. De Kinder J, Tulleners F, Thiebaut H. Reference ballistic imaging database performance. Forensic Science International 2004; 10; 207-215

37. Senin N, Groppetti R, Garofano L, Fratini P, Pierni M. Three-dimensional surface topography acquisition and analysis for firearm identification. Journal of Forensic Sciences 2006; 51(2); 282-295

38. Banno A, Masuda T, Ikeuchi K. Three dimensional visualization and comparison of impressions on fired bullets. Forensic Science International 2004; 140; 233-240

39. Song J, Vorburger T. Topography measurements and applications. SPIE Conference Proceedings, Third International Symposium on Precision Mechanical Measurements 2006; 6280

40. Thompson E. Editorial: Two dimensional versus three dimensional characteristics. AFTE Journal 2006; 38(1); 10-13

41. Roberge D, Beauchamp A. The use of BulletTrax-3D in a study of consecutively manufactured barrels. AFTE Journal 2006; 38(2); 166-172

42. Vorburger TV, Yen JH, Bachrach B, Renegar TB, Filliben JJ, Ma L, Rhee HG, Zheng A, Song JF, Riley M, Foreman CD, Ballou SM. Surface topography analysis for a feasibility assessment of a national ballistics imaging database. NISTIR 7362 (National Institute of Standards and Technology), Gaithersburg, MD, USA, 2007, http://www.mel.nist.gov/div821/webdocs-13/NISTIR2007-7362.pdf

43. Forensic Technology Inc. The development of IBIS-TRAX 3D™: BulletTRAX-3D™ and BrassTRAX-3D™. http://www.forensictechnologyinc.com/

44. Roberge D, Beachamp A. The use of BulletTRAX-3D in a study of consecutively manufactured barrels. AFTE Journal 2006; 38(2); 166-172

45. Haag LC. Shooting incident reconstruction. Academic Press (Elsevier) USA 2006; ISBN-13:978-0-12-088473-5; ISBN-10:0-12-088473-9.

46. Haag LC. Sequence of shots through tempered glass. AFTE Journal 2004; 36(1); 54-64

47. Haag LC; Garrett, ML. Bullet length to diameter ratios and caliber determination of bullets in surviving gunshot victims. AFTE Journal 2007; 39(1); 31-43

48. Moran B. Shooting incident reconstruction. Chapter 8 (215-312) in the book entitled Crime Reconstruction by Chisum and Turvey. Academic Press (Elsevier) USA 2006; ISBN-10:0-12-369375-6.

49. Klees GS. The Un-expanded hollow point bullet-observations of terminal effects from a shooting scene examination. AFTE Journal 2005; 37(3); 184-186

50. Rowe WF. The distribution of shotgun pellets after ricochet from an intermediate target surface. Forensic Science International 2005; 155; 188-192

51. Sims E, Barksdale L. The importance of careful interpretation of shell casing ejection patterns. Journal of Forensic Identification 2005; 55(6); 726-740

52. Jussila J. Preparing ballistic gelatine–-review and proposal for a standard method. Forensic Science International 2004; 141; 91-98

53. Jussila J. Measurement of kinetic energy dissipation with gelatine fissure formation with special reference to gelatine validation. Forensic Science International 2005; 150; 53-62

54. Jussila J. Ballistic skin stimulant. Forensic Science International 2005; 150; 63-71

55. The Scientific Working Group SWGGUN: http://www.swggun.org/

56. Wright DM, Trimpe MA. Summary of the FBI Laboratory's Gunshot Residue Symposium, May 31-June 3, 2005. Forensic Science Communications 2006; 8(3)

57. De Forest PR, Martir K, Pizzola PA. Gunshot residue particle velocity and deceleration. Journal of Forensic Sciences 2004; 49(6); 1237-1243

58. Haag LC, Tew J. The effect of revolver cylinder gap on GSR production and projectile velocity. AFTE Journal 2006; 38(3); 204-212

59. Yang J, Gunn A, Palmbach T, Wei D, Sinha S. Nanoparticles in gun-shot-residue. 2006 IEEE Conference on Emerging Technologies - Nanoelectronics 2006; 269-272

60. Oommen Z, Pierce S. Lead-free primer residues: a qualitative characterization of Winchester Winclean™, Remington/UMC LeadLess™, Federal BallistiClean™, and Speer Lawman CleanFire™ handgun ammunition. Journal of Forensic Sciences 2006; 51(3); 509-519

61. Fojtasek L, Kmjec T. Time periods of GSR particles deposition after discharge-final results. Forensic Science International 2005; 153(2-3);132-135

62. Berk RE, Rochowicz SA, Wong M, Kopina MA. Gunshot residue in Chicago police vehicles and facilities: an empirical study. Journal of Forensic Sciences 2007; 52(4); 838-841

63. Mejia R. Why we cannot rely on firearm forensics. New Scientist 2005;188(2527); 6-7

---

64. Biedermann A, Taroni F. A probabilistic approach to the joint evaluation of firearm evidence and gunshot residues. Forensic Science International 2006; 163(1-2); 18-33

65. Cardinetti B, Ciampini C, Abate S, Marchetti C, Ferrari F, Di Tullio D, D'Onofrio C, Orlando G, Gravina L, Torresi L, Saporita G. A proposal for statistical evaluation of the detection of gunshot residues on a suspect. Scanning 2006; 28; 142-147

66. Cardinetti B, Ciampini C, D'Onofrio C, Orlando G, Gravina L, Ferrari F, Di Tullio D, Torresi L. X-ray mapping technique: a preliminary study in discriminating gunshot residue particles from aggregates of environmental occupational origin. Forensic Science International 2004, 143;1-19

67. Roeterdink EM, Dadour IR, Walting RJ. International Journal of Legal Medecine 2004; 118; 63-70

68. Niewoehner L, Andrasko J, Biegstraaten J, Gunaratnam L, Steffen S, Uhlig S. Maintenance of the ENFSI proficiency test program on identification of GSR by SEM/EDX (GSR2003). Journal of Forensic Sciences 2005; 50(4); 877-882

69. Nichols RG. Gunshot proximity testing: a comprehensive primer in the background, variables and examination of issues regarding muzzle-to-target distance determinations. AFTE Journal; 2004 36(3); 184-203

70. Nichols RG. Shotgun proximity testing: a review of the literature regarding muzzle-to-target distance determinations involving shotguns. AFTE Journal 2006; 38(3); 192-203

71. Haag M. Shotgun pellet patterning: federal's FLITCONTROL$^{\text{TM}}$ law enforcement shotshell. AFTE Journal 2006; 38(3); 231-238

72. Haag LC. Shotgun range of fire determinations from skin stippling by plastic buffer material. AFTE Journal 2007; 39(1); 50-61

73. Rawls DD, Ryan JP. Modified Feigl test for lead. AFTE Journal 2006; 38(3); 213-222

74. Haag M, Haag L. Trace bullet metal testing for copper and lead at suspected projectile impacts. AFTE Journal 2006; 38(4); 301-309

75. Adeyi O, Duval JV, Dupre ME, Andrew TA. Role of chemical tests and scene investigation in determination of range of fire. American Journal of Forensic Medecine Pathology 2005; 26(2); 166-169

76. Malikowski SG. Alternative Modified Griess test paper. AFTE Journal 2003; 35(2); 243

77. Hess PA, Poole LL. The validation of inkjet photographic paper for use with the Modified Griess Test. AFTE Journal 2005; 37(3); 213-223

78. Gamboa FA, Kusumi R. Evaluation of photographic paper alternatives for the Modified Griess Test. AFTE Journal 2006; 38(4); 339-347

79. Bailey JA. Enhancement of gunshot residue patterns on dark colored fabric using sodium hypochlorite. AFTE Journal 2005; 37(3); 169-171

80. Bailey JA, Casanova RS, Bufkin K. A method for enhancing gunshot residue patterns on dark and multicolored fabrics compared with the Modified Griess Test. Journal of Forensic Sciences 2006; 51(4); 812-814

81. Marshall J. Visual and chemical variability in gunpowder residue deposition on different fabric media. Canadian Society Forensic Science Journal 2006; 39(3); 115-124

82. Jason A. Effect of hair on the deposition of gunshot residue. Forensic Science Communications 2004; 6(2)

83. Martini L. Craft foam: a target material for distance determination. AFTE Journal 2004; 36(3); 242

84. Chaklos DL, Davis AL. Visualization of gunpowder residue patterns using a digital infrared camera and optical filters. AFTE Journal 2005; 37(2); 117-122

85. Giroux BN. Non-destructive techniques for the visualization of gunshot residue. AFTE Journal 2006; 38(4); 327-338

86. Atwater C.S, Durina ME, Durina JP, Blackledge RD. Visualization of Gunshot Residue Patterns on Dark Clothing. Journal of Forensic Sciences 2006; 51(5); 1091-1095

87. Berendes A, Neimke D, Schumacher R, Barth Martin. A Versatile Technique for the Investigation of Gunshot Residue Patterns on Fabrics and Other Surfaces: m-XRF. Journal of Forensic Sciences 2006; 51(5); 1085-1090

88. Mathis JA, McCord BR. Gradient reversed-phase liquid chromatographic-electrospray ionisation mass spectrometric method for the comparison of smokeless powders. Journal of Chromatography A 2003; 988; 107-116

89. Mathis JA, McCord BR. Mobile phase influence on electrospray ionisation for the analysis of smokeless powders by gradient reversed phase high-performance liquid chromatography-ESIMS. Forensic Science International 2005; 154; 159-166

90. West C, Baron B, Minet JJ. Detection of gunpowder stabilizers with ion mobility spectrometry. Forensic Science International 2007; 166; 91-101

91. McCrehan WA, Bedner M. Development of smokeless powder reference material for propellant and explosives analysis. Forensic Science International 2006; 163; 119-224

92. Hopper KG, McCord BR. A comparison of smokeless powders and mixtures by capillary zone electrophoresis. Journal of Forensic Sciences 2005; 50(2); 307-315

93. Muller D, Levy A, Vinokurov A, Ravreby M, Shelef R, Wolf E, Eldar B, Glattstein B. A novel method for the analysis of discharged smokeless powder residues. Journal of Forensic Sciences 2007; 52(1); 75-78

94. Laza D, Nys B, De Kinder J, Kirsch-De Mesmaeker A, Moucheron C. Development of a quantitative LC-MS/MS method for the analysis of common propellant powder stabilizers in gunshot residues. Journal of Forensic Sciences 2007; 52(4); 842-850

95. Zeichner A, Eldar B, Glattstein B, Koffman A, Tamiri T, Muller M. Vacuum collection of gunpowder residues from clothing worn by hooting suspects, and their analysis by GC/TEA, IMS, and GC/MS. Journal of Forensic Sciences 2003; 48(5); 961-972

96. Zeichner A, Eldar B. A novel method for extraction and analysis of gunpowder residues on double-side adhesive coated stubs. Journal of Forensic Sciences 2004; 49(6); 1194-1206

97. Bird DK, Agg KM, Barnett NW, Smith TA. Time-resolved fluorescence microscopy of gunshot residue: an application to forensic science. Journal of Microscopy 2007; 226(1); 18-25

98. Mahoney CM, Gillen G, Fahey AJ. Characterization of gunpowder samples using time-of-flight secondary ion mass spectrometry (TOF-SIMS). Forensic Science International 2006; 158(1); 39-51

99. Hanson A, Springer F. An evaluation of Instant Shooter Identification (Isid^{TM}) gunshot residue kits. AFTE Journal 2005; 27(3); 172-178

100. Hall D, Fairley M. A single approach to the recovery of DNA and firearm discharge residue evidence. Sience & Justice 2004; 44(1); 15-19

101. Avissar YY, Sagiv AE, Mandler D, Almog J. Identification of Firearms Holders by the $[Fe(PDT)_3]^{+2}$ complex. Quantitative determination of iron transfer to the hand and its dependence on palmar moisture levels. Journal of Forensic Sciences 2004; 49(6); 1215-1219

102. Avissar YY, Sagiv AE, Mandler D, Almog J. Identification of firearms handling by the $[Fe(PDT)_3]^{+2}$ complex: chemical and time-dependent factors. Talanta 2005; 67; 328-333

103. Zeichner A, Ehrlich S, Shoshani E, Halicz L. Application of lead isotope analysis in shooting incident investigations. Forensic Science International 2006; 158(1); 52-64

---

104. Haag LC, Niewoehner L. The source and persistence of lead in gun barrels. AFTE Journal 2007; 39(1); 8-23

105. Randich E, Duerfledt W, McLendon W, Tobin W. A metallurgical review of the interpretation of bullet lead compositional analysis. Forensic Science International 2002; 127; 174-191

106. Koons RD, Buscaglia J. Forensic significance of bullet lead compositions. Journal of Forensic Sciences 2005; 50(2); 341-351

THE FORENSIC EXAMINATION OF MARKS

– A Review: 2004 to 2007 –

Nadav Levin, MSc

Head, Toolmarks and Materials Laboratory
Division of Identification and Forensic Science (DIFS)
Israel National Police Headquarters
Jerusalem 91906, Israel

Phone: +972-2-542-9453
Fax: +972-2-542-9464
Mobile: +972-50-627-5319
E-mail: simanim@police.gov.il

Contents

Introduction

The examination of contact marks covered in this review is one of the core issues of forensic science. Even though these types of evidence may sometimes have the highest evidential values in definitely linking suspects to scenes of crime, the techniques used are usually straightforward and simple. This review covers advances in scientific methods applied to the forensic examination of various marks since the 14th INTERPOL International Forensic Science Symposium (IFSS) in October 2004. Until the last IFSS (2004), these topics (e.g. footwear impressions and toolmarks) were included in a wider report, under the title "Fingermarks, shoesole and footprint impressions, tire impressions, ear impressions, toolmarks, lipmarks, bitemarks".

This paper is based mainly on a literature review, derived from the UK Forensic Science Service (FSS) FORS (Forensic Bibliography Database, www.forensic.gov.uk/forensic_t/inside/products/fors/), which covers articles published in the principle forensic science and other relevant journals over the period in question. This has been supplemented by a search of the Internet for articles related to forensic examination of marks. Valuable assistance was courteously provided by Prof. Christophe Champod and his colleagues (Institut de Police Scientifique, Université de Lausanne, headed by Prof. Pierre Margot).

Toolmarks, footwear impressions, and other contact marks form important types of evidence found in major or volume crimes. Their efficient classification and treatment play an important role in identification and crime analysis. Current developments in these fields are highlighted in the present review. The impact of *Daubert*-type challenges has forced practitioners to review their discipline and its basic foundations. Several organizations are active in these fields, such as the newly formed Scientific Working Group on Shoeprint and Tire Tread Evidence (SWGTREAD) (1), the European Network of Forensic Institutes (ENFSI) Expert Working Group (EWG) Marks, the Association of Firearms and Toolmark Examiners (AFTE) and the International Association for Identification (IAI).

Footwear and Tire-tread Impressions

SWGTREAD has recently published several guidelines covering many aspects of these disciplines (2-13). These manuals describe the duties of footwear and tire tread examiners (2), establish their minimum qualification and training (10), and set a standard terminology for use (13). They also delineate procedures for the detection and collection of impressions, both in the field and in the laboratory (3-6, 8, 9), as well as instructions for photographing (11) and examining (12) these marks (Also available at the SWGTREAD web page http://www.theiai.org/guidelines/swgtread/).

The systematic use of footwear (among other) evidence, collected at scenes of crime, was studied by Burrows and Tarling of the FSS (14). Although the value of this type of evidence is well established both at intelligence or court proceedings levels, this study showed apparent differences in the way police services exploit the collected marks. Some services were shown to use a pro-active approach, taking advantage of crime analysis before the arrest of potential offenders; others adopted a purely reactive approach, waiting for potential suspects to be brought to their attention. A similar trend, focusing mainly on shoeprint evidence, was also observed by Rix (15).

Detection and Recording

Photography

Footwear impressions can be digitally photographed or scanned. Shor *et al.* examined the evidential value of shoeprint images received from the scene or taken deliberately at an angle out of proper perspective (16). This study demonstrated that shoeprint images taken at an angle less than 40° to the perpendicular still preserve the evidential value of the acquired characteristics. At larger angles the original image could not be adequately restored. These findings may be highly useful in digitally rectifying distorted images to their proper dimensions.

A complementary approach was proposed by Chung using a Tilt-and-Shift lens for photographing impressions on reflective surfaces or on partially shielded areas (17).

Buck *et al*. demonstrated that the non-destructive method of 3D optical surface scanning (by using the GOM ATOS II system) delivers more detailed results of higher accuracy than the conventional casting techniques (18). According to their findings the software calculates, within seconds, the high-precision 3D coordinates of up to 1.3 million object points per measurement. The results of this mobile 3D optical surface scanner were very satisfactory in different meteorological and snow conditions. The method is also suitable for impressions in soil, sand or other materials.

Casting and 3D Test Impressions

Dental stone obtained from dental suppliers has been used worldwide at crime scenes for more than thirty years (*e.g.*, Castone or Glastone by Dentsply International). A common practice consists of weighing a portion of dental stone (*e.g.*, 1kg portions) into sturdy Ziploc or heat-sealed bags, which are carried to the crime scenes to be used if needed by adding a known amount of water (500cc per 1kg, usually). Bodziak and Hammer (19) provided basic information about dental stone and its recommended usage and compared it with the new "ready-to-go" kits (such as Traxtone and Crime-cast). Even if the novel products gave excellent detail and adequate hardness, the authors finally recommended the use of bulk dental stone for the following reasons: it offers more flexibility regarding the size and amount needed, it is readily available from many dental suppliers, it costs less, and it sets up quickly.

To obtain three-dimensional test impressions of known shoes examiners tend to use commercially available Biofoam. Some cases require test impressions for photographic work only, without need for preservation. For these circumstances Massey developed an inexpensive formula of Play-Dough that allows rapid production of high quality three-dimensional impressions (20), which will last for a few days or weeks before becoming crumbly.

Wilson proposed using expandable polyurethane foam for producing 3D test prints of the tires in question (21). The polyurethane foam tested gave detailed, durable, cost-effective and lightweight tire casts, showing this method to be the most practical compared with other three-dimensional casting techniques.

Naples and Miller proposed hands-on laboratory-based activities to introduce forensic sciences to students, by casting and comparing shoemarks (22). This article is clearly intended for teachers and the general audience.

Three-dimensional shoeprints and tire tracks in snow are enhanced and preserved prior to casting using various brands of aerosol spray wax, paraffin, or sulphur, following traditional photography methods. Other approaches utilize dry powder layers to build a protective "base" prior to the application of plaster or dental stone. Aerosol waxes, such as "Snow Print Wax", are more commonly used to form a protective layer between the snow impression and subsequent dental stone backing. Adair *et al*. proposed a method for casting shoe or tire impressions in snow using Quikrete fast-setting concrete powder in conjunction with dental stone casting material (23). If the snow is somewhat "dry" or icy, the authors have found that pre-application of cold water to the impression improves the Quikrete powder preparation. The Quikrete method gave good results with regard to retention of fine details and is thus presented as an alternative to aerosol waxes. One disadvantage is that small voids, appearing as small defects in the outsole, can be formed where the powder material has not fully set.

In another article Adair and Tewes also proposed a solution to harden sulphur casts of snow impressions (24). These casts are highly fragile (even minor abrasive forces can damage or obliterate the fine detail), so the researchers used Plasti-dip, a multipurpose rubber coating material, to coat the sulphur casts. The Plasti-dip coating provided an extremely tough protective layer with minimal to negligible effect on details.

Detecting and Lifting 2D Impressions

Gelatine lifters are commonly used to lift dusty shoeprints off porous surfaces. Shor *et al.* proposed a novel technique to clean gelatine lifters from interfering contaminations using adhesive lifters (25). The technique consists of applying the adhesive lifter directly to the surface of the gelatine lifter and removing it instantly. The upper layer of the attached material on the gelatine filter is removed through this procedure and the quality of the visualized imprint is consequently improved. The cleaning process can be applied repeatedly, and the optimum number varies with substrate. The proposed procedure is routinely used in casework; nevertheless, the authors suggested that repeating the procedure too many times could harm the quality of the print severely. A similar approach, with comparable results, was later taken also by Ford and Baldwin (26).

The Electrostatic Dust Print Lifter (EDPL) and the Electrostatic Detection Apparatus (ESDA) were compared by Craig *et al.* The goal of the study was to determine the optimal combination and order of application of these processes for lifting footwear impressions of the same or similar quality in order to develop the highest quality footwear impression (27). They determined that the EDPL gave impressions of better comparative value than the ones developed with the ESDA. On average, 72.4% of the individual characteristics from the known impression were identified using the EDPL, with an average of only 38.9% for the ESDA. If only one technique is used EDPL is thus highly recommended. The authors also recommended using ESDA before EDPL, to avoid any reversal of the colour that could appear if EDPL is used first. In an earlier work Licht and Murano, while focusing on indented writings, also studied the factors influencing the quality of the recovered impressions when using the ESDA (28).

Adair and Doberson demonstrated the feasibility of lifting dusty shoeprints from human skin using the electrostatic dust print lifter (ESDL) (29). Footwear impressions differing in quality were tested using two widely used ESDLs. The test results confirm that this approach may be useful for lifting dusty footwear impressions from human skin.

The routinely used method for lifting dust prints using the EDSL is not suitable for conductive surfaces. In order to overcome this limitation, Adair proposed using a non-conductive film barrier, placed underneath the metallic film (30). The author reported obtaining good results with this modification.

Adair and Tewes also demonstrated excellent results with a novel method for recovering footwear impressions from cylindrical surfaces, by applying the impression-carrying object to the lifting film, instead of the conventional way (31).
Adair also showed that 2D bloody impressions on various surfaces, including human skin, could be easily transferred on alginate casting material (32). Alginate was the only casting materials tested to yield very good results with all surfaces tested, both with leucocrystal violet (LCV) treated and untreated bloody footwear impressions. Similar results, yet unpublished, were also obtained by the Israeli Police DIFS.

Michaud and Brun-Conti proposed another method for lifting and enhancing impressions made in blood by impregnation of nylon transfer membranes with LCV (33). The lifted and/or enhanced impressions exhibited excellent detail, especially when the impression was made with very small quantities of blood supported by a nonporous surface.

A comprehensive review of the methods used for the recovery of latent marks from human skin, focused mainly on fingerprints, was presented by Sampson and

Sampson (34). Apparently, some of these methods may be applicable to footprints as well.

Wilgus reported a case of shoeprint recovery from human skin, using cyanoacrylate fuming followed by the application of black magnetic powder and Mikrosil lifting (35). The recovered shoeprint from the victim's right forearm was found to match, by class characteristics, a shoe found in the possession of a suspect.

Digital treatment of footwear marks

Digital image enhancement tools have become more accessible to handle footwear marks, mainly due to the availability of computer power to handle large images.

Smith enhanced images by manipulating colour channels (36). The technique is well suited when the impression is distracted by colour backgrounds or detected by colour-based detection techniques. Berger *et al*. used a similar approach (37).

Wen and Chen describe the use of an image fusion method, based on multi-resolution analysis, for forensic examinations (38). These authors use simulated and actual images to illustrate how the multi-resolution image fusion technique works. Hamiel, and Yoshida reported a similar technique (39).

Several authors have studied the automatic classification of footwear marks achieved using various image processing and matching techniques such as Fourier transform (40, 41) or MSER feature detectors (42). To the best of this author’s (NL) knowledge none of these developments is yet known to be in operational use.

Su *et al*. proposed pre-processing algorithms to transform the initial grayscale image into a binary image, taking advantage of the pixel context (43). This group also studied automatic detection of quality of the input image using first- and second-order statistics combined with gradient-based and ridgelet-based quality measures (44). Tests using a database of 'good' and 'poor' shoeprint images indicated that the proposed approaches give a reasonable estimate of shoeprint image quality.

Individualization Process

The basis for the evidential value of shoeprints examination, as with other types of contact marks, derives from the selectivity of manufacturing or acquired features found in the shoe sole. Kainuma (45) published a study based on a die-cut footwear model (100 pairs of Zori-Zori beach sandals). The study shows enormous variability in results of the die-cut process, and no two slipper soles involved were found to be identical. Nevertheless, the orientation of the patterns should still be regarded as a class, or at least sub-class, characteristic.

Wyatt *et al*. showed that two months of regular wear can affect the ability to individualise, but even after this period of use positive shoeprint identification is still sometimes possible (46). Adair *et al*. demonstrated that following 7 hours of hiking, sufficient acquired features had been left on the soles of Altitude II hiking boots from Hi-Tec Corporation to distinguish all of them (47). The results obtained support the use of these features for the identification of footwear impressions and confirm the random formation of such damage by the wearer's use of the footwear.

Stone suggested a statistical model to predict probabilities of theoretical types of acquired features present in shoeprints (48). The author stated that when the marks or combinations of marks are relatively complex, the magnitudes of the resulting numbers are remarkable, despite being entirely abstract and based on conservative assumptions. It should be stressed that the basic assumptions of the model (independence and uniform distribution of defects in the shoe sole) need to be taken with caution.

Reporting the Results

The conclusions of the ENFSI EWG Marks Conclusion Scale Committee (CSC) have been published (49, 50). The committee collected conclusion scales, used by various forensic science laboratories throughout the world, and proposed a six-level harmonized verbal (not numerical) scale for reporting the evidential value of the examination’s findings. The harmonized scale incorporates also the Bayesian approach, as well as likelihood ratio, for interpreting evidence. The proposed scale was also adopted by the SWGTREAD (13). The assumptions made by the CSC regarding equal priors at the origin of the proposed scale, has been discussed by Taroni and Biederman (51) as well as by Biederman *et al.* (52). In any case, the rich discussion with regards to the scale of conclusions should force all examiners to rethink their reporting procedures.

Kerstholt *et al*. investigated the influence of expectations and complexity on shoe print examinations in order to determine whether results depend on the examiner’s experience (53). It was found that neither expectation nor experience affected results; the quality of the print was shown to be the primary factor influencing the assessment. When there was a noisy background, the acquired features were given a lower evidential value than when there was a clear background. Apparently examiners compensated for the quality of the print and drew more cautious conclusions in cases where the print was less clear.

Assessing the evidential value of a footwear impression, Black reported a case where the data obtained from the manufacturer regarding the distribution of a specific brand of shoe was used in strengthening the conclusion reached (54). In a later letter-to-the-editor, Black noted that multiple uppers from the same or different manufacturers might share a common outsole design (55).

Another case report, by Brooks Jr., showed how manufacturer’s information (in that case from Reebok) was useful in establishing the precise size, model and date of production of shoes that had left marks at a crime scene (56).

At this point it should be mentioned that the ENFSI EWG Marks maintains an internet-based forum for exchanging information regarding unknown footwear impressions (www.intermin.fi/intermin/hankkeet/wgm/home.nsf).

Other

The routine production of a shoemark cast taken in soil may provide information other than shoe size and gait. Indeed, material adhering to the surface of the cast is a potentially fruitful source of information for forensic reconstruction. Bull *et al*. addressed issues of experimental design and reproducibility for routine comparisons of source and transferred soil samples (57). These principles were later demonstrated in reference to a murder case, which took place in the English Midlands (58). In this case pollen analysis, together with analysis of fibre and of physical and chemical characteristics of the soil, allowed reconstruction of three phases of previous activity of the wearer of the boot prior to leaving the footprint in the field after the murder had taken place.

Linking the suspect to a pair of shoes, on the other hand, may be achieved by DNA analysis, as demonstrated by Bright and Petricevic (59). These researches studied the variation in the amount of the wearer's DNA recovered from shoe insoles. A procedure for sampling and subsequent DNA extraction was developed. The usefulness of this technique was illustrated by a casework example where DNA from shoe insoles had provided useful forensic evidence. In a similar study, Hillier *et al*. examined whether a wearer's identity could be determined consistently on the basis of DNA analysis (60). The results obtained suggest that, in some cases, DNA profiles can be obtained, but frequently the DNA profile was mixed, having multiple contributors, indicating secondary transfer.

Ozden *et al*. developed regression formulae for the estimation of individuals' sex and stature based on foot and shoe dimensions (61). This study confirmed that foot and shoe sizes can be used to estimate an individual's stature, and that the relationship between foot and shoe length and width can be used to aid stature estimation. Shoe lengths are more useful than widths in determination of sex of wearer, and shoe measurements are preferable to foot measurements.

Another example of reconstruction of a criminal event involved the use of tire track analysis. Tracks found on the clothing and corpse of a victim led Park *et al.* (62) to refute the suspect driver's version of events.

Toolmarks

The Identification Process

Recently, toolmark (as well as firearms) examinations have come under the same scrutiny as other classic identification areas. One of the main challenges to toolmark examination is exemplified by papers by Schwartz (63, 64) in the aftermath of the *United States v. Kain*, Crim. No. 03-573-1 (E.D. Pa. 2004). According to Schwartz, adequate statistical empirical foundations and proficiency testing do not exist for firearms and toolmark identification; all firearms and toolmark identifications should be excluded until the development of firm statistical empirical foundations for identifications and a rigorous regime of blind proficiency testing.

These arguments were not left without rebuttal, especially by Nichols (65-67). In his response to the challenges raised by Schwartz, Nichols systematically critiqued Schwartz's articles, reviewing their bibliographic references one-by one. He concluded, in contrast, that in fact a substantial body of literature demonstrates that toolmark and firearm examination have been critically studied according to the precepts of the scientific method and empirically validated.

Addressing the statistical issues regarding toolmarks and firearms examinations, Miller and Neel investigated the scientific reliability of using the concept of consecutive matching striae (CMS) as a toolmark criterion for striation marks, and discussed the application to the CMS for the assessment of toolmark patterns (68). It was concluded that an incorrect identification could not be made if the CMS criteria were strictly adhered to, although such strict adherence could also eliminate certain identifications where only one land impression could be compared.

As part as a more general trend suggesting to adopt a framework based on a likelihood ratio to interpret evidence, Buckleton *et al*. published a Bayesian model for assessing firearms and toolmark evidence (69). The proposed model was based on a CMS summary of the visual image of a striated tool mark comparison, and according to its authors the preliminary results are promising. The trend towards the adoption of a probabilistic approach may seem unavoidable, but its operational deployment and reporting procedures are not straightforward, as discussed by Deinet and Katterwe (70).

Marks of Various Types of Tools

A statistical study on the defects observed on the faces of twenty hammers subjected to various degrees of wear and abuse through normal use was performed by Collins (71). The results of this study have led to a re-evaluation of Stone's work (72, 73) and to modifications of the related formulae. The new formulae were used to calculate practical, conservative probabilities associated with impressed toolmarks using the collected data.

Miller and Beach examined several types of consecutively manufactured tools, including pliers, cutters, punches, and chisels, for the presence of subclass characteristics and any possible effect of the tool on the toolmarks (74). The AFTE Glossary defines *Subclass Characteristics* as "discernible surface features of an object, which are more restrictive than *Class Characteristics* in that they are produced incidental to manufacture, are significant in that they relate to a smaller group source (a subset of the class to which they belong) and can arise from a source which changes over time" (75). Identification based on subclass characteristics and not on individual characteristics is considered fallacious and the aim of this article was to observe whether subclass characteristics were noted for each studied tool. In this study some subclass characteristics were found to have no influence on the resulting toolmarks.

Walsh & Newton presented a case of sabotaged wooden power poles cut by a chainsaw (76). The article focused on the possibility that corresponding toolmarks found on one of the wood poles and the chainsaw of a suspect were subclass characteristics rather than individualizing ones. In order to test this conclusion consecutively manufactured chainsaw links were obtained from the manufacturer and studied to assess the reproducibility of marks arising from their manufacture.

Miller performed a comparative study between marks left 10 years ago by bolt cutters on lead, and the toolmarks left nowadays by the same cutters after several years of use (77). The toolmarks were examined for subclass characteristics, for the persistence of identifiable individual characteristics and changes that occurred on the tools from use.

Apart from the well-established mark-producing tools, other types of “tools” were also studied. Van Beest *et al*. studied the marks left by professional heat-sealing machines on plastic bags, mainly used in drug packing (78). They established relevant class and subclass characteristics, and individual marks (caused by manufacturing defects or due to use).

Akao *et al*. studied the spur mark evidence on inkjet-printed documents, in the domain of counterfeit banknotes, securities, and passports (79). Spur marks are toolmarks created by the spur gears in the paper conveyance system of many inkjet printers. The relationship between printouts and printers was investigated by comparing spur marks found on printed documents with reference spur marks samples from known printers. Spur marks were considered to be effective class characteristics to identify certain brands of inkjet printers since spur gears are used in many types of these machines. It is, however, necessary to build a database allowing isolating families or groups of suspect printers.

Novoselsky *et al*. reported the findings of a case where a motor vehicle, suspected of being stolen, was found severed (80). One of the sections was found in the possession of a suspect, while the other parts were deserted elsewhere. Physical match of the sections was incomplete, due to the width of the abrasion disc used for cutting them apart, but instead the parts were matched on the basis of brush strokes (striations) of a polymer sealant which had been applied when the vehicle was manufactured. These marks were found to continue on both sides of the cut.

In an article dealing with counterfeit 10 New Israeli Shekel (NIS) Coins in Israel, Tsach *et al*. describe various processes used for producing counterfeit coins, including the manufacturing defects (individual marks) associated with several of these processes (81). Kuppuswamy studied the formation, temporal evolution and forensic applications of camera "Fingerprints” (82). Negative films were exposed in various makes and models of cameras and exposures were performed at regular time intervals over a two-year period. The processed film negatives were then examined using transmitted light to detect the presence of discriminating features on the frame edges. The edge-marks were found to originate mainly from imperfections received on the film mask from the camera's manufacturing process, and that camera settings have a considerable influence on recording of frame-edge marks with film exposure.

Gorn and Hamer examined cable ties of different make and sizes, and found that these items may bear manufacturing-processes marks that can be used for comparison (83).

Many other works dealing with toolmarks produced by firearms-related processes, such as the manufacturing of ammunition, are outside the scope of this review.

The Examination of Stabbing and Cutting Marks

Identification of the weapon in a murder case by stabbing is one of the difficult problems faced by forensic pathologists. In *Ramirez v. State of Florida*, 810 So.2d 836 (2001), the court excluded toolmark comparison from marks left in cartilage after a *Frye* hearing. In a commentary to this court decision, Meyers argued that the words novel, science fiction, and junk science (as used by the Florida Supreme Court in this case) are inapplicable to toolmark identification in general or, more specifically, to the procedure involved in this case (84). The possibility to identify the knife as the source of marks left in cartilage after stabbing has been thoroughly re-investigated by Clow, showing the quality of cartilage as a medium to accept toolmark and the ability to distinguish consecutively manufactured knives (85). The results of this study support the validity of previous studies into the uniqueness of toolmarks in cartilage stabbed by knives.

A case study reported by Sitiene *et al* evaluated wounds and lesions of clothing in the area of injury (86). Their study revealed that precise knowledge of the assault circumstances enabled identification of the instrument of assault.

In another work general class characteristics of cuts on human bone were shown to correlate with specific sharp (single blade knife) or sharp-blunt (hatchet) instruments (87). Similarity of macroscopic findings led to the conclusion that microscopic analysis is more effective in distinguishing sharp from sharp-blunt injury to the bone. Emphasis has been placed on the value of the scanning electron microscope (SEM) as an anthropologist's tool in bone lesion injuries.

A case report by Ostrowski (88) concluded that toolmark findings from the skull of a victim could prove the injury had been inflicted by a hatchet.

The examination of damage to a paper towel, an item of evidence in a murder case, was described by Causin *et al*. (89). Simulations carried out with various tools and comparison of the lacerations present on the towel showed that the towel had been used to clean a sharp, pointed instrument. The paper towel also exhibited marks deemed characteristic of scissors. These findings were effectively used to challenge the suspect's version of events.

Another study focused on different characteristics expected to be seen in knife cuts to tires (90). Different styles of knives were shown to yield a variety of characteristic marks. Toolmark findings may also be utilized in puncture marks.

Food products can be intentionally contaminated by injection through the polypropylene packaging of certain foodstuffs. A paper by Abe and Matsuda describes a method designed to make controlled holes by needles at different angles on polypropylene bags (91). Their study demonstrated that almost all of the control holes were accompanied by scratch marks and that there was some correlation between needle diameters and scratch widths.
Finally, from an historical point of view, Smith and Brickley proposed an analysis of toolmarks found on bones of a Neolithic tomb, consistent with the use of flint tools (92).

Observation Methods

Toolmark test exemplars can be produced by applying a tool's working surface to a piece of soft metal such as lead, since the lead will replicate the microscopic grooves of the tool surface. An alternative material for preparation of test toolmarks was presented by Petraco *et al.*, who used carving waxes (jewellery modelling) (93). The replicas obtained from wax were exact, highly detailed 1:1, negative impressions of the exemplar tool's working surface, had a long shelf-life, and were suitable for use in toolmark examination and comparison cases.

The comparison microscope is the basic tool used by toolmarks and firearms examiners. In 2004, Leica Microsystems released a new comparison macroscope, named the FSC (Forensic Solution Comparison). Dutton presented a review of the instrument’s main features and showed its ability to compare bullet and cartridge cases (94).

Schecter *et al*. proposed a simple method to enhance the visualization of toolmarks found in the firing pin impressions (95). The proposed technique consisted in placing drops of a liquid on the base of cartridge cases so that the liquid forms a lens that enhances illumination and resolution of marks. Various liquids were tested and all presented disadvantages of some sort. However, acetone was shown to be the best adapted. The usefulness of this improvisation for toolmarks examination seems, however, quite limited.

Firearms and cartridge cases are often treated for latent fingerprints prior to the firearms identification examination. Bishop *et al*. studied the influence of cyanoacrylate (superglue) fuming on the identification of unique, microscopic marks within the barrel of a firearm (96). Their findings were that in most cases superglue masks the microscopic marks to a minimal extent but does not interfere with conventional methods of firearms identification. These findings are likely to be applicable to other types of toolmark examinations as well.

Demoli *et al*. proposed an original method for identifying toolmarks based on SEM observations of the striation patterns, combined with an optoelectronic correlator device (97). The method includes acquiring striation patterns as digital image files by using an environmental scanning electron microscope (ESEM), followed by selection and extraction of features from the striation patterns and identifying tools by calculating the correlation measures. This approach relies on transforming the 2D striation patterns to 1D “bar-code” information, by which the starting information is well preserved and the obtained information is robust to deformations and noise.

Physical Match

Physical match, or fracture match, namely linking two or more objects by the morphology of fractured or torn surfaces, is usually viewed as one of the strongest ways for establishing common origin. De Forest recently stated, for instance, that “If the fracture surface is large enough, the detail present may be sufficient to allow a unique association to be demonstrated between the two portions” (98, p. 8). The evidential value of such physical matches, and their admissibility in court, seem to be taken for granted, considering the limited number of articles published in this discipline. Even so, several recent articles were aiming toward the foreseen *Daubert*-type challenges in this field.

Bradley *et al.* used duct tape as the fractured medium, to study the validity and error rate associated with conducting end match (fracture match) examinations on this material (99). Five test designs, which varied either the source roll of tape or manner of separation (torn or cut) from the roll, were administered to four analysts with instructions to examine the assigned test sets for end matches. Results indicated that while tape grade did not hinder end match identification, the manner of separation could affect results.

Tsach *et al*. took a more controlled approach, by using a tensile machine with set force and speed for rupturing homogeneous samples (100). The torn samples were then submitted for examination by several experts. The results obtained showed that, even when rupture is carried out under repetitive conditions, each ruptured sample has a different contour, demonstrating the individuality of the process. Katterwe (101) and Orench (102) also took a similar approach.

In a study by Stone, consideration was given to the formation of two- and three-dimensional fractures formed in brittle metals, and mathematical probability models were derived for the interpretation of fracture evidence (73). This study presents a model that, when validated, may assist examiners to quantify such fractures in casework.

Miller and Kong reviewed the types of fracture patterns described in the literature, and considered the fracture process in metal objects (103). Actual samples were also examined in order to observe the pattern of the external break and the pattern of the internal fracture.

In addition to these research papers, several case reports were also published in this field. Streine describes the use of physical match in a murder case where the victim was dragged alongside a car for some distance (104). Pieces of material from which the wheel well was composed of, broke off and were recovered at the scene. These pieces were submitted to the author's laboratory together with part of a wheel well from the suspect's vehicle. A physical fracture match between the items was confirmed.

Karim reported an atypical pattern-fit identification of two parts of a severed exhaust pipe (105). One of the sections was severed from a vehicle that departed the scene of a murder and was found at the scene. The other section remained attached to the vehicle. After the vehicle was recovered one year later, a pattern-fit identification between the two parts was made.

Restoration of Obliterated Marks

Several articles have been published, regarding methods for the restoration of obliterated marks. Katterwe published a review on methods for serial numbers restoration in vehicles (106). Katterwe suggested a method to restore erased numbers from polymers surfaces using clove powder. Burke *et al.* explored this technique, presenting that clove powder, and especially the active component Eugenol, can be used to restore obliterated numbers from a wide range of polymers (107).

Kuppuswamy and Senthilkumar proposed a procedure for the examination of vehicles involved in forgeries (i.e., vehicles whose engine numbers, chassis numbers or other identifying marks have been obliterated) (108). Several cases, where these procedures were utilized, are presented at this article. The Fry's reagent (a solution of cupric chloride, concentrated hydrochloric acid, and water), was found to be the favourable solution for steel surface, as already reported by others.

In a later article, Azlan Mohd. Zaili *et al.* studied reagents for the restoration of erased numbers on steel surfaces (109). Good results have been obtained by a reagent made of 5 g copper sulphate, 60 ml water, 30 ml concentrated ammonium hydroxide and 60 ml concentrated hydrochloric acid. This reagent restored marks erased to a depth of 0.04 mm below the engraving depth.

Hogan and Smith compared MAPP gas (a stable, high energy fuel made of a mixture of methyl-acetylene-propadien and liquefied petroleum gas) with oxyacetylene in terms of its ability to restore obliterated vehicle identification numbers (110). The results obtained indicate that MAPP has significant benefits in terms of equipment weight and cost.

Malikowski describes a case where digital photography and Adobe Photoshop software were used to enhance and restore a partially obliterated laser-etched barcode on a Smith & Wesson Sigma pistol, enabling the barcode to be scanned and recovered using a barcode reader (111).

Utrata and Johnson studied the conditions that increase the likelihood of successfully applying the magnetic particle method to forensic casework (112). It was found that success depends on the magnitude and the orientation of the magnetic field, the correct nature of the magnetizing current, and an appropriate choice of magnetic particle suspension.

Crowe and Morgan-Smith reported that the metallurgical reagent aqua regia was proved to be effective in recovering an erased jeweller's mark on the inner band of a stolen 18-carat gold-and-diamond ring (113).

Barratt and Smith report a case in which the printed serial number on a tax disc had been partially removed (114). In this case, the obliterated bar code could be restored and manually decoded, allowing the complete recovery of the serial number of the tax disc and the retrieval of the original entries.

References

(1) Wiersma, S. SWGTREAD. *Journal of Forensic Identification*, 2005, 55 (1), 47-48.

(2) SWGTREAD. Scope of work relating to forensic footwear and/or tire treads examiners. Journal of Forensic Identification, 2005, 55 (6), 764-765.

(3) SWGTREAD. Guide for the detection of footwear and tire impressions in the field. *Journal of Forensic Identification*, 2005, 55 (6), 766-769.

(4) SWGTREAD. Guide for the collection of footwear and tire impressions in the field. *Journal of Forensic Identification*, 2005, 55 (6), 770-773.

(5) SWGTREAD. Guide for the detection of footwear and tire impressions in the laboratory. *Journal of Forensic Identification*, 2005, 55 (6), 774-777.

(6) SWGTREAD. Guide for the collection of footwear and tire impressions in the laboratory. *Journal of Forensic Identification*, 55 2005, (6), 778-780.

(7) SWGTREAD. Guide for the preparation of test impressions for footwear and tires. *Journal of Forensic Identification*, 2005, 55 (6), 781-786.

(8) SWGTREAD. Guide for lifting footwear and tire impression evidence. *Journal of Forensic Identification*, 2006, 56 (4), 630-634.

(9) SWGTREAD. Guide for casting footwear and tire impression evidence. *Journal of Forensic Identification*, 2006, 56 (4), 635-641.

(10) SWGTREAD. Guide for minimum qualifications and training for a forensic footwear and/or tire tread examiner. *Journal of Forensic Identification*, 2006. 56 (5), 788-793.

(11) SWGTREAD. Guide for the forensic documentation and photography of footwear and tire impressions at the crime scene. *Journal of Forensic Identification*, 2006, 56 (5), 794-799.

(12) SWGTREAD. Guide for the examination of footwear and tire impression evidence. *Journal of Forensic Identification*, 2006, 56 (5), 800-805.

(13) SWGTREAD. Standard terminology for expressing conclusions of forensic footwear and tire impression examinations. *Journal of Forensic Identification*, 2006, 56 (5), 806-808.

(14) Burrows, J. and Tarling, R. Measuring the impact of forensic science in detecting burglary and autocrime offences. *Science and Justice*, 2004, 44, 217-222.

(15) Rix, B. (2004) The contribution of shoemark data to police intelligence, crime detection and prosecution. *Findings, Home Office, Research, Development and Statistics Directorate* (No. 236).

(16) Shor, Y., Chaikovsky, A. and Tsach, T. The evidential value of distorted and rectified digital images in footwear imprint examination. *Forensic Science International*, 2006, 160 (1), 59-65.

(17) Chung, J. W. Use of Tilt and Shift Lens in Forensic Photography. *Journal of Forensic Identification*, 2006, 56 (1), 6-17.

(18) Buck, U., Albertini, N., Naether, S. and Thali, M. J. (2007) 3D documentation of footwear impressions and tyre tracks in snow with high resolution optical surface scanning. *Forensic Science International*, 2007, In Press.

(19) Bodziak, W. J. and Hammer, L. An evaluation of dental stone, traxtone, and crime-cast. *Journal of Forensic Identification*, 2006, 56 (5), 769-787.

(20) Massey, S. L. Fingertips: Three-dimensional test impressions of footwear using home made play dough. *Identification Canada*, 2007, 30 (1), 19-22.

(21) Wilson, J. D. Casting Tyres with Expandable Polyurethane Foam and Other Materials. *Journal of Forensic Identification*, 2004, 54 (2), 158-169.

(22) Naples, V. L. and Miller, J. S. Making tracks: The forensic analysis of footprints and footwear impressions. *The anatomical record (Part B: New Anat.)*, 2004, 279B, 9-15.

(23) Adair, T. W., Hisey, S. and Tewes, R. Casting snow prints with "Quikrete" Fast setting concrete: An alternative to aerosol wax products. *The Information Bulletin for Shoeprint/Toolmark Examiners*, 2005, 11 (1), 34-40.

(24) Adair, T. W. and Tewes, R. Strengthening sulfur casts with plasti-dip. *The Information Bulletin for Shoeprint/Toolmark Examiners*, 2006, 12 (2), 16-21.

(25) Shor, Y., Tsach, T., Wiesner, S. and Meir, G. Removing interfering contaminations from gelatin lifters. *Journal of Forensic Sciences*, 2005, 50 (6), 1386-1393.

(26) Ford, A. and Baldwin, D. Cleaning the Surface of Gelatine Lifts. *FSS Report*, 2006; No. TN896, 1-8.

(27) Craig, C. L., Hornsby, B. M. and Riles, M. Evaluation and comparison of the electrostatic dust print lifter and the electrostatic detection apparatus on the development of footwear impressions on paper. *Journal of Forensic Sciences*, 2006, 51 (4), 819-826.

(28) Licht, G. and Murano, E. ESDA Effects in Light of Current Discussions. *Journal of the American Society for Questioned Documents*, 2004, 7 (1), 7-48.

(29) Adair, T. W. and Dobersen, M. Lifting Dusty Shoe Impressions from Human Skin: A Review of Experimental Research from Colorado. *Journal of Forensic Identification*, 2005, 56 (3), 333-338.

(30) Adair, T. W. Electrostatic dust lifting on metallic surfaces using automotive window tinting film as a nonconductive barrier. *Journal of Forensic Identification*, 2005, 55 (5), 605-610.

(31) Adair, T. W. and Tewes, R. Lifting Shoe Impressions from Cylindrical Objects: A Simple Method. *The Information Bulletin for Shoeprint/Toolmark Examiners*, 2006, 12 (1), 7-13.

(32) Adair, T. W. Casting two-dimensional bloody shoe prints from concrete, fabric and human skin: A review of several methods with recommendations. *International Association of Bloodstain Pattern Analyst (I.A.B.P.A.) News*, 2005, March, 4-8.

(33) Michaud, A. L. and Brun-Conti L. A method for impregnating Nylon transfer membranes with leucocrystal violet for enhancing and lifting bloody impressions. *Journal of Forensic Sciences*, 2004, 49 (3), 511-516.

(34) Sampson, W. C. and Sampson, K. L. Recovery of latent prints from human skin. *Journal of Forensic Identification*, 2005, 55 (3), 362-385.

(35) Wilgus, G. Latent shoeprint recovery on human skin. *Journal of Forensic Identification*, 2004, 54 (4), 428-432.

(36) Smith, J. Image enhancement and Adobe Photoshop: Using calculations to extract image detail. *Journal of Forensic Identification*, 2007, 57 (4), 493-505.

(37) Berger, C. E. H., de Koeijer, J. A., Glas, W. and Madhuizen, H. T. Color separation in forensic image processing. *Journal of Forensic Sciences*, 2006, 51 (1), 100-102.

(38) Wen, C. Y. and Chen, J. K. Multi-resolution fusion technique and its application to forensic science. *Forensic Science International*, 2004, 140 (2-3), 217-232.

(39) Hamiel, J. S. and Yoshida, J. S. Evaluation and application of polynomial texture mapping in the area of shoe and impression evidence. *Journal of Forensic Identification*, 2007, 57 (3), 414-434.

(40) de Chazal, P., Flynn, J. and Reilly, R. B. (2005) Automated processing of shoeprint image based on the Fourier transform for use in forensic science. *IEEE Transactions on Pattern Analysis and Machine Intelligence (PAMI)*, 2005, 27 (3), 341-350.

(41) Hannigan, T. J., Fleury, L. M., Reilly, R. B., O'Mullane, B. A. & de Chazal, P. Survey of 1276 shoeprint impressions and development of an automatic shoeprint pattern matching facility. *Science and Justice*, 2006, 46 (2), 78-89.

(42) Pavlou, M. and Allinson, N. M. (2006) Automatic extraction and classification of footwear patterns. *Proc. Intelligent Data Engineering and Automated Learning (IDEAL06)*, 2006, Lecture Notes in Computer Science 4224 721-728.

(43) Su, H., Crookes, D. and Bouridane, A. Thresholding of noisy shoeprint images based on pixel context. *Pattern Recognition Letters*, 2007, 28 (2), 301-307.

(44) Su, H., Bouridane, A. and Crookes, D. Image quality measures for hierarchical decomposition of a shoeprint image. *Forensic Science International*, 2006, 163 (1-2), 125-131.

(45) Kainuma, A. Manufacturing variations in a die-cut footwear model. *Journal of Forensic Identification*, 2005, 55 (4), 503-517.

(46) Wyatt, J. M., Duncan, K. and Trimpe, M. A. Aging of shoes and its effect on shoeprint impressions. *Journal of Forensic Identification*, 2005, 55 (2), 181-188.

(47) Adair, T. W., Lemay, J., McDonald, A., Shaw, R. and Tewes, R. The Mount Bierstadt study: An experiment in unique damage formation in footwear. *Journal of Forensic Identification*, 2007, 57 (2), 199-205.

(48) Stone, R. S. Footwear examinations: Mathematical probabilities of theoretical individual characteristics. *Journal of Forensic Identification*, 2006, 56 (4), 577-599.

(49) Katterwe, H. Annual report 2003. *The Information Bulletin for Shoeprint/Toolmark Examiners*, 2004, 10 (1), 8-22.

(50) ENFSI Expert Working Group Marks Conclusion Scale Committee. Conclusion scale for shoeprint and toolmarks examination. *Journal of Forensic Identification*, 2006, 56 (2), 255-280.

(51) Taroni, F. and Biederman, A. (2005) Inadequacies of posterior probabilities for the assessment of scientific evidence. *Law Probability and Risk*, 2005, 4, 89-115.

(52) Biedermann, A., Taroni, F. and Aitken, C. G. G. Letter to the editor - conclusion scale for shoeprint and toolmarks examinations. *Journal of Forensic Identification*, 2006, 56 (5), 685-693.

(53) Kerstholt, J. H., Paashuis, R. & Sjerps, M. Shoe print examinations: Effects of expectation, complexity and experience. *Forensic Science International*, 2007, 165 (1), 30-34.

(54) Black, J. P. An interesting case involving footwear distribution information. *Journal of Forensic Identification*, 2005, 55 (4), 499-502.

(55) Black, J. P. Letter to the editor - an interesting case involving footwear distribution information. *Journal of Forensic Identification*, 2005, 55 (6), 685-686.

(56) Brooks Jr., J. M. Identifying and sharing class characteristics of outsole impressions. *Journal of Forensic Identification*, 2006, 56 (5), 737-743.

(57) Bull, P. A., Morgan, R. M., Dunkerley, S. and Wilson, H. E. Multi-technique comparison of source and primary transfer soil samples: An experimental investigation. A comment. *Science & Justice*, 2004, 44 (3), 173-178.

(58) Bull, P. A., Parker, A. and Morgan, R. M. The forensic analysis of soils and sediment taken from the cast of a footprint. *Forensic Science International*, 2006, 162 (1-3), 6-12.

(59) Bright, J. A. and Petricevic, S. F. Recovery of Trace DNA and Its Application to DNA Profiling of Shoe Insoles. *Forensic Science International*, 2004; 145 (1), 7-12.

(60) Hillier, E., Dixon, P., Stewart, P., Yamashita, B. and Lama, D. Recovery of DNA from Shoes. *Journal of the Canadian Society of Forensic Science*, 2005, 38 (3), 143-150.

(61) Ozden, H., Balci, Y., Demirustu, C., Turgut, A. and Ertugrul, M. Stature and Sex Estimate Using Foot and Shoe Dimensions. *Forensic Science International*, 2005, 147, 181-184.

(62) Park, S., Kim, T., Choi, Y. and Chae, S. Analysis of Two Tyre Marks on the Head and Clothing. *Japanese Journal of Forensic Science and Technology*, 2006, 11 (1), 125-129.

(63) Schwartz, A. A challenge to the admissibility of firearms and toolmark identifications: Amicus brief prepared on behalf of the defendant in United States v. Kain, crim. 03-573-1 (e.D. Pa. 2004). *The Journal of Philosophy, Science and Law*, 2004, 4 (December 7), www.psljournal.com/archives/all/kain.cfm

(64) Schwartz, A. A systemic challenge to the reliability and admissibility of firearms and toolmark identification. Science and Technology Law Review, 2005, 6, 1-42.

(65) Nichols, R. G. The scientific foundations of firearms and tool mark identification – a response to recent challenges. *The CAC News*, 2006 (Second Quarter), 8-27 (available also at www.firearmsid.com).

(66) Nichols, R. G. Defending the scientific foundations of the firearms and tool mark identification discipline: Responding to recent challenges. *Journal of Forensic Sciences*, 2007, 52 (3), 586-594.

(67) Nichols, R. G. Firearm and tool mark identification: The scientific reliability and validity of the AFTE theory of identification discussed within the framework of a study of ten consecutively manufactured extractors. *AFTE Journal*, 2004, 36 (1), 67-88.

(68) Miller, J. and Neel, M. Criteria for identification of toolmarks part III – supporting the conclusion. *AFTE Journal*, 2004, 36 (1), 7-16.

(69) Buckleton, J. S., Nichols, R. G., Triggs, C. and Wevers, G. An exploratory Bayesian model for firearms and tool mark interpretation. *AFTE Journal*, 2005, 37 (4), 352-361.

(70) Deinet, W. and Katterwe, H. Comments on the application of theoretical probability models including Bayes theorem in forensic science relating to firearm and tool marks. *AFTE Journal*, 2007, 39 (1), 4-7.

(71) Collins, E. R. (2005) How "Unique" Are impressed toolmarks? - an empirical study of 20 worn hammer faces. *AFTE Journal*, 2005, 37 (4), 252-395.

(72) Stone, R. S. How unique are impressed toolmarks? *AFTE Journal*, 2003, 35 (4), 376-383.

(73) Stone, R. S. A probabilistic model of fractures in brittle metals. *AFTE Journal*, 2004, 36 (4), 297-301.

(74) Miller, J. & Beach, G. Toolmarks: Examining the possibility of subclass characteristics. *AFTE Journal*, 2005, 37 (4), 296-345.

(75) The AFTE Training and Standardization Committee (editors). Glossary of the Association of Firearms and Toolmark Examiners. 2001, 4th Edition (CD version).

(76) Walsh, K. A. J. and Newton, A. W. N. An investigation into the individualization of chainsaw cuts in wood and the general toolmark identification process. *AFTE Journal*, 2006, 38 (1), 14-40.

(77) Miller, J. An evaluation of the persistence of striated and impressed toolmarks encompassing a ten-year period of tool application, and a summary of forensic research on bolt cutters. *AFTE Journal*, 2006 38 (4), 310-326.

(78) Van Beest, M., Migeot, G. and De Kinder, J. Toolmarks left by heat sealing machines. *AFTE Journal*, 2004, 36 (4), 302-307.

(79) Akao, Y., Kobayashi, K. and Seki, Y. Examination of spur marks found on inkjet-printed documents. *Journal of Forensic Sciences*, 2005, 50 (4), 915-923.

(80) Novoselsky, Y., Tsach, T., Volkov, N. and Shor, Y. Matching Vehicle Parts Using Brush Strokes. *Journal of Forensic identification,* 2005, 55 (5), 624-632.

(81) Tsach, T., Shor, Y., Volkov, N. and Novoselsky. Counterfeit NIS 10 coins in Israel. *Journal of Forensic Identification*, 2005, 55 (4), 433-441.

(82) Kuppuswamy, R. Studies on the formation, temporal evolution and forensic applications of camera "fingerprints ". *Forensic Science International,* 2006; 159 (2-3), 210-217.

(83) Gorn, M. E. and Hamer P. S. The forensic examination of cable ties. *Journal of Forensic Identification*, 2006, 56 (5), 744-755.

(84) Meyers, C. Commentary: Tool marks - "Novel scientific evidence?" (Ramirez revisited). AFTE Journal, 2005, 37 (3), 197-200.

(85) Clow, C. M. Cartilage stabbing with consecutively manufactured knives: A response to Ramirez v. State of Florida. *AFTE Journal*, 2005, 37 (2), 86-116.

(86) Sitiene, R., Varnaite, J. and Zakaras, A. Complex investigation of body and clothing injuries during the identification of the assault instrument. *Forensic Science International*, 2004, 146 (Supplement 1), S59-S60

(87) Alunni-Perret, V., Muller-Bolla, M., Laugier, J.-P., Lupi-Pégurier, L., Bertrand, M.-F., Staccini, P., Bolla, M. and Quatrehomme, G. Scanning electron microscopy analysis of experimental bone hacking trauma. *Journal of Forensic Sciences*, 2005, 50 (4), 796-801.

(88) Ostrowski, S. H. Identification of a toolmark on human skull utilizing cattle blade bones as test medium. *AFTE Journal*, 2006, 38 (4), 348-355.

(89) Causin, V., Marega, C. and Schiavone, S. Cuts and tears on a paper towel: A case report on an unusual examination of damage. *Forensic Science International*, 2005, 148 (2-3), 157-162.

(90) Locke, R. L. Characteristics of knife cuts in tires. *AFTE Journal*, 2006, 38 (1), 56-65.

(91) Abe, T. and Matsuda, J. Needle marks on polypropylene film. *Japanese Journal of Forensic Science and Technology*, 2006, 11 (2), 193-204.

(92) Smith, M. J. and Brickley, M. B. Analysis and interpretation of flint toolmarks found on bones from West Tump Long Barrow, Gloucestershire. *International Journal of Osteoarchaelogy*, 2004, 14, 18-33.

(93) Petraco, N., Petraco, N. D. and Pizzola, P. A. () An ideal material for the preparation of known toolmark test impressions. *Journal of Forensic Sciences*, 2005, 50 (6), 1407-1410.

(94) Dutton, G. LEICA FSC comparison macroscope. *AFTE Journal*, 2004, 36 (4), 256-261.

(95) Schecter, B., Giverts, P., Siso, R. and Finklestein, N. Creating a temporary liquid lens for amplification of toolmarks. *AFTE Journal*, 2005, 37 (4), 362-367.

(96) Bishop, B., Rosati, C., Leas, R., Ennis, M., Lee, J. and Janeksela, V. Does superglue hinder traditional firearms identification? *AFTE Journal*, 2005, 37 (1), 3-7.

(97) Demoli, N., Sariri, K., Stanic, Z., Mastruko, V. and Milat, O. Toolmarks identification using SEM images in an optoelectronic correlator device. *Optik - International Journal for Light and Electron Optics*, 2004, 115 (11-12), 487-492.

(98) De Forest P. R. What is trace evidence? In: Caddy B. (Editor). *Forensic Examination of Glass and Paint*. London, New York: Taylor & Francis, 2001, 1-25.

(99) Bradley, M. J., Keagy, R. L., Lowe, P. C., Rickenbach, M. P., Wright, D. M. and LeBeau, M. A. A Validation study for duct tape end matches. *Journal of*

Forensic Sciences. 2006, 51 (3), 504-508 (Also in: *Forensic Science Communications*, 2007, 9 (3), 1-7, www.fbi.gov/hq/lab/fsc/current/research/2007_07_research01.htm).

(100) Tsach, T., Wiesner, S. and Shor, Y. Empirical proof of physical match: systematic research with tensile machine. *Forensic Science International*, 2007, 166 (1), 77-83.

(101) Katterwe, H. W. Fracture matching and repetitive experiments: A contribution of validation. *AFTE Journal*, 2005, 37 (3), 229-241.

(102) Orench, J. A. A validation study of fracture matching metal specimens failed in tension. *AFTE Journal*, 2005, 37 (2), 142-149.

(103) Miller, J. and Kong, H. Metal fractures: matching and non-matching patterns. *AFTE Journal*, 2006, 38 (2), 133-165.

(104) Streine, K. M. An interesting physical fracture match. *AFTE Journal*, 2007, 39 (1), 68-69.

(105) Karim, G. A pattern-fit identification of severed exhaust tailpipe sections in a homicide case. *AFTE Journal*, 2004, 36 (1), 65-66.

(106) Katterwe, H. Restoration of serial numbers. In: Stauffer, E. and Bonfanti, M. (Eds.) *Forensic investigation of stolen-recovered and other crime-related vehicles*. Academic Press, 2006, 177-206.

(107) Burke, K., Lewis, S. W., Bett, J., Southhurst, T. E., Lim, K. F. and Gutowski, S. J. () Preliminary investigations into using Eugenol to recover erased characters on polymers. *Journal of Forensic Identification*, 2007, 57 (4), 522-529.

(108) Kuppuswamy, R. and Senthilkumar, M. Restoration of vehicle identification numbers. *Journal of Forensic Identification*, 2004, 54 (1) 13-21.

(109) Azlan Mohd. Zaili, M., Kuppuswamy, R. and Harun, H. Restoration of engraved marks on steel surfaces by etching technique. *Forensic Science International*, 2007, 171 (1), 27-32.

(110) Hogan, B. E., Smith, D.R. and Hall, B. R. MAPP gas: An alternative to oxyacetylene. *Journal of Forensic Identification*, 2006, 56 (2), 232-241.

(111) Malikowski, S. G. The Restoration of an obliterated serial number and barcode using digital photography and Adobe Photoshop. *AFTE Journal*, 2004 36 (2), 237-238.

(112) Utrata, D. and Johnson, J. Development of magnetic particle method for forensic recovery of serial numbers. *Review of Quantitative and Non-destructive Evaluation*, 2004, 23, 1438-1444.

(113) Crowe, G. and Morgan-Smith, R. (2005) Restoration of a jeweller's mark in gold jewellery. *AFTE Journal*, 37 (4), 379-381.

(114) Barratt, E. M. and Smith, Y. Examination of an altered bar code on a vehicle tax disc. *Science & Justice*, 2005, 45 (3), 135-139.

FORENSIC GEOLOGY

– A Review: 2004 to 2007 –

Sugita R, MSc [1], Suzuki S, PhD [2] and Katsumata Y, PhD[3]
1) Senior Scientist in Trace Evidence Section
2) Chief of Trace Evidence Section
3) President
National Research Institute of Police Science, Japan

Corresponding author:
Ritusko Sugita
National Research Institute of Police Science
6-3-1 Kashiwanoha, Kashiwa-shi
Chiba 277-0882, Japan

Contents

Introduction

This review of “Forensic geology” includes not only “geological” but also related sciences such as palynology and microscopy since geology is basically an integrated science.

The number of meetings was increased rapidly during this review period. International Workshop on Criminal and Environmental Soil Forensics was held in Perth, Australia in which nineteen presentations were provided (1-19) and networking of forensic geologists was also discussed. Forensic Remote Sensing and Geophysics Conference organized by the EIGG and the Remote Sensing and Photogrammetry Society in 2004 (20-31).Joint Environmental and Industrial Geophysics Group (EIGG) and the Forensic Science Group Meeting was held on the December 2006 with 15 oral and 2 poster presentations (32-47). Many sessions on forensic geology and related sciences have been held as a part of meetings: palynology session in 17th ANZFSS 2004 (48-57), “Forensic Geology: Practical Geologic Experiences that Helped CSI’s” at the 41st Annual Meeting of Northeastern Section of the Geological Society of America (58-68), “Forensic Geoscience: In Practice and in Teaching” session at the Annual Meeting of the Geological Society of America 2006 (69-83). Moreover, the number of presentations in other general meetings such as the annual meetings of the Japanese Association of Forensic Science and Technology has increased. A special issue of Forensic Science International on palynology and books (84, 85) related to forensic geology have also been published.

Analysis of soil

There were many studies on the mineralogical and analytical approach to geological evidence such as soil and mineral grains that employed traditional and newly developed methods.

Microscopy is the most traditional method and continues to be a powerful method. Basic knowledge on the maintenance of light microscopes was discussed by Speir (86). Hietpas (87) explained the differentiation of calcite and dolomite by using dispersion colors. Soil color analysis by using an instrumental method was evaluated by Croft and Pye (88). Marumo and Sugita (89) presented a simple examination of a coarse fraction of soil by microscopic observation. The importance of particles in soil evidence as indices of discrimination was described by Sugita and Marumo (90).

Reports on the usage of a scanning electron microscope (SEM) and an energy dispersive X-ray analyzer (EDX) attached to an SEM were presented by many researchers (91-93). Bull and Morgan (94) observed quartz by using an SEM and classified it according to the grain type and surface texture. This technique provides exclusionary results and is a powerful tool in the forensic interpretation of soil and sediments. Instrumental analysis has been applied for the discrimination and characterization of quartz. Bernet and Bassett (95) analyzed single-quartz-grain SEM-CL to assume the provenance where the grain originally derived from. A new method for the determination of three-dimensional grain shapes was described by Blott et al. (96) by using a nitrogen gas adsorption technique for provenance analysis.

Particle size analysis was another traditional method of soil examination. Pye and

Blott (97), Blott et al. (98), and Blott and Pye (99) examined the use of a laser diffraction method for the particle size analysis of soil evidence; the authors also studied the effect of the shape of particles on the application of the laser device.

Analyses of elements in soil are often used as an indicator of discrimination of soil evidence. The relation between soil types and agricultural use in Japan was examined on fifty seven soil samples by Takeda et al. (100), and the effect of accumulation of uranium derived from long-term fertilizer application in cultivated Andisol in comparison to noncultivated land was investigated by Takeda et al. (101). Sterckman et al. (102) analyzed trace elements in soils developed on sedimentary materials and described the correlation of the elements with the depth, types of sediments, and anthropogenic influence. Cengiz et al. (103) performed an experiment involving sieved and pressed soil samples by using SEM-EDS for discrimination. Jarvis et al. (104) investigated the element variability of small amounts of soil and sediments by inductively coupled plasma (ICP) optical emission spectrometry (OES) and mass spectrometry (MS). Pye and Croft (105) and Pye et al. (106) performed elemental analysis of soil using ICP-OES and ICP-MS to investigate repeatability and reproducibility were closely investigated for forensic soil examination. Sasajima et al. (107) and Sasajima et al. (108) analyzed soil collected from mountains and rivers of a single prefecture to provide basic information for their discrimination. Scheinost et al. (109) examined Sb species in soil samples of six shooting ranges by using EXAFS. It was found that there were only two species of Sb in all the samples although the geology of the sampling sites was varied. Rawlins and Cave (110) examined elemental data obtained by X-ray fluorescence (XRF) spectrometry through statistical comparison and inferred that statistical comparison could be used to help establish provenance when performed according to a strict protocol. Yoshida et al. (111) used synchrotron radiated XRF for forensic soil analysis.

The analysis of the stable isotope ratio in the field of forensic geology is a fairly new method. The application of stable carbon isotope analysis in forensic geology was reported by Croft and Pye (112).

A series of presentations by Naganuma et al. (113-115) and Arikawa et al. (116) clarified that a combination of methods could provide regional information reflecting both the geological and vegetation background; these researchers combined the analysis of magnetic minerals using electron probe microanalysis (EPMA) and the observation of plant opal with a microscope. The mineralogical analysis of weathered biotite for forensic discrimination was investigated by Sugita and Suzuki (117).

Apart from elemental analytical methods, the X-ray diffraction method, thermal analysis, and optical spectroscopy were also studied and applied. By using X-ray diffraction, Ruffell and Wiltshire (118) examined soil samples obtained from tire marks and compared them with soil collected from tire treads. Quantitative and qualitative analyses were performed and the results were compared. Friolo et al. (119) examined the use of thermal analysis for the examination of a crystalline or amorphous phase when the amount of sample was small. By employing Raman and infrared spectroscopy, Kurata (120) performed experiments on synthesized and natural quartz that were relatively large-sized for the nondestructive identification of seal materials.

Organic matters in soil were also studied as indices of soil discrimination. Dawson et al. (121) described the use of plant hydrocarbons in forensic soil characterization. Fiedler et al. (122) characterized soil containing adipocere and suggested that there was a need for additional approaches in forensic research.

The evaluation and interpretation of the results obtained through multitechniques were enthusiastically studied during the review period. Pye et al. (123) compared different methods by using instrumental analyses performed on 18 samples obtained from two sites. They examined both the distinguishing ability of the methods and the number of samples that should be analyzed to ensure the representativeness of the site under study. Rawlins et al. (124) tested independent and collective interpretations of four different methods, including a mineralogical technique, palynology, and organic analysis, performed by experts. The results indicated that collective interpretation was very effective but anthropogenic redistribution of materials may affect the result. Isphording (125) pointed out several problems pertaining to quality assurance, quality control, and statistical interpretation of geochemical data presented in courts. Morgan and Bull (126) presented two case studies in which difficulties in data interpretation arose. Bayesian analysis was applied for fingerprinting sediments and its suitability was discussed by Small et al. (127).

Nocerino et al. (128) emphasized the importance of sampling and subsampling to ensure representativeness. Gilbert and Pulsipher (129) also described the role of sampling designs in the collection of representative data.

Geophysical survey

Many researches have been performed during the review years on geophysical survey. The determination of burial sites is the main purpose of this survey.

The general information and methods were described by Fenning and Donnelly (130). Details of the techniques and progress were also described by Watters and Hunter (131) and Scott and Hunter (132). As already mentioned, the Forensic Remote Sensing and Geophysics Conference was held in London in 2004, which was organized by the EIGG and the Remote Sensing and Photogrammetry Society.

Schultz et al. (133) experimented with a ground-penetrating radar (GPR) to monitor burials of pig cadavers and blank graves under several conditions. Ruffell (134) examined quantitative probe measurements for the search of grave sites. Kalacska and Bell (135) reported an ongoing long-term experiment on detecting clandestine mass graves using remote sensing techniques. Ruffell (136) reported a case in which GPR had been used to search for the IRA Disappeared at a location that was suspected to be a burial site.

Palynology

There was significant development of palynology during the review period. Palynology is a part of geoscience and is very useful in identifying soil types and determining the environment at the scene of a crime by using pollen and spores derived from plants. A special issue of Forensic Science International on forensic palynology was published in 2006. It started with a brief summary of the history and status of palynology as a part of forensic science (Mildenhall et al. (137)) and discussed some important factors to be considered when practicing forensic palynology (138). There were also articles on the current status of forensic palynology in several countries (139, 140), case reports that included criminal and war crime investigations (141–145), examinations to establish a crime pollen calendar for criminal investigations (146).

The preparation of pollen samples for a forensic examination was described by Horrocks (147) and a general description of forensic palynology was also given in a chapter of the book “Forensic Botany” by Milne et al. (18). There were also case reports by Mildenhall (149).

Other biological materials

The application of techniques of molecular biology to soil has slowly but steadily increased the number of reports. Moreno et al. (150) compared the experimental data on microbial communities with elemental analysis by performing ICP-OES with soil samples. The potential for using bacterial DNA for the discrimination of soil was examined by Narihara et al. (151) and Heath and Sunders (152). Kuske et al. (153) reported the result of a survey on four pathogenic bacteria and closely related species in soil and aerosol. They found a large number of *Bacillus cereus* group bacteria in soil, while other pathogenic and related species were very small in number. Attempts to utilize *Bacillus cereus* were also reported by Kikkawa (154).

Edwards et al. (155) examined archaeological ivory from different ages and provenances and with different taphonomic histories by using FT-Raman spectroscopy. The report also discussed the problems faced in matching the results with the standard spectra.

Urban soil, dust analysis, and related matters

Urban soil and roadside sediments are important geological evidence in crime investigations. They have not been considered in detail in traditional geology, but have been investigated by forensic and environmental scientists.

Roadside sediments from urban and local cities in Kyoto, Japan, were examined using X-ray fluorescence analysis for a forensic application (156); a monograph on this topic has also been published in 2005 (157). Aoki et al. (158) studied various methods for the characterization of urban soil. A database of coastal dune sediments, including data on particle size and chemical composition, has been developed for forensic investigations (159).

Studies on environmental investigations have high potential of providing useful information to forensic science. Anagnostopoulou and Day (160) examined lead concentrations in roadside dust from streets, national gardens, and school playgrounds. They revealed that the lead concentrations were reduced as compared to the concentrations seventeen years ago, and they also found a significant difference of concentrations between various types of streets. Heavy metals are often examined due to environmental concerns, and therefore there are many studies on the issue. Zanders (161) revealed that freshly collected road sediment contains a large portion of materials that are finer than 250 m and that the particles in these materials have the highest concentrations of metals. PGE and some other traffic-related elements in roadside soils of Saõ Paulo, Brazil, were examined by Morcelli et al. (162). They concluded that the concentrations of PGE and traffic-related elements were high in the vicinity of traffic. A low ratio of Pb/PGE indicates the use of gasoline that is considerably less unleaded as compared to Europe. There were quite a large number of reports (164–173, for example) in the issue of urban soil examinations that could provide background information in criminal investigations.

The transfer of soil indoors was examined by Hunt et al. (174), and Turner et al. (175) described a standard approach for determining the characteristic composition of common indoor dust by using a polarized microscope.

Case report

Bull et al. (176) introduced a case report in which soil and sediment obtained from a footprint cast were utilized. This analysis showed the advantage of integrating different independent techniques. Stam (177) reported a case of sexual assault/attempted homicide in which soil was significant evidence. Morgan et al. (178) reported the application of geoscientific examination to wildlife crime detection by employing the analyses of soil, sediment, and pollen. Finley (179), Sever (180), and Murray (181) described the usefulness of forensic geology by showing how it has been applied to real case studies.

Miscellaneous

Hanson (182) showed the importance of stratigraphy, which is rarely found in forensic geological papers, in criminal investigations. Cameron (183) described the use of diatoms in forensic science, and Horton et al. (184) examined a quantitative reconstruction technique based on diatom analysis and discussed its application to two drowning cases.

Hills (185) provided a general outline of cement and concrete, which are often subjected to forensic examinations as a part of geological materials.

The application of a geological technique to study bone minerals was mentioned by Trueman (186). Pye (187) also described the application of isotopes and trace elemental analysis to the examination of human bone and teeth for forensic purpose.

References

1. Fitzpatrick R, Raven M, McLaughlin M. Forensic Soil Science: An overview with reference to case investigations and challenges. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 9.
2. Clarke R, Brmner G . The use of heavy mineral analysis to establish the provenance of suspect shellfish. Program and Book of Abstracts of

International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 11.

3. Stam M. Soil as evidence in a Southern California forensic case and the development of a searchable soil profile database. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 12.
4. Raven M, Fitzpatrick R. Overview of x-ray methods and application to forensic soil examinations with case studies. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 13.
5. Verrall M. Mineral identification using the AutoGeoSEM. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 14.
6. Forrester S, Fitzpatrick R, McLaughlin M, Janik L. Mid–Infrared spectroscopy (MIR): Overview of methods for rapid soil analyses in forensic soil examinations. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 15.
7. Tibbett M. Forensic Taphonomy and Decomposition Processes in Gravesoils. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 16.
8. Nobes D. Clay vs Silt vs Sand: Does geophysical surveying of burials work all the time? Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 17.
9. Moffat I, Wallis L, Mill P, Keane B, Woogwer Valley Aboriginal Corporation. Geophysical investigations at the Alleged Woolgar Massacre site, NW Queensland. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 18.
10. Fitzpatrick R, Baker A. Magnetic susceptibility and low altitude aerial photography using a helium balloon: applications to forensic soil examinations. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 19.
11. Nobes D, Bateman L, Butland C, Flintoft M, Geiger F, Lea J et al. From Kaikoura to Kaitorete: Non-invasive geophysical imaging of Maori burial sites. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 21.
12. Zarcinas B, McLaughlin M, Ohmsen G. Case study involving lead and cadmium contamination around a lead smelter. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 22.
13. Scheckel K. Distinguishing, Anthropogenic and Geogenic Impacts of Environmental Contamination. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 23.
14. Andrew A. Isotopes in soils: application to forensic science. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 24.
15. Walker S. Very Wet Soil. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 25.
16. Fitzpatrick R, Baker AKM, Raven M, Rodgers S, Degens B, George R et al. Terrestrial Environmental Forensic Investigation: Case Study of elevated

levels of metals in drains in the WA wheatbelt. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 26.

17. Horswell J, Parkinson R, Macdonald C, Cordiner S, Speir T,Chambers G et al. DNA Fingerprinting Soils - Dirt, Death and DNA. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 27.
18. Waters JM, Chan HJA, Rodgers CDG, Burgoyne L, Catcheside DEA. Profiling and diversity estimations with soil DNA. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 28.
19. Dawson L, Macdonald LM. Identification of crime scene origin through use of soil organic evidence. Program and Book of Abstracts of International Workshop on Criminal and Environmental Soil Forensics 2006; April 8-9: 29.
20. Cheetham P. Geophysics and the locating of clandestine graves - out of its depth? Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
21. Hunter JR, Simpson B. Geophysics in the wider context of forensic search. Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
22. Wilson P, Ruffell A. Searching for the IRA disappeared : ground-penetrating radar survey of cemetery graves, N. Ireland. Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
23. Cheetham P. Review of recent work in forensic geophysics at Bournemouth University Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
24. Graham C, Meneely J. Cyrax Laser Scanning aids Criminal, Built Environment and Archaeological Investigations. Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
25. Smith P, Hunter J, Baber C, Woolley S, Cross J. The integration of Wearable Computer Technology into Forensic Archaeological Practice. Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
26. Challis K, Henderson J. Extending the Remote Sensing Record: Using Declassified Intelligence Satellite Imagery for Landscape Reconstruction in the Middle East. Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
27. Wagstaff B, Dyer D. Bedfordshire Police and Photogrammetry. Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
28. Fowler MJF. Archaeological uses of satellite imagery: lessons for forensic remote sensing. Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
29. Sykes J. Current MOD remote sensing techniques, including photogrammetry for rapid response operations. Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
30. Boyd G. Use of thermal helicopter video transmitted to hand held devices and dogs for criminal tracking, and body searching. Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.

31. Harrison M. Current practice in body search & recovery. Abstract Booklet of Forensic Remote Sensing and Geophysics Conference; 2006; December 16.
32. Pringle JK, Cassella, JP, Middleton H, Rogers D, Summers R, Cassidy N. Multi-disciplinary studies and taught site material on a simulated clandestine grave site. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
33. Hunter J, Reddick A, Sterenberg J. Integrated approach to mass grave detection. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
34. Tempest AL, Cheetham PN. An assessment of geophysical methods for locating animal mass graves and observations pertinant to their use in locating human mass graves. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
35. Smith AS. Geomaterials from Civil to Criminal Law; one small step for the Geoscientist. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
36. Harrison M. Search Methodologies. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
37. McKinley J, Keaney A. Different scales of spatial sampling in forensic investigations: case studies from the macro to micro scale. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
38. Sablock J. Using The Non-Quartzose Components of Local Sands For Forensic Comparison. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
39. Bergslien E, Bush P, Bush M. Application of Field Portable X-ray Fluorescence (FPXRF) Spectrometry in Forensic and Environmental Geology. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
40. Wiltshire P. Diversity, resolution, and scale in forensic palynology and botany. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
41. Riding JB, Rawlins BG, Coley KH. The effect of the habitual wearing of footwear on the pollen content of adherent materials. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
42. Lombardini G. A forensic geologist's experiences in Italy. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
43. Dawson L, Macdonald L. Integration of Soil Fingerprinting Techniques for Forensic Application. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
44. Pirrie D, Power M.QemScan. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.

45. Sugita R. Altered biotite as an index of forensic discrimination of granitic saprolite. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
46. Guedes A, Dória A, Noronha F. Application of micro-Raman spectroscopy in Forensic Geosciences. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
47. Gallego C. Colombian Forensic Science. Programme and Abstracts of Geoscientists at Crime Scenes, Joint EIGG & Forensic Geology Group Meeting 2006 December 20.
48. Wiltshire P. Current Applications Of Environmental Profiling And Forensic Palynology In The United Kingdom. Abstract of the 17th ANZFSS International Symposium on the Forensic Sciences 2004 March 31.
49. Milne L. Use Of Forensic Palynology: The Microscopic World Of Pollen And Spores. Abstract of the 17th ANZFSS International Symposium on the Forensic Sciences 2004 March 31.
50. Munroe R. Window Screens - Forensic Evidence Collectors. Abstract of the 17th ANZFSS International Symposium on the Forensic Sciences 2004 March 31.
51. Ryan S. Copped By Cannabis Pollen: Practical Applications Of Forensic Palynology. Abstract of the 17th ANZFSS International Symposium on the Forensic Sciences 2004 March 31.
52. Mildenhall D.An example of the use of forensic palynology in assessing alibi. Abstract of the 17th ANZFSS International Symposium on the Forensic Sciences 2004 March 31.
53. Gavrilova O. Pollen Diagnostic Characteristics In The Tribe Rinoreae (Violaceae). Abstract of the 17th ANZFSS International Symposium on the Forensic Sciences 2004 March 31.
54. Milne L. Hitchhikers Guide To The Neighborhood. Abstract of the 17th ANZFSS International Symposium on the Forensic Sciences 2004 March 31.
55. Mildenhall D. Forensic Palynology In The United States: An Underused Technique. Abstract of the 17th ANZFSS International Symposium on the Forensic Sciences 2004 March 31.
56. Wiltshire P. Palynology And QEMSCAN: A Powerful Combination For Forensic Investigation. Abstract of the 17th ANZFSS International Symposium on the Forensic Sciences 2004 March 31.
57. Munroe R. Forensic Geology. Abstract of the 17th ANZFSS International Symposium on the Forensic Sciences 2004 March 31.
58. Andrews S, Geology goes to court. Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20–22. Available from: http://gsa.confex.com/gsa/2006NE/finalprogram/abstract_102589.htm
59. Benimoff AI. Forensic geology: using scenes from a popular TV crime series in an introductory geology course. Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20–22. Available from: http://gsa.confex.com/gsa/2006NE/finalprogram/abstract_100716.htm
60. Stephens GC, Starrs JE. Forensic geology: all that remains are the remains . Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20–22.

Available from: http://gsa.confex.com/gsa/2006NE/finalprogram/abstract_99563.htm

61. Caldwell DW. A case of lust in Massachusetts. Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20–22. Available from: http://gsa.confex.com/gsa/ 2006NE/finalprogram/abstract_99055.htm

62. Smith JP, Olsen CR, Gontz AM, Benedict LA, Bopp RF, Pleil JD et al. Conducting environmental forensics in dynamic, highly urbanized estuarine systems: lessons learned from investigating the impact of the world trade center attack on the sediments of New York harbor. Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20–22. Available from: http://gsa.confex.com/gsa/ 2006NE/finalprogram/abstract_100263.htm

63. Gontz AM, Smith JP, Li L, Wallace GT, Olsen CR, Pala F. Hey where did that come from? - a combined geochemcial and geophysical approach to sediment transport dynamics. Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20–22. Available from: http://gsa.confex.com/gsa/2006NE/finalprogram/abstract_100826.htm

64. Horton BP, Boreham S, Hillier C. The development and application of a diatom-based quantitative reconstruction technique in forensic science. Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20–22. Available from: http://gsa.confex.com/gsa/ 2006NE/finalprogram/abstract_99703.htm

65. Snader TV, Kozlowski AL. A breath of life to the dead: applications of three-dimensional impulse ground penetrating radar for the delineation of late 19th - early 20th century unmarked graves in Milton, PA. Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20–22. Available from: http://gsa.confex.com/gsa/ 2006NE/finalprogram/abstract_100268.htm

66. Beem K, Dippold A, Horner J, Snader T, Kozlowski A. A multi-method geophysical approach to locate unmarked graves in Milton, Pennsylvania. Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20–22. Available from: http://gsa.confex.com/gsa/ 2006NE/finalprogram/abstract_100364.htm

67. Bergslien E. X-ray diffraction identification of geologic trace evidence: in the classroom and for the courtroom. Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20–22. Available from: http://gsa.confex.com/gsa/2006NE/finalprogram/abstract_99976.htm

68. Junger EP. Copper, bentonite and brutality. Abstract of 41st Annual Meeting of Northeastern Section of Geological Society of America [Homepage on Internet]; 2006 March 20 22. Available from: http://gsa.confex.com/gsa/ 2006NE/finalprogram/abstract_102585.htm

69. Murray R. Sherlock Holmes To The Present-Progress In Forensic Geology. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_105331.htm

70. Palenik S, Palenik CS. Developing Forensic Investigative Leads Through The Microscopical Examination Of Trace Evidence. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_116541.htm
71. Ruffell A. Novel Ground-Penetrating Radar Applications For Scenes Of Crime Mapping. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_106266.htm
72. Di Maggio RM, Nuccetelli L. Forensic Soil Analyses Applied To The Laura M. Homicide Case. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_111553.htm
73. Horita J, Lavelle M, Riciputi LR, Duckworth DC, Bostick DA, Bürger S et al. Isotopic And Elemental Analysis For The Forensics And Attribution Of Biological Agents. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_114003.htm
74. Bottrell MC. The Forensic Disconnect: Research V Real World. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_114719.htm
75. Bergslien E. XRD And Cremated Human Remains: What Is In This Urn Anyhow ?. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_110907.htm
76. Crelling JC. Teaching Critical Observation With Forensic Geology. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_109509.htm
77. Isphording WC. Outline And Goals For A Contemporary Forensic Geology Course. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_110408.htm
78. Williams TJ. Tools In The Toolbox: Instrumentation In The Forensic Geology Classroom. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_111042.htm
79. Nehru CE. Tell-Tale Sand Grains In Forensic Work. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_108476.htm
80. Bundy ME. Murder (Most Foul!). Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_115612.htm
81. Riding JB, Rawlins BG, Kemp SJ, Hodgkinson EH, Vane CH, Poulton C et al. Establishing The Provenance Of Surface Samples In Forensic Investigations. Abstract of 2006 Annual Meeting of Geological Society of America

[Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_111123.htm

82. Korejwo DA. Forensic Geology At The FBI: Why Does The FBI Need A Geologist? Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_114990.htm
83. Roemmel JS. Comparison Of Environmental And Forensic Geology. Abstract of 2006 Annual Meeting of Geological Society of America [Homepage on Internet]; 2006 October 22–25. Available from: http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_108943.htm
84. Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004.
85. Coyle HM editor. Forensic Botany: principles and applications to criminal casework. Boca Raton: CRC Pres:s 2005.
86. Speir JA,. Cleaning, maintenance and adjustment of the light microscope. Microscope 2006; 54(2): 61-70.
87. Hietpas J. Differentiation of calcite and dolomite using dispersion colors. Microscope 2006; 54(1): 37-41.
88. Croft DJ, Pye K. Colour theory and the evaluation of an instrumental method of measurement using geological samples for forensic applications. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 49-62.
89. Marumo Y, Sugita R. Validity of simple examination on soil coarse particle fraction. Japanese Journal of Forensic Science and Technology 2006; 11(Supplement): 85.
90. Sugita R, Marumo Y. `Unique' particles in soil evidence. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 97-102.
91. Pye K. Forensic examination of rocks, sediments, soils and dusts using scanning electron microscopy and X-ray chemical microanalysis. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 103-121.
92. Pirrie D, Butcher AR, Power MR, Gottlieb P, Miller GL. Rapid quantitative mineral and phase analysis using automated scanning electron microscopy (QemSCAN); potential applications in forensic geoscience. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 123-136.
93. Graham GA, Kearsley AT, Drolshagen G, Mcdonnell JAM, Wright IP, Grady MM. Mineralogy and microanalysis in the determination of cause of impact damage to spacecraft surfaces. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 137-146.
94. Bull PA, Morgan RM. Sediment fingerprints: A forensic technique using quartz sand grains. Science and Justice 2006; 46(2): 107-124.

95. Bernet and Bassett. Provenance analysis by single-grain SEM-CL/optical microscopy. Journal of Sedimentary Research 2005; 75: 492-500.

96. Blott SJ, Al-Dousari AM, Pye K, Saye SE. Three-dimensional characterization of sand grain shape and surface texture using a nitrogen gas adsorption technique. Journal if Sedimentary Research 2004; 74: 156-159.

97. Pye K, Blott SJ. Particle size analysis of sediments, soils and related particulate materials for forensic purposes using laser granulometry. Forensic Science International 2004; 144: 19-27.

98. Blott SJ, Croft DJ, Pye K, Saye SE, Wilson HE. Particle size analysis by laser diffraction. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 63-73.

99. Blott SJ and Pye K.Particle size distribution analysis of sand-sized particles by laser diffraction: an experimental investigation of instrument sensitivity and the effects of particle shape. Sedimentology 2006; 53: 671-685.

100. Takeda A, Kimura K, Yamasaki S. Analysis of 57 elements in Japanese soils, with special reference to soil group and agricultural use. Geoderma 2004; 119: 291-307.

101. Sterckman T, Douay F, Fourrier H, Proix N, Schvartz C. Trace elements in soils developed in sedimentary materials from Norhtern France. Geoderma 2006; 136: 912-929.

102. Takeda A, Takeda H, Takaku Y, Hisamatsu S, Nanzyo M. Accumulation of uranium derived from long-term fertilizer application in a cultivated Andisol. Science of the Total Environment 2006; 367: 924-931.

103. Cengiz S, Karaca AC, Çakır _, Üner HB, Sevindik A. SEM-EDS analysis and discrimination of forensic soil. Forensic Science International 2004; 141: 33-37.

104. Jarvis KE, Wilson HE, James SL. Assessing element variability in small soil samples taken during forensic investigation. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 171-182.

105. Pye K, Blott SJ. Comparison of soils and sediments using major and trace element data. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 183-196.

106. Pye K, Blott SJ, Wray DS. Elemental analysis of soil samples for forensic purposes by inductively coupled plasma spectrometry - precision considerations. Forensic Science International 2006; 160: 178-192.

107. Sasajima Y, Suenami K, Sato K, Takekoshi Y, Kanno S. Discrimination of soil samples of mountains in Gifu by means of multivariate analysis of X-ray fluorescence spectrometry data. Japanese Journal of Science and Technology for Identification 2004; 9(Supplement): 70.

108. Sasajima Y, Suenami K, Sato K, Takekoshi Y, Kanno S. Discrimination of soil samples of rivers in Gifu by means of multivariate analysis of X-ray fluorescence spectrometry data. Japanese Journal of Forensic Science and Technology 2006; 11(Supplement): 87.

109. Scheinost A, Rossberg A, Vantelon D, Xifra I, Kretzshmar R, Leuz A-K, et al. Quantitative antimony speciation in shooting-range soils by EXAFS spectroscopy. Geochimica et Cosmochimica Act 2006; 70: 3299-3312.
110. Rawlins BG, Cave M. Investigating multi-element soil geochemical signatures and their potential for use in forensic studies. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 197-206.
111. Yoshida T, Ishiwata T, Miyata K, Ishizawa F, Suzuki S, Yaita T. Analysis of trace elements in soil samples by SR-XRF and XRF. Japanese Journal of Science and Technology for Identification 2004; 9(Supplement): 71.
112. Croft DJ, Pye K. Stable carbon and nitrogen isotope variations in soils: forensic applications. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 257-267.
113. Naganuma K, Iwamoto M, Arikawa T, Udatsu T, Nagatomo Y. The environmental information for micro-particles in trace samples. Japanese Journal of Science and Technology for Identification 2004; 9(Supplement): 68.
114. Naganuma K, Arikawa T, Iwamoto M, Udatsu T, Nagatomo Y. Extraction of information for criminal investigation in small amount of soil samples (III): Investigation of the effectiveness of some specific particles in identifying the surface geology of Miyazaki Prefecture. Japanese Journal of Forensic Science and Technology 2006; 11(Supplement): 86.
115. Naganuma K, Arikawa T, Iwamoto M, Udatsu T, Nagatomo Y. Studies on extraction of information for criminal investigation in very small amount of soil samples: Significant of information from ferromagnetic minerals. Japanese Journal of Forensic Science and Technology 2005; 10(Supplement): 105.
116. Arikawa T, Naganuma K, Iwamoto M, Udatsu T, Nagatomo Y. Studies on extraction of information for criminal investigation in very small amount of soil samples: Construction of the database for estimation of area in Miyazaki Pref. Japanese Journal of Forensic Science and Technology 2005; 10(Supplement): 126.
117. Sugita R, Suzuki S. Examination of biotite in granitic saprolite for forensic discrimination of soil. Japanese Journal of Forensic Science and Technology 2006; 11(Supplement): 88.
118. Ruffell A, Wiltshire P. Conjunctive use of quantitative and qualitative X-ray diffraction analysis of soils and rocks for forensic analysis. Forensic Science International 2004; 145: 13-23.
119. Friolo KH, Ray AS, Stuart BH, Thomas PS. Thermal analysis of heritage stones. Journal of Thermal Analysis and Calorimetry 2005; 80: 559-563.
120. Kurata S. Nondestructive Identification of Synthetic Quartz Crystal Seals Using Spectroscopy. Japanese Journal of Forensic Science and Technology 2006; 11(2): 205-211.
121. Dawson LA, Towers W, Mayes RW, Craig J, Vaisanen RK, Waterhouse EC. The use of plant hydrocarbon signatures in characterizing soil organic matter. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 269-276.

122. Fiedler S, Schneckenberger K, Graw M. Characterization of soils containing adipocere. Archives of Environmental Contamination and Toxicology 2004; 47: 561-568.
123. Pye K, Blott SJ, Croft DJ, Carter JF. Forensic comparison of soil samples: Assessment of small-scale spatial variability in elemental composition, carbon and nitrogen isotope ratios, colour, and particle size distribution. Forensic Science International 2006; 163: 59-80.
124. Rawlins BG, Kemp SJ, Hodgkinson EH, Riding JB, Vane CH, Poulton C, et al. Potential and pitfalls in establishing the provenance of earth-related samples in forensic investigations. Journal of Forensic Sciences 2006; 51(4): 832-845.
125. Isphording WC. The right way and the wrong way of presenting statistical and geological evidence in a court of law (a little knowledge is a dangerous thing!). In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 281-288.
126. Morgan RM, Bull PA. Data interpretation in forensic sediment and soil geochemistry. Environmental Forensics 2006; 7: 325-334.
127. Small IF, Rowan JS, Franks SW, Wyatt A, Duck RW. Bayesian sediment fingerprinting provides a robust tool for environmental forensic geoscience applications. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 207-213.
128. Nocerino JM, Schumacher BA, Dary CC. Role of laboratory sampling devices and laboratory subsampling methods in representative sampling strategies. Environmental Forensics 2005; 6: 35-44.
129. Gilbert RO, Pulsipher BA. Role of sampling designs in obtaining representative data. Environmental Forensics 2005; 6: 27-33.
130. Fenning PJ, Donnelly LJ. Geophysical techniques for forensic investigation. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 11-20.
131. Watters M, Hunter JR. Geophysics and burials: field experience and software development. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 21-31.
132. Scott J, Hunter JR. Environmental influences on resistivity mapping for the location of clandestine graves. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 33-38.
133. Schultz JJ, Collins ME, Falsetti AB. Sequential monitoring of burials containing large pig cadavers using ground-penetrating radar. Journal of Forensic Sciences 2006; 51(3): 607-616.
134. Ruffell A. Burial location using cheap and reliable quantitative probe measurements. Forensic Science International 2005; 151: 207-211.
135. Kalacska M, Bell LS. Remote sensing as a tool for the detection of clandestine mass graves. Canadian Society of Forensic Science Journal 2006; 39(1): 1-13.

136. Ruffell A. Searching for the IRA "Disappeared": Ground-penetrating radar investigation of a churchyard burial site, Northern Ireland. Journal of Forensic Sicneces 2005; 50: 1430-1435.
137. Mildenhall DC, Wiltshire PEJ, Bryant VM. Forensic Palynology: Why do it and How it works. Forensic Science International 2006; 163: 163-172.
138. Wiltshire PEJ. Consideration of some taphonomic variables of relevance to forensic palynological investigation in the United Kingdom. Forensic Scinece International 2006; 163: 173-182.
139. Bryant VM, Jones GD. Forensic palynology: Current status of a rarely used technique in the United States of America. Forensic Science International 2006; 163: 183-197.
140. Mathewes RW. Forensic palynology in Canada: An overview with emphasis on archaeology and anthropology. Forensic Science International 2006; 163: 198-203.
141. Brown AG. The use of forensic botany and geology in war crimes investigations in NE Bosnia. Forensic Science International 2006; 163: 204-210.
142. Mildenhall DC. An unusual appearance of a common pollen type indicates the scene of the crime. Forensic Science International 2006; 163: 236-240.
143. Wiltshire PEJ. Hair as a source of forensic evidence in murder investigations. Forensic Science International 2006; 163: 241-248.
144. Wiltshire PEJ, Black S. The cribriform approach to the retrieval of palynological evidence from the turbinates of murder victims. Forensic Science International 2006; 163: 224-230.
145. Mildenhall DC. Hypericum pollen determines the presence of burglars at the scene of a crime: An example of forensic palynology. Forensic Scinece International 2006; 163: 231-235.
146. Montali E, Mercuri AM, Grandi GT, Accorsi CA. Towards a "crime pollen calendar" - Pollen analysis on corpses throughout one year. Forensic Science International 2006; 163: 211-223.
147. Horrocks M. Sub-sampling and preparing forensic samples for pollen analysis. Journal of Forensic Sciences 2004; 49(5): 1024-1027.
148. Milne LA, Bryant VM, Mildenhall DC. Forensic Palynology. In: Coyle HM editor. Forensic Botany: principles and applications to criminal casework. Boca Raton: CRC Pres:s 2005. p. 217-252.
149. Mildenhall DC. An example of the use of forensic palynology in assessing alibi. Journal of Forensic Sciences 2004; 49: 312-316.
150. Moreno LI, Mills DK, Entry J, Sautter RT, Mathee K. Microbial metagenome profiling using amplicon length heterogeneity-polymerase chain reaction proves more effective than elemental analysis in discriminating soil specimens. Journal of Forensic Sciences 2006; 51(6): 1315-1322.
151. Narihara M, Nishi E, Nishida K, Tsutsumi K, Ito S, Sakai K et al. An attempt of trace soil discrimination using microbial DNA. Japanese Journal of Forensic Science and Technology 2005; 10(Supplement): 104.
152. Heath LE, Saunders VA. Assessing the potential of bacterial DNA profiling for forensic soil comparisons. Journal of Forensic Sciences 2006; 51(5): 1062-1068.

153. Kuske CR, Barns SM, Grow CC, Merrill L, Dunbar J. Environmental survey for four pathogenic bacteria and closely related species using phylogenetic and functional genes. Journal of Forensic Sciences 2006; 51(3): 548-558.
154. Kikkawa H, Sugita R, Fujinami Y, Yasuda J, Suzuki S. Microbial genotyping of soil samples for forensic discrimination. Japanese Journal of Forensic Science and Technology 2006; 11(Supplement): 89.
155. Edwards HGM. Forensic applications of Raman spectroscopy to the non-destructive analysis of biomaterials and their degradation. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 159-170.
156. Hiraoka Y. Chemical properties of road sediments in urban areas : A case study in Kyoto Prefecture, central Japan. Journal of the Geological Society of Japan 2004; 110(11): 661-670.
157. Hiraoka Y. Assessment for urban environment based on analyses of road sediments -Its applications to Geo-Environments and Forensic Geology. Monograph of The Association for the Geological Collaboration in Japan 2005; 55: pp65.
158. Aoki E, Hokura A, Nakai I. Fundamental research for forensic characterization of soil samples (3). Japanese Journal of Science and Technology for Identification 2004; 9(Supplement): 69.
159. Saye SE, Pye K. Development of a coastal dune sediment database for England and Wales: forensic applications. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 75-96.
160. Anagnostopoulou MA, Day JP. Lead concentrations and isotope ratios in street dust in major cities in Greece in relation to the use of lead in petrol. Science of the Total Environment 2006; 367: 791-799.
161. Zanders JM. Road sediment: characterization and implications for the performance of vegetated strips for treating road run-off. Science of the Total Environment 2005; 339: 41-47.
162. Morcelli CPR, Figueiredo AMG, Sarkis JES, Enzweiler J, Kakazu M, Sigolo JB. PGEs and other traffic-related elements in roadside soils from São Paulo, Brazil. Science of Total Environment 2005; 345: 81-91.
163. Eberel DD. Quantitative mineralogy of the Yukan River system: Changes with reach and season, and determining sediment provenance. American Mineralogist 2004; 89: 1784-1794.
164. Kutle A, Ore__anin V, Obho_a_ J,Valkovi_ V. Trace element distribution in geochemical environment of the island Krk and its influende on the local population. Journal of Radioanalytical and Nuclear Chemistry 2004; 259: 271-276.
165. Li X, Lee S, Wong S, Shi W, Thornton I. The study of metal contamination in urban soils of Hong Kong using a GIS-based approach. Environmental Pollution 2004; 129: 113-124.
166. Marques JJ, Schulze DG., Curi N, Mertzman SA. Trace element geochemistry in Brazilian Cerrado soils. Geoderma 2004; 121: 31-43.
167. Minato S. Uranium, thorium and pottasium concentrations in Japanese soils. Radioisotopes 2005; 54: 509-515.

168. Norra S, Lanka-Panditha M, Kramar U, Stuben D. Mineralogical and geochemical patterns of urban surface soils, the example of Pforzheim, Germany. Applied Geochemistry 2006; 21: 2064-2081.
169. Ohta A, Imai N, Terashima S, Tachibana Y, Ikehara K, Nakajima T. Geochemical mapping in Hokuriku, Japan: influence of surface geology, mineral occurences and mass movement from terristrial to marine environments. Applied Geochemistry 2004; 19: 1453-1469.
170. Rodrigeus S, Pereira ME, Sarabando L, Lopes L, Cachada A, Duarte A. Spatial distribution of total Hg in urban soils from an Atlantic coastal city (Aveiro, Portugal). Science of the Toatl Environmet 2006; 368: 40-46.
171. Sutherland A., Tack FMG, Ziegler AD,Bussen JO. Metal extraction from road-deposited sediments using nine partial decomposition procedures. Applied Geochemistry 2004; 19: 947-955.
172. Ozaki H, Watanabe I, Kuno K. As, Sb and Hg distribution and pollution sources in the roadside soil and dust around Kamikouchi, Chubu Sangaku National Park, Japan. Geochemical Journal 2004; 38: 473-484.
173. Ziadat AH, Batarseh M, El-Hasan T, Berdanie BW, Jiries A. Chemical and mineralogical characteristics of dry deposition in the surrounding of a cement factory in Jordan. Environmental Forensics 2006; 7: 169-174.
174. Hunt A, Johnson DL, Griffith DA. Mass transfer of soil indoors by track-in on footwear. Science of the Total Environment 2006; 370: 360-371.
175. Turner WL, Millette JR, Boltin WR, Hopen TJ. A standard approach to the characterization of common indoor dust constituents. Microscope 2005; 53(4): 169-177.
176. Bull PA, Parker A, Morgan RM. The forensic analysis of soils and sediment taken from the cast of a footprint. Forensic Science International 2006; 162: 6-12.
177. Stam M. Soil as significant evidence in a sexual assault attempted homicide case. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 295-299.
178. Morgan RM, Wiltshire P, Parker A, Bull PA. The role of forensic geoscience in wildlife crime detection. Forensic Science International 2006; 162: 152-162.
179. Finley JA. Geologic materials as physical evidence. FBI Law Enforcement Bulletin 2004; 73(3).
180. Sever M. Murder and mud in the Shenandoah. Geotimes 2005; January:.
181. Murray R. Collecting crime evidence from earth. Geotimes 2005; January:.
182. Hanson ID. The importance of stratigraphy in forensic investigation. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 39-47.
183. Cameron NG. The use of diatom analysis in forensic geoscience. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 277-280.
184. Horton BP, Boreham S, Hillier C. The development and application of a diatom-based quantitative reconstruction technique in forensic science. Journal of Forensic Sciences 2006; 51(3): 643-650.

185. Hills LM. From rocks to skyscrapers: the life of a cement grain. Microscope 2005; 53(2): 89-93.
186. Trueman CN. Forensic geology of bone mineral: geochemical tracers for post-mortem movement of bone remains. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 249-256.
187. Pye K. Isotope and trace element analysis of human teeth and bones for forensic purposes. In: Pye K, Croft DJ editors. Forensic Geocience: Principles, Techniques and Applications. Geological Society Special Publication 232. London: Geological Society; 2004. p. 215-236.

Paint and Glass

– A Review: 2004 to 2007 –

PAINT
Maureen J. Bradley, Ph.D.
Maureen.Bradley@ic.fbi.gov
Andria L. Hobbs, M.S.
Diana M. Wright, Ph.D.

GLASS
Robert D. Koons, Ph.D.
rkoons@fbiacademy.edu
Federal Bureau of Investigation Laboratory
Quantico, Virginia, U.S.A. 22135

Contents

Introduction

This review covers relevant publications in paint and glass since the last review presented at the 14th Interpol Forensic Science Symposium in October 2004. This is the first paint and glass review written by the United States (US) Federal Bureau of Investigation (FBI) Laboratory. Sincere appreciation is expressed to colleagues at the Bundeskriminalamt (BKA) for writing past reviews, which have served as excellent models.

An estimated 1000 articles and presentations with potential interest to the forensic science community concerning the areas of paint and glass have been published since mid-2004. Articles selected and included in this review provide a good representation of the technical fields covered and were deemed to be either of the most importance or of the most interest to paint and glass examiners. There has been considerable change in the distribution of literature among topics since the last report. The distribution of papers among technical topics reflects the level of active research and publication and not the level of importance or frequency of utilization of methods by crime laboratories. For example, there are many papers describing elemental characterization of glass, but few detailing methods for refractive index measurement, although the latter is more frequently used by the forensic community. Similarly, Raman spectroscopy is widely reported on in the literature for the analysis of paint, although, at this time, relatively few forensic laboratories utilize the technique. Also, the number of studies concerning paint and glass analysis in the fields of art and archaeology far exceeds the forensic applications, although these disciplines have much in common. Therefore, art and archaeological applications are included in this review.

Conferences focused on specific topics provide in-depth coverage of their respective fields. Proceedings and abstracts from these conferences may serve as additional resources to determine what techniques are being explored, what studies are being undertaken, and by whom. However, abstracts often contain too little information and do not always capture the totality of the materials presented. Therefore, only a few conference presentations have been included in this review.

This review is divided into two distinct sections, paint and glass, with further subject headings used within each section to assist the reader in delineating pertinent areas of interest.

Paint

Formulations And Technology

Two underlying themes were apparent when reviewing relevant articles in paint and coating trade journals; reduce both cost and the negative impact paint formulations have on the environment. The industry is being directed away from solventborne formulations toward waterborne, high solids, and powder coatings. Paint suppliers are faced with meeting these challenges, while trying to fulfill or exceed customer expectations.

Automotive Paints

Paint application is historically the most expensive and time consuming step in the automobile assembly process and requires the largest energy consumption. Compounded by the push to lower volatile organic compound (VOC) emissions and reduce solventborne formulations, automobile manufacturers' paint suppliers are developing new technologies that are being implemented in assembly plants. Typically, the basecoat and clearcoat are a wet-on-wet application. This means that after the basecoat is applied, it is "flashed off". Lower temperatures and shorter times are used to set the basecoat rather than fully curing it prior to application of the clearcoat. Once the clearcoat is applied, the vehicle is passed through a drying zone or oven to fully cure the top coats. Ford Motor Company's new "Paint Shop of the Future" is being pilot tested at its Ohio assembly plant (1). It consolidates the application of the primer surfacer, basecoat, and clearcoat in a single step (wet-on-wet-on-wet). This eliminates the need for separate applications, spray booths, and ovens. Typically, because they are wet-on-wet applied, basecoats and clearcoats have comparable chemistries. It is not evident from this article whether this will also be the case for the paints applied in a wet-on-wet-on-wet process.

In a 2005 article, Spielman (2) wrote about how increasing environmental regulations have an affect on developments in automotive paint formulations. BASF's SlurryGloss, a solventless clearcoat, is given as an example. CathoGuard500 and Powercron 8000, from BASF and PPG, respectively, are also provided as examples. These are both lead- and chromium-free, low VOC electrocoats. Schoff (3) stated in his 2005 paper that the use of electrodeposition coatings containing lead will be replaced with lead-free versions. He also predicted that wet-on-wet-on-wet applications will become more common in the industry.

Another way to reduce costs is to modify the processes to reduce or eliminate layers while still maintaining quality. In Spielman's 2005 article cited above, BASF's Integrated Process II was mentioned. It is discussed in further detail in Pianoforte's 2007 article (4). Basically, one layer replaces the basecoat and primer surfacer layers. The layer is specially formulated to combine the function of both layers, including stone chip protection and ultraviolet resistance. The new system has been successfully implemented in the Mini production line at the BMW Group's Oxford, UK plant. Since the primer application and oven sections are no longer needed, they have been converted to a second basecoat/clearcoat line to increase production capacity at the plant.

This article also reports on a wet-on-wet two tone process developed by DuPont that was implemented at Ford's Kentucky truck plant. This has increased capacity and lowered production costs. DuPont has also developed EcoConcept, a primerless waterborne top coat system. This system also eliminates an entire step in the paint application process; the basecoat is applied directly to the electrodeposition coat. The system is in place at two Volkswagen (VW) facilities; one of theVW Jetta paint lines in Puebla, Mexico, and in the VW paint shop in Pamplona, Spain.

In 2007, BASF introduced a transparent cathodic electrodeposition coating (5). It differs from conventional electrodeposition coatings in that it is not pigmented. The article did not specify whether or not this product would be used in automotive original equipment manufacture (OEM) production.

Pretreatments

Changes may be in store for surface pretreatment as well. Giles reported that many pretreatment companies have invested huge research dollars to develop a coating that limits the dependence on zinc, a regulated heavy metal (6). Gichuhi et al. (7) discussed how zinc phosphate is a low cost alternative to lead- and hexavalent chromium-based corrosion inhibitors. The article stressed that many health authorities classify zinc, strontium, and barium (excluding barium sulfate) as heavy metals and consequently may be regulated. The focus of the remainder of the paper was the use and performance of organic corrosion inhibitors as viable alternatives.

Laminated Films on Plastics

As an alternative to the way paint is traditionally applied to a vehicle, manufacturers are exploring dry paint films (8, 9). Paint films are laminated and applied to plastic substrates such as thermoplastic olefins (TPO), acrylonitrile-butadiene-styrene copolymers (ABS), and polycarbonate (PC). In a 2006 article, Chouinard (8) elaborated on how the films are manufactured and stated that current paint chemistries are not used to make the laminated films. In contrast to a traditional painting operation, the films start with the clearcoat being cast on a heat stabilized polyester carrier. The colorcoat can then be applied in a second pass as a wet-on-wet application. An appropriate adhesive or “primer” allows the laminated film to then be applied to the plastic part. The thermoplastic nature of the film provides significant improvement in chip resistance and allows it to conform to any shape. Soliant, a manufacturer of exterior durable films, estimated that between 2001 and 2006, over 40 million exterior automotive components have been surfaced with dry paint film with explosive growth expected over the next three to five years. Current applications include, but are not limited to, rocker panels, fascias, body side moldings, grilles, and bezels. Acura, Audi, Chrysler, Ford, General Motors, Honda, Mercedes, Saab, Toyota, and Volvo are cited as currently using this technology.

In Whitfield’s article (9), the SMART roadster is noted as creating momentum in the marketplace. It has a filmed plastic roof which demonstrates this technology can be used to create larger body parts. The advantage of plastic over traditional steel is that it is half the weight and can be molded into shapes that defy a stamping press, translating into better fuel economy and more aggressive exterior styling and curves to differentiate product lines.

Pigments and Additives

In a 2006 article on pigments, Challener (10) reported that the largest application for pigments is in paints and coatings, followed by inks. Wright (11) corroborated this statement in a 2007 article summarizing metallic pigments. The article stated that the highest demand for aluminum pigments continues to be the automotive industry for use in paints, plastics, and wheel rims. The 'liquid metal' effect can be produced by utilizing vacuum metallized aluminum flake. Vacuum metallized pigments (VMP) are produced by deposition of vaporized metal, in this case aluminum, onto a smooth surface. The thin layer is then stripped from the surface and broken down into particles of suitable size for their use as a pigment in surface coatings. Unlike conventional aluminum flake, the resulting flakes are extremely smooth resulting in a mirror-like finish. Venturini et al. stated in their US patent (12) that the VM aluminum flakes are on the order of one tenth the thickness (0.01 m – 0.05 m) of conventional aluminum flake (0.1 m – 0.5 m). Both Venturini et al. as well as Yates and Mitchell (13) discussed that the use of VMP aluminum pigments at lower loads than conventional aluminum flake resulted in films with higher reflectivity and higher opacity. Yates and Mitchell went on to report that this type of pigment is currently used on Giant bicycles. Pianoforte's 2007 article (14) on high performance pigments reported that Mercedes is the first car manufacturer to utilize the liquid metal effect in a waterborne paint system.

Traditionally, aluminum pigment manufacturers supplied their product in the form of a paste containing 60-80% pigment in a mixture of hydrocarbon solvents. However, in order for it to be compatible with new paint formulations, modifications including application of a surface treatment, dispersement of the pigment in a resin rather than a solvent, and silica encapsulation needed to be made (15,16). The type of modification depends on whether the formulation is waterborne, high solids, or a powder coating.

A pigment available from EMD chemicals that will find its widest application in automotive and other OEM coatings is Xirallic® crystal effect pigment. These pigments are based on aluminum oxide platelets coated with metal oxides. They provide more glitter effect and stronger color saturation than traditional effect pigments (10). New pigments available from Ciba and BASF include reflective, opaque organic reds, and transparent oranges and blues. Huebach also introduced Tico™ and Bitan products, which combine properties of different pigment chemistries such as hiding power and color. Brussaard and Genn stated that using a Tico™ (titanium color pigment) as opposed to blending titanium dioxide (TiO_2) with colored organic pigments resulted in less pigment loads with more vibrant colors achieved (17). Heubach also introduced a yellow azo pigment that is designed for polymer applications. It has a temperature resistance of 320°C. The company has also introduced a green shade of bismuth vanadate for use in industrial and automobile coatings.

Another product available from Heubach is micronized rutile yellow (18). It was reported that when used in place of conventional high-performance TiO_2, less organic pigment load is necessary. In addition to saving costs on both organic pigments and TiO_2, higher hiding power and better weatherability were achieved in the cured films.

As reported by Wilker (19), a new yellow organic pigment, Hostaperm Yellow H5G (Pigment Yellow 213), has been accepted by all major automotive OEM paint manufacturers and can be used in waterborne and high solids formulations.

Traditionally, aluminum flake of the cornflake type has been used as the substrate for effect pigments. In a 2004 article, Schmid and Mronga (20) reported that BASF was working on a new generation of effect pigments by coating aluminum flakes of the silver dollar type with iron oxide. The resulting golden, orange, and red pigments produced high chroma, hiding power, and sparkling effects. They went on to report on the development of iron oxide plates; effects such as opacity, color, and level of sparkle can be altered by varying the thickness of the resulting flakes.

An excellent overview of diffractive pigment technology was provided in Parker's article (21). It included theory, definitions, compositions, and photomicrographs depicting the grating structure present on their surface.

A US patent issued in 2005 covers novel black pigments that are prepared by mixing carbon black with particular organic pigment intermediates and pigment derivatives (22). The resulting black pigments are suitable for use in paints and inks and produce a deep color characteristic that cannot be achieved with carbon black alone.

BASF launched Near Infrared (NIR)-transparent black pigments in 2006 (23). These pigments have been designed to reduce the solar heat buildup of dark-colored or black-colored construction elements by up to one-half. Aside from their use in construction, potential applications for these pigments include the coatings and printing inks industries. A similar product is reported on by Hope (24); specially engineered additives, termed Total Solar Reflectance (TSR) technology, keep painted and coated surfaces cool by reflecting infrared energy leading to lower energy costs and increased life of the substrate. These additives can be integrated into current product lines for industrial maintenance coatings and coatings applied to wood, automobiles, and concrete.

Recent developments in nanotechnology have enabled paint formulators to create more advanced coatings. So called "smart" architectural coatings have been developed that use nanosized particles of TiO_2 to trigger photo catalytic activity that reduces air pollution (25,26). Nitrogen oxide gas permeates the paint and is converted to nitric acid when exposed to sunlight. It is then neutralized and washed away with rain. Researchers at PPG applied for two patents in 2003 in which they utilized aluminum silicate nanoparticles in their automotive coatings to achieve better chip and scratch resistance (27). In addition, Nanophase Technologies Corp. has developed two grades of alumina nanoparticles that can improve scratch resistance significantly (28).

The addition of hollow glass microspheres as an extender in a paint or coating can improve the paint's properties, cut down on the VOCs and decrease the amount of TiO_2 needed (29). Due to their size (18-30 m) and shape, they reduce the coating's viscosity, which was generally controlled by the addition of solvent. They also impart some opacity to the paint thereby reducing the amount of TiO_2 needed. Research conducted by Shinkareva and Safonova demonstrated that metallized hollow microspheres, made possible by advances in plasma technology, can be incorporated into coatings to serve as conductive and heat insulating fillers (30).

A number of new ultraviolet (UV) absorbers [hindered amine light stabilizers (HALs)] that meet the continually stringent demands of coating formulators are reported by Rogers (31). Advantages achieved by using these new UV absorbers included their non-migratory nature, compatibility with waterborne formulations, and improved UV-resistance at thinner coating thicknesses.

Formulators use smectite clays, such as Bentonite, in coatings to develop certain rheological and performance properties. In his article, Bradford discussed the synthesis of a new grade of smectite clay, and its utility as both a thickener and to control metal flake orientation in automotive paint formulations (32).

Microspheres, HALs, and smectite clays are just three of the classes of additives defined in Paint and Coatings Industry's Additives Guide (33). Updated and published annually, this guide is an excellent resource. It includes definitions and examples of various additives in a format that is easily understood regardless of the readers' paint experience.

Automotive Color Popularity

Silver continued to be the top automotive color choice globally over the last three years. White/white pearl and black were among the top three, while blue, red and light metallic neutrals (shades of beige, champagne, gold, and copper) jockeyed for fourth and fifth position (34-37). Color designers and forecasters from DuPont, PPG, and BASF all report that brighter, more vibrant colors such as red and blue are expected to grow in popularity within the next three to five years. They also report on the new colors being offered that infuse color, such as blue and red, or other metallics like copper and gold, to silver to add diversity to this popular color choice. Developing new colors is not the only way paint companies alter or enhance their products. As previously reported, specialty formulated pigments can provide a 'liquid metal' effect (14). In contrast, BASF Coatings introduced a matte clearcoat which provides a satin-finish to the surface (37).

Marine and Maintenance Coatings

Although not encountered frequently in case work, the forensic scientist should be aware of changes occurring in marine and industrial maintenance coatings. Anti-fouling paints are applied to structures and areas of a vessel that are submerged in water. These paints are designed to release a biocide to kill organisms before they become permanently attached to the surface. If left untreated, fouling organisms such as algae, barnacles, and mussels attach to the surface thereby affecting the weight and fuel efficiency of the vessel.

Concerns, regulations, and legislation regarding the environment do not only affect paint suppliers to the automotive and architectural markets. A resolution adopted by the International Maritime Organization (IMO) in 1999 banned the application of tributyl-tin (TBT) paints on all vessels by 2003. This treaty also called for the elimination or effective containment of organo-tin compounds from all ships' hulls by January 2008 (38, 39). Therefore, most global antifouling paint suppliers discontinued paint products containing TBT between 2003 and 2005. Most antifouling paints used today are copper-based. However, they may face the same future as their tin-based predecessors. In two separate citations (39, 40), the authors reported that dissolved copper levels in the water collected close to boatyards and marinas exceeded both state and federal allowable levels.

International Paint's marine and protective coatings unit has developed a silicone-based foul release coating. This product does not use biocides but rather relies on the slippery, low friction surface to which fouling organisms have difficulty adhering. They also introduced a fluoropolymer coating in February 2007, which had been applied to 20 vessels as of May 2007 (38). Other technologies being explored are silica encapsulation of the copper biocide (41) and the use of natural materials such as algae and tubeworms (42).

In a 2004 estimate, over $1.5 billion/year was spent on maintenance marine and industrial maintenance coatings (43). Approximately 80% of industrial maintenance paints applied to steel and concrete structures are solventborne, with epoxy, polyurethane, and alkyds being the most predominant resins. Regulatory pressures will continue to move industrial coatings toward waterborne, high solids solventborne, and other technologies that comply with recent standards. Procopio, et al. (44) reported on an acrylic latex formulation developed for industrial maintenance use. Based on the results presented, the specially- engineered polymer developed showed promise in this application. Borst and his colleagues (43) reported on the use of epoxy-functional silicone resins as a suitable replacement for polyurethanes. Their findings are reinforced in Kukachova's paper (45) where it was reported that rather than the traditional application of an epoxy layer followed by a polyurethane topcoat, these two layers can be replaced by one epoxy-silane coating. This resulted in significant cost savings and increased corrosion- and UV-resistance.

Paint Analysis In Art And Archaeology

As was reported in the last review of paint literature that was compiled for the Interpol Forensic Science Symposium in 2004, over 50 articles concerning art and archaeological materials analysis were found in the relevant scientific literature. A two part series of articles written by Skelton in 2004 describe the history of pigments used in the Western art world from prehistoric times through modern day (46, 47). These publications provide context for both inorganic and organic pigment development and usage and collectively include over 400 citations.

Adriaens compiled a good overview of European research conducted in the first half of this decade for non-destructive analysis of art and archaeological artifacts (48). Van Grieken and Janssens also edited a book entitled *Cultural Heritage Conservation and Environmental Impact Assessment by Non-Destructive Testing and Micro-Analysis* (49), which covers a broad range of art conservation methods and technique. Paint, as well as glass, bronze, gold, and marble, are featured surfaces discussed in the chapters of this book.

Much of the remaining published literature is specific to a given work of art or type of analysis. In general, these articles provide a good foundation for the continuing use and prevalence of non-destructive techniques in disciplines similar to forensics. Consideration of these methods may no longer be beyond the scope or resources of forensic laboratories. Therefore, the applications of the analytical methods presented herein may be applicable to objects known as “evidence” as well as those termed “artifacts.”

The following table lists a wide range of techniques described for the analysis of pigments, binders, and resins in historical art works and archaeological artifacts. The relevant citations are also provided for easy reference.

Technique	Number of citations	Citations
Pigments		
Raman Spectroscopy	23	(50-72)
Energy Dispersive X-ray Fluorescence (EDXRF)	14	(51, 73-85)
Scanning Electron Microscopy with Energy Dispersive ray Spectroscopy (SEM/EDS)	14	(53, 56, 65, 82, 83, 86-94)
Infrared (IR) Spectroscopy	8	(70, 81, 83, 84, 86, 87, 89, 93)
Particle (or Proton) Induced X-ray Emission (PIXE)	5	(65, 66, 84, 95, 96)
Laser Ablation – Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)	2	(77, 97)
Pyrolysis – Gas Chromatography/Mass Spectrometry GC/MS)	2	(100, 113)
X-ray Diffraction (XRD)	2	(77, 93)
Chemical Testing	1	(53)
Fiber Optic Diffuse Reflectance Spectroscopy	1	(98)
High Resolution Electron Microscopy	1	(71)
Laser Induced Breakdown Spectroscopy (LIBS)	1	(99)
Light Microscopy	1	(91)
Neutron Activation Analysis (NAA)	1	(65)
Polarized Light Microscopy (PLM)	1	(53)
Secondary Ion Mass Spectrometry (SIMS)	1	(91)
Total Reflection X-ray Fluorescence (TXRF)	1	(74)
X-ray Photoelectron Microscopy	1	(101)
Binders		
GC/MS	5	(102-106)
IR Spectroscopy	5	(65, 70, 107-109)
Secondary Ion Mass Spectrometry (SIMS)	2	(91, 110)
Thermally Assisted Hydrolysis and Methylation (THM) GC/MS	2	(107, 108)
Direct Temperature Resolved Mass Spectrometry (DT	1	(90)
Electrochemical Impedance Spectroscopy (EIS)	1	(73)
High Performance Liquid Chromatography (HPLC) wi Fluorescence	1	(106)
Nanotechnology	1	(111)
Nuclear Magnetic Resonance (NMR)	1	(112)
Raman Spectroscopy	1	(72)
Size Exclusion Chromatography (SEC)-FTIR	1	(109)
XRF	1	(79)
Resins		
GC/MS	6	(103-105, 114-116)
Py-GC/MS	4	(92, 100, 113, 114)
Capillary Electrophoresis (CE)	1	(117)
Matrix Assisted Laser Desorption Ionization Time of F (MALDI-TOF)-MS	1	(118)

In addition to these individual discussions of science applied to art conservation and restoration, Schnell et al. published a chapter in Volume 100 of *Lasers in the Conservation of Artwork* describing analytical testing using such techniques as environmental SEM (ESEM), XRD, FTIR and NMR to determine the energies at which pigments were discolored by exposure to lasers during cleaning techniques (119). In this work, inorganic pigments and organic binding media were tested using laser irradiation set at 1064 nm.

Kendix and colleagues applied micro-Raman spectroscopy to embedded cross sections of architectural paints in an examination of the interior decoration of a historical building (120). When complemented by SEM/EDS analysis of the same samples, both the elemental distribution and the molecular structures of the pigments used were able to be discerned. In a separate study of historic architectural design using Raman spectroscopy, Castro et al. presented an overview of the use of FTIR and Raman in the analysis of nineteenth century wallpaper (54). The combination of vibrational techniques allowed for the evaluation of the pigments, binders, and degradation of the cellulose substrates. The authors noted that the wallpaper industry was a reflection of the prosperity of the era and as such depicted a timeline for the introduction of new pigments into society in the same way other craft-oriented objects would. Both antique (carbon back and red oxides) and more modern (synthesized) pigments such as copper-arsenic and ultramarine blue were able to be characterized in this study.

Castro and collaborators also published a 2005 paper regarding development of spectral databases for cataloguing and searching fine art pigments using both dispersive Raman and FT-Raman spectroscopy (55). Both sets of data are loaded into an e-vibrational spectroscopic database (e-VISART), which contains spectra, pigment names in multiple languages with chemical compositions, reference numbers, period or year of first use, compatibility with other pigments or media, and applications. The user can also obtain access to previously reported FTIR data at this site as well. The databases can be accessed via the internet using the website address as follows: http://www.ehu.es/udps/database/database.html. The login for the site is: spectra. The password is: database. Both dispersive and FT-Raman spectra were collected to offset problems from fluorescence encountered with the 785 nm laser employed for the dispersive Raman data collection. FT-Raman measurements obtained for pigments such as kaolin were made possible using a 1064 nm laser excitation source.

Edwards and Chalmers edited a text in 2005 regarding the use of Raman spectroscopy in archaeology and art history (58). This book, which was favorably reviewed by Ariese in 2005, contains 25 chapters that have been authored by over forty scientists (121). It covers basic theory, the usefulness of Raman spectroscopy in the fields of art and archaeology, the comparison of Raman to other microscopic and spectroscopic techniques, and the core chapters of the book, which are divided into four application areas. There is a section dedicated to dyes and pigments, which includes a case study by Bersani, Lottici, and Casoli of frescoes analyzed by micro-Raman and GC/MS and another section by Withnall, Shadi, and Chowdhry on the analysis of dyes by surface enhanced resonance Raman spectroscopy (SERRS). Chapters in the third section are devoted to analysis of artifacts. An overview by Vandenabeele and Edwards as well as the case study of museum objects by Burgio seem most relevant to topics discussed herein.

Other specific applications of Raman spectroscopy for the analysis of regional pigment use were documented by Wang et al. (71) for an ancient Chinese tomb, by Ambers (50) for Egyptian objects and paintings dated between 2600 to 2300 BC, and Hernanz et al. (62) on Spanish prehistoric rock paintings. Chen et al. (57) also published research regarding the application of a surface enhanced Raman scattering (SERS) technique for the characterization of anthraquinone dyes used in artwork. This latter study determined that a 50 nm layer of silver nanoparticles coated on an alumina substrate could detect alizarin dye at about 7×10^{-15} femtograms. The concept was effectively tested when alizarin was identified in a solution extracted from a silk textile known to have been dyed with an alizarin-containing compound.

Vandenabeele and coauthors published multiple articles in recent years on the use of a mobile fiber optic based Raman instrument capable of in situ analysis of museum artifacts (52, 67-69). One of these studies demonstrated the ability to characterize an indigo pigment not previously associated with Bronze Age Greek painted plaster (67). Another describes the instrument design and capabilities in detail, including the use of a portable computer for ease of transport and a fiber optic probe in conjunction with a variety of positioning tools and stages to best effect focus and sample-to-instrument distancing.

The 2005 and 2007 papers by Vandenabeele's group (68, 69) describe the practical challenges associated with in situ analysis of artifacts in their display setting or a conservation laboratory. In the former, research can be conducted without gratuitous handling or movement of the object or painting. However, museum visitors' safety and curiosity become factors for consideration in addition to the positioning of the fiber optic probe in relation to the object's surface. For example, in the analysis of a painting, the angle of the probe had to be adjusted in accordance with the angle at which the art had been hung. The display angle had been chosen to maximize the viewing experience and minimize aesthetic and destructive effects of the room's lighting conditions. The authors report that manipulation of the versatile probe design allowed for effective, non-invasive analysis despite this situation. Analysis in the conservation laboratory proved challenging as well, due in part to the excessive ambient lighting conditions which tended to overwhelm the background signal.

Similar work was also reported by Andrikopoulos et al. (51). However, this study utilized an instrument capable of both Raman and XRF analyses. Data was collected from the same spots on the painting in order to provide complementary information for pigment elucidation, even in areas where over-painting had been introduced to the original artwork.

In addition to the aforementioned text, Edwards and colleagues also published about specific uses of Raman spectroscopy in art characterization and authentication (59, 60, 63, 64). Of note, Edwards, Wolstenholme, and others report on their use of Raman spectroscopy to characterize pigments used in black, blue, gray, green, red, and white paints associated with a noted church architect, Sir Ninian Comper (59). This work determined the chemical composition of the pigments used to create colors known as *Comper red* and *Comper green*, which had not previously been reported in the scientific literature. For the characteristic strawberry red color of the former, a mixture of vermilion, hematite, and barytes were used. The dark green *Comper green* effect was achieved by the combination of Prussian blue with chrome yellow, also known as lead (II) chromate.

Edwards also co-authored two papers that call into question the use of titanium, particularly anatase, as an indicator of modernity in artworks purported to be of ancient design and construction (60, 64). Raman spectroscopy identified the presence of anatase in Roman pottery that predates known uses of titanium dioxide as a whitening pigment. While the amounts are small enough to be considered a natural but not deliberate addition to kaolinitic clay, the authors state that its presence cannot be disputed. The second paper by Edwards on this topic yields findings that the authors state are strongly indicative of anatase as a pigment in Europe approximately two thousand years ago. They further suggest that its presence cannot be attributed to impurities within the raw materials used in construction or sedimentary accumulation on the artifact after its burial.

Weis, Jiang, and Grant published a paper on the use of second derivative preprocessing of Raman spectra in order to diminish interference from fluorescence (72). Partial least squares regression algorithms were applied to pigment libraries as well as to the analysis of oils commonly used as binding media (linseed, walnut, and poppyseed oils). The findings led the authors of the study to conclude that this approach can identify pure pigments, pigments present in dilute quantities in binding media, and fatty acids of similar chemical compositions.

An NMR publication (112) described analysis as applied to the study of aged binding media used in paintings. The study was carried out in attempt to determine the amount of degradation of aged binders and to verify the ability of NMR to differentiate binding media. Stated advantages of NMR include speed, simplicity, non-destructiveness, and minimal sample preparation. Through NMR the state of hydrolysis and oxidation of linseed and egg tempera binders was successfully established. Further, the copolymer composition of acrylic media was determined and the presence of various additives included in their formulation was established.

The use of multiple techniques in the analysis and restoration efforts being pursued in conservation research is highlighted in separate articles by Pavlidou, Higgitt, and others (53, 65, 83, 89). Pavilodou et al. (83) described micro-FTIR, optical microscopy, TXRF, and SEM/EDS in the analysis of paint samples from wall paintings in churches throughout Albania and Greece which have been attributed to the artist Onoufrios. Pigments such as red and yellow ochre, carbon black, green earth, and calcium carbonate were used in all of the churches from which samples were taken. Deterioration, both from environmental air pollution and lichens, is also noted in the article.

In Higgitt's paper, it is reported that paintings at the United Kingdom's National Gallery are developing small white inclusions on the surfaces of paintings of different types and from different periods (89). The common denominator in these works has been identified as the use of two lead-based pigments, namely red lead

(Pb_3O_4) and lead-tin yellow ($PbSnO_4$). Analysis of these inclusions was conducted using SEM/EDS and FTIR. Further work indicated that zinc-based pigments also result in the same type of small white inclusions, which have been identified as metal carboxylates that form as a result of reaction between these metal-based pigments and drying oils in the paint formulations. However, these inclusions seem to be self-contained such that the marks have not been observed to get progressively larger or more prevalent with time. Ortega-Avilés and colleagues discuss attempts to date and authenticate an unsigned Mexican painting through pigment analysis (65). Their work concluded that the painting in question was created in the mid-18th century or early decades of the 19th century.

SEM/EDS was also used by Haswell and colleagues to quantitatively analyze extender pigments used in oil paintings as a means of determining the extent to which priming of the canvas influenced the quality of the actual paints used (88). This research is a preliminary step in analysis of Van Gogh's work that is being conducted in the Netherlands. SEM/EDS initially was used to determine that lead white mixtures were typical with chalk, barium sulfate, gypsum, and clay as bulking agents. This research sought to examine the capability of SEM/EDS to determine quantities of these components within the mixtures. The authors concluded that relative amounts of pigment and extenders in canvas preparation layers could be determined with a relative accuracy of 10% or less. This analysis has significance for authenticity and dating studies of artwork. It also allows conservationists and art historians to construct reference samples for the investigation of artistic painting techniques.

White et al. (94) used an ESEM for in situ hydration studies of pigment discoloration processes caused by the interaction of cadmium yellow (CdS) with malachite ($CuCO_3\_Cu(OH)_2$). The commingling was visually observed to produce either a dark-colored interface between the two pigments or an overall darkening of a mixed pigment layer. Moisture seemed to hasten this process, giving rise to the concept of studying the reaction using ESEM. These researchers determined that copper sulfide resulted from the cadmium sulfide and copper-based pigment interaction. The process is thought to occur when copper ions from the malachite pigment diffuse into the cadmium yellow pigment layer when in the presence of linseed oil and water. The reaction occurs at the interacting surface to produce copper sulfide, the darker layer observed at the interface between the colored pigments.

SEM/EDS was one of many techniques used by van Loon and Boon in characterization of degradation products observed in 17th-century Dutch paintings located in the central hall of The Hague (93). Areas of paintings known to contain pigments used to impart a black or dark brown color were observed to contain whitened "crust-like" surfaces on top of the original painted layer. This phenomenon was previously thought to have only appeared on frescoes. Cross-sections of the affected areas were sampled and compared to "healthy" areas of the same surface. Visible, UV-fluorescence, SEM/EDS, and specular reflectance FTIR were all used to then image the samples being compared. Transmission FTIR and XRD were also used to analyze the white material. Imaging of the layered paint surfaces revealed that the canvas pre-treatment was undertaken with an oil-based lead carbonate

($2PbCO_3\_Pb(OH)_2$) ground that included brown umber particulates, an earth pigment comprised of hydrated iron oxide, and manganese dioxide. The next layer was light-brown and semi-transparent, containing white, red earth, and brown pigments. It served as a primer for the regions where dark hair was depicted in the painting. The topmost layer of dark brown or black paint was quite thick in relation to the underlayers and was composed primarily of bone black pigment with very little red earth. DTMS was used to determine that the binder for this layer was linseed oil.

UV fluorescence imaging also provided information as to the true depth of the white degradation product. In addition to being a thin layer on the top of the surface, it was observed within some regions of the bone black layer. SEM/EDS confirmed the presence of calcium (Ca), phosphorous (P), carbon (C), and oxygen (O), as well as some lead (Pb) and magnesium (Mg) in the "healthy" and white degraded areas of the painting's dark brown/black surface layer. The bone black pigment is an aromatic matrix containing charred bone fragments which impart color and composition via calcium phosphates and carbon black. The bone as a starting material also results in a small amount of magnesium, roughly an atomic mass ratio of 1:18 with respect to calcium. The lead is thought to be present as a result of lead driers used to absorb the oil within their porous structure and decrease the drying time of black pigments, which as anti-oxidants can slow down the drying process of oils. This finding for the lead use was confirmed with DTMS.

SEM/EDS in conjunction with FTIR and XRD analyses of the inorganic species within the topmost layer do not support the notion that changes to the calcium phosphate composition were the cause of the color change observed for the dark brown/black regions of the painting. While the calcium and phosphorous were evenly distributed throughout the topmost layer, the lead and carbon were not. SEM/EDS revealed that the carbon was slightly less at the surface and the lead more concentrated there. The observed lead intensities correspond to the white areas on the surface as well as in cracks within this topmost layer. FTIR also noted that phosphate was the dominant peak in spectra collected for the black and white samples and showed a marked difference in intensity bands in the "aromatic network" region for the black versus white samples. It is suspected from this data that the lead from the added driers migrated to the surface and acted as a catalyst for UV photo-oxidation of the black layer, thereby causing the discoloration to white. Therefore, preservation of the organic binder might serve to prevent the migration of the lead and diminish the effects of UV and oxidation forces on the painted surface.

Van Ham et al. (110) attempted to measure the molecular composition of pigments in paintings using static SIMS with a time of flight mass spectrometer (TOF-MS). The primary conclusion of the authors is that for such a sensitive analytical technique, more refined sample preparation procedures are needed than what has historically been used. A possible advantage of the technique, claimed the authors, is the potential ability to characterize and image both inorganic and organic analytes.

Since the last review, Keune and Boon have continued their use of SIMS for the study of pigment degradation in works of art (91). In 2005, they published a study of the combined use of static SIMS data with light and electron microscopy as well as X-ray analysis to identify and localize the various reaction products of degraded vermilion. This work has allowed them to hypothesize an alternative depiction of the reaction mechanism that produces the photodegradation of vermilion. When exposed to light, the vermilion (HgS) in an artwork degrades into elemental mercury and sulfur. The chlorine naturally present in the vermilion acts as a catalyst for this reaction, in which the now elemental mercury deposits as nanoparticles on the surface of the remaining vermilion, turning it from red to black. Exogenous chloride begins to accumulate in the black layer allowing the metallic mercury and the remaining HgS to continue the reaction until a resultant white powder of $HgCl_2$ is formed on the surface of the artwork. This proposed degradation path was concluded to be an accurate depiction of the color changes in vermilion on two different paintings created by different painters and housed under different storage conditions.

Further, light microscopy provided images of the white degradation product above and around the black product. Most of the black product was observed as a top layer over a red underlayer. Both the black and the red colors remained true under UV light observation. SEM/EDS also provided elemental distribution data and information about the structural changes between the three colored phases, including confirmation of the presence of elemental mercury nanoparticles through visualization of “hot” spots smaller than 100 microns via back scatter electron imaging (BSI). SIMS detected traces of chloride in the native vermilion, which were not noted in the EDS analysis. SIMS imaging also enabled identification of the white product as mercuric chloride, which has not been reported in previous studies of vermilion degradation in paintings.

Just as nanoparticles were observed as a byproduct in the Keune and Boon study, they can also be created for use as a restorative layer in conservation of paintings and de-acidification of historic paper and wood products (111). Baglioni and Giorgi report that the traditional approach to restoration of wall paintings can be enhanced by nanoparticulate technology. Wall paintings that have undergone severe degradation of the calcium carbonate binding as a result of exposure to sulfur need to be treated chemically in order to revert the resulting sulfate salts back to carbonate in order to halt their migration to other areas of the artwork. Following this process with an application of a nanoparticulate dispersion restores the binder to its original condition.

The example cited in the study describes in situ restoration of wall paintings in the Yucatan peninsula in Mexico. In this region, there is relatively high humidity year round and short periods of rain. These conditions accelerate degradation processes of the wall art, particularly those which have previously been treated with non-compatible polymeric materials. Several paintings exhibited fissures and powdered paint layers that needed to be reconstituted. An application of calcium hydroxide nanoparticles were gently brushed onto the surface as a dispersion ten to thirty times more concentrated than conventional lime water. The treated area was kept wet for a period of 8 hours in order to maintain conditions favorable to the slow carbonation of hydroxide. After a second treatment of the nanoparticle dispersion, the treated area's color passed testing that determined the restoration was successful. Thus, nanotechnology has been demonstrated to provide significant contribution to wall painting restoration with minimal effort and cost expenditures.

Analysis of pigment use and recipes by LA-ICP-MS was the subject of two recent independent publications that studied specific populations and the pottery they manufactured. Duwe and Neff reported on the viability of TOF-LA-ICP-MS in studies of east-central Arizona Pueblo IV period ceramics (97). Results indicated that of the sherds tested, three distinct paint recipes could be distinguished within the community studied based on levels of iron, copper, antimony, and lead. These researchers concluded that careful sample selection and analysis of homogeneity in pigment use over the entirety of a vessel's surface are critical in order to best describe pigment recipes used within communities of potters. Moreover, elemental analyses of these recipes and the subsequent inferred existence of pottery-making familial communities could then be used to differentiate households, and allow for a more thorough understanding of the Pueblo social organization.

In the second LA-ICP-MS study, Green and Watling continued Watling's previous work in authentication studies via trace element analysis (77). This study used trace element fingerprinting of Australian ocher to establish provenance and subsequent authentication of Aboriginal art. Growing appreciation for indigenous art has spawned increased demand and pricing as well as the need for authentication techniques to combat the rise in fraudulent sales of copies. Aboriginal art usually incorporates a naturally occurring mixture of iron oxide and clay, namely ocher, which varies in color from white to dark brown. The researchers state that ocher mixtures are often specifically associated with regional artists who use the material from an area of cultural or ancestral significance. Therefore, sourcing facilitates determination of authenticity. The authors report that the analytical reproducibility achieved in this work sufficiently proves that a single sample of ocher from a specific site is all that is needed to derive an analytically robust trace element profile of that area. Therefore, a single sampling from a questioned artwork would be sufficiently homogenous to determine authenticity. This work initiated the creation of a database of ocher samples for future use in authenticity studies.

Detection of forgeries was also reported on by Hynek and colleagues in a 2004 article that described the analysis of a 19th-century painting by MALDI-TOF in order to determine the binding media used (118). While attempts to verify authenticity by analytical means is of great importance to the relevant scientific community, far more work has been published on conservation and restoration methodologies. As an example, Erhardt described work by Carretti et al. also in 2004 involving the use of "rheoreversible" gels which remove surface contaminants without altering the original design layer (116). The gelled solvent mixture reported on by Carretti and colleagues reverts to a free-flowing liquid when a few microliters of a dilute acetic acid solution are added to it. This process of liquefying the gel makes it much easier to remove from the surface along with the contaminants it has enveloped.

Analysis of the gel by FTIR and SEM/EDS after removal from a painted surface showed that none of the binder or pigmentation had been transferred from the original artwork. This work was noted by Erhardt to be significant progress in the restoration field.

Additional papers of note that have been published since the last review in relation to paint analysis of art works include the use of a three dimensional micro-XRF technique for analysis of in-situ paint layers (79) and two papers in the journal *Applied Physics A* from 2006. In the first, Krug and colleagues present the use of synchrotron-based K-edge absorption imaging as applied to paintings in order to develop elemental mapping profiles over large areas (80). This technique is also referred to as dichromography, which is the process of taking two images ideally acquired with a monochromatic X-ray beam and logarithmically subtracting one from the other to obtain two orthogonal images. One of the resulting images is the mapping of a specific element, while the second contains the map of the background. This approach allows for the detection of a specific pigment throughout the paint layer system. For example, paintings can be imaged such that each brush stroke may be examined through use of the high atomic number elements in the pigments. Common elements in historic artists' pigments such as cadmium, mercury, lead, barium, antimony, and tin can be examined in this way. Color information on individual paint layers can then be determined non-intrusively by art historians and conservators. The described approach is noted to allow for quick data acquisition and elemental sensitivity throughout the paint stratigraphy.

In the second article from this journal, Dupuis and Menu described the use of fiber optic diffuse reflectance spectroscopy (FORS) for the non-invasive, quantitative identification of artistic reference paint mixtures (98). This paper describes initial work in this area with testing of the methodology on genuine artworks to be presented in future studies. The purpose of this preliminary research was to determine if reflectance measurements of paint mixtures could yield identification of individual components, which was accomplished to the authors' satisfaction.

Another application of fiber optic reflectance spectroscopy as applied to in situ analysis of paintings makes use of FTIR in conjunction with XRF (81). Principal components analysis (PCA) was used to discriminate patterns in the initial FTIR data collected from a Renaissance era fresco located in a church in Italy. Of the initial 65 reflectance spectra, a group of 56 data points was subjected to a further PCA algorithm in order to better differentiate the results. From this work, it was observed that the painting surface had at some point in time been subjected to a layer of casein, probably as a protective finish. Other areas contained a protein-based binder such as animal glue or egg tempera. The FTIR and XRF techniques were used in concert to evaluate pigment composition. The FTIR analysis allowed for identification of mixtures of blue and green pigments such as malachite and azurite. When combined with XRF for elemental information, a complex mixture of green colorants containing malachite, green earth, and smalt (potassium glass containing cobalt ions) was able to be identified without any sampling of the fresco. The authors concluded that this work demonstrates the abilities of noninvasive techniques to provide an abundance of chemical information as well as the possibility of limiting the extent to which an artwork should be considered for further invasive testing.

Several studies published in recent years discuss the use of portable XRF spectrometers for in situ analysis of painted surfaces. Bonizzoni et al. reported on the use of energy dispersive XRF to determine chemical composition of pigmented layers in sequence (75). In combination with visible and/or near-infrared reflectance spectroscopy analysis of lighter elements in the surface layer, which cannot be detected by XRF methods, is also made possible. Angelini and colleagues analyzed a red decorative pigment (iron oxide in natural clay or as the mineral hematite) using a portable XRF instrument (73). They also conducted surface analyses with this same technique in an attempt to discover if environmental contaminants were affecting the stonework under examination. Cesareo et al. identified the pigments used by the artist, the potential for deterioration of the surface by contaminants such as chlorine and sulfur, and previous restoration areas as noted by the presence of cadmium, zinc, and titanium in the golden haloes depicted in a painting completed in the 14th century (76).

Of course, the allure of transportable equipment to authenticate artwork in real time has numerous applications in forensic work as well. A partnership of these two fields most often occurs in authentication studies, particularly after a suspected forgery has been purchased at genuine prices. Szökefalvi-Nagy and associates in Budapest conducted authentication paint analyses on three suspected forgeries (85). The authors stated that titanium white has only been available since 1920, whereas the disputed artworks were said to have been created by artists who predeceased this timeline. Therefore, the presence of titanium in any of the suspected paintings would clearly indicate that they were not authentic. Recent work by Edwards and colleagues raises questions as to the use of titanium as a marker for forged (i.e., non-ancient) artwork (60). Nonetheless, for the disputed paintings attributed to Géza Mészöly, titanium was readily observed using a portable XRF spectrometer with a ^{55}Fe ring source in the two questioned works, but not in the known painting by this artist.

A painting reported to have been by Tivadar Csontváry Kosztka was also under suspicion as a forged work. The owner of the painting allowed multiple examinations by these authors to settle the question of authenticity, first using microsamplings from the painting's surface and then in situ with a portable XRF. Both analytical methods were used in order to determine if the presence of barium influenced a previous determination that titanium was present in the painting. Using the same excitation source as was used on the other paintings, it was determined that detection of titanium was being influenced by the L-lines of barium. Moreover, numerous attempts to isolate the K-lines of titanium were reported as unsuccessful. Therefore, the authors reported that XRF could not confirm the presence of titanium in the microsamplings. Subsequent in situ measurements taken at 12 points on the painting, in both white and colored areas, revealed that the best curve fit for the detection of either barium or titanium was achieved when both were accounted for in the equation. The authors conclude from this study that analysis of titanium in authenticity examinations can be very effective and readily achieved with a portable

X-ray spectrometer equipped with a ^{55}Fe excitation source provided that barium is not also present in the pigments used. If barium is suspected, the K-lines for this element can be confirmed with an ^{241}Am source.

Given the evidence that portable XRF equipment is greatly facilitating the in situ examination of art and artifacts, it is noted that Ida and Kawai have published an article on the use of a portable X-ray spectrometer equipped with a pyroelectric X-ray generator which allows for quantitative analysis of Fe down to 180 parts per million in an aluminum foil sample (78). The geometry of the current design also has the potential to be further improved such that the size of the spectrometer could be further reduced, possibly allowing for even greater portability and versatility in the examination of large or irregularly shaped objects.

PIXE has been utilized by conservators and archaeologists as a complement to electron based X-ray analytical techniques, such as EDS, because it offers better peak to noise ratios and consequently much higher trace element sensitivities (www.mrsec.harvard.edu.) As such, it is described in analyses of pigments in three paintings and on a multi-colored wooden altarpiece (66, 95, 96). In Pagès-Camagna and Calligaro's article (66), PIXE was used by the authors to confirm pigment results obtained by micro-Raman analysis. Grassi describes the use of differential PIXE measurements using different beam energies or incident angles on the same analytical spot in order to obtain depth assessments of inhomogeneous layered paint samples (95). In the third paper in this set, Reiche and colleagues (96) were able to report on the existence of both zinc and tin-containing pigments from works not previously determined to contain these elements. The authors conclude that their findings raise the question as to whether these works are authentic. If so, these paintings could provide evidence that zinc pigments were already in use in India before their known synthesis and application in Europe around 1850.

Two articles published in 2005 by Chiavari's group at the University of Bologna describe reactive pyrolysis methylation and silylation procedures used with GC/MS applications (100, 113). Methylation-pyrolysis and silylation-pyrolysis are two derivatization techniques whose purposes are to provide information on carboxylic acids and other polar compounds not typically observed in conventional pyrolysis. The first paper by Chiavari examined the use of pyrolysis methylation and silylation in identifying indigo dyes in a particular work of art (100). In this study, indigo was able to be positively identified by reactive Py-GC/MS along with some binder information. The presence of the dye was also confirmed by Raman spectroscopy.

In the second paper (113), the effect of three inorganic pigments, namely cinnabar (HgS), lead white ($2PbCO_3\_Pb(OH)_2$), and zinc white (ZnO) in linseed oil layers, were examined with respect to the analysis of fatty acids by pyrolysis with in situ derivatization. Both applications were found to be affected by the presence of these pigments, causing a significant decrease in the relative content of an analyte of interest, azelaic acid. It was surmised that zinc white and lead white might also be problematic for analysis of siccative oil in egg tempura.

A 2004 publication principally authored by Mazzeo was also a product of work performed in Chiavari's group (92). In this study, multiple techniques were used to analyze decorative materials on ancient Chinese wooden architecture. Both the inorganic pigments, such as clay and lime, and the binding media, which was concluded to be a siccative oil, were analyzed using optical microscopy of paint cross-sections, SEM/EDS, XRD, and Py-GC/MS with methylation conditions. According to the authors, the obtained data confirms historical information and provides a base of knowledge for future conservation efforts of Chinese artworks.

Reports of advances in the analysis of binding media for artistic and historic artworks unilaterally contain discussion of the use of GC/MS in one form or another. For example, synthetic resins used in binding media of two 20th century paintings were studied by Cappitelli using thermally assisted hydrolysis and methylation (THM) GC/MS) in conjunction with FTIR (107). This work served as a precursor to later research by Cappitelli and Koussiaki in which both synthetic and natural binders were identified in three works by Picasso using THM-GC/MS and FTIR (108). This research demonstrated that Picasso experimented with mixing artists' paints with other materials such as animal fats and alkyd resins, the latter combination being unusual for that era.

Pitthard published two articles describing direct chemolysis using (*m*-trifluoromethyl-phenyl) trimethylammonium hydroxide (TFTMAH) as a starting point for the analysis of drying oils in works of art by GC/MS (103, 104). The first of these articles includes some history on the various derivatization techniques for the analysis of fatty acids, including methylation-pyrolysis as well as analysis of partially degraded drying oils. This work was followed by a paper in 2006 in which specific applications of binding media ageing and degradation analysis at the Kunsthistoriches Museum in Vienna were reported by Pitthard, Griesser, and Stanek (105).

Other publications of note in art conservation and analysis of binding media or the starting resins used to make them also involved GC/MS with methylation, direct chemolysis, and/or pyrolysis. Andreotti and colleagues described the identification of animal glue, egg, linseed oil, beeswax, Pinaceae resin, dammar, and shellac in three "old paint" microsamples (115). Using a combination of a multi-step pretreatment of solvent extractions and microwave-assisted chemolysis prior to GC/MS analysis, the authors were able to describe these materials as original or restoration agents within the samples analyzed. Scalarone and Chiantore reported on their comparative analyses of Py-GC/MS data for acrylic emulsion paints to SEC-FTIR results for the same samples (109). The authors contend that while the latter approach is not as sensitive as GC/MS, it does allow for the simultaneous identification of polymeric components and additives in emulsion paints using calculated molecular weights and extensive FTIR libraries without thermal degradation caused by the GC/MS procedure.

P_ikryl et al. described the merits of HPLC-fluorescence detection (FD) and GC/MS analyses of proteins in binding media (106). Both techniques required pre-derivatization steps and involved long analysis times, high cost, and/or safety concerns with respect to the methyl chloroformate (MCF) derivatization agent. However, the paper gives researchers guidance into alternative approaches to identifying proteins in works of art. Further uses of GC/MS in studies of binding media include papers by Kouloumpi et al. (102) and De la Cruz-Cañizares et al. (114).

An exception to the use of GC/MS to analyze binding media was published by Harrison et al. in 2005 (117). In that paper, the use of CE is described in the identification of long-chain fatty acid constituents of drying oils and their degradation products, short-chain dicarboxylic acids. Plant and animal glues were found to interfere with other methods of analysis, but even as much as a ten-fold excess of this type of material with respect to the oils sampled on a ceremonial mask were not found to cause interferences when analyzed by CE.

Forensic Analysis Of Paint

Ryland's review article (122) is an excellent reference for trends in the forensic examination of paints and coatings, including how coatings evidence is encountered in a forensic laboratory and a detailed outline of the technical approach used for their analysis. The analytical approach used by most United States laboratories includes a combination of microscopic, microchemical, and instrumental techniques, of which microspectrophotometry (MSP), FTIR, Py-GC, SEM/EDS, XRD, XRF, and LA-ICP-MS are discussed. An evaluation of evidential significance, including the use of databases in make, model, year investigations, is included. This publication is a good primer for new and experienced paint examiners alike desiring an overview of current practices in forensic paint analysis.

Saferstein (123, 124) published both the 8th and 9th editions of his popular *Criminalistics* textbook in 2004 and 2007, respectively. The chapter on paint gives a brief but accurate description of the layers comprising an automotive paint chip, instrumental techniques, and resources utilized in make-model-year determinations. It also provides case examples and a current bibliography. Although no substantive changes to this chapter were made between the two editions, the color photographs, figures, and overall layout of the present edition are notable improvements over its predecessors.

Also of note is Kubic and Petraco's chapter (125) entitled "Microanalysis and Examination of Trace Evidence" in a different introductory forensic science textbook. It provides an excellent overview of all types of trace evidence as well as the various microscopic techniques and instrumentation used to analyze these different types of materials. Topics include paint, glass, fibers, polarized light microscopy (PLM), FTIR, SEM, MSP, and Py-GC/MS.

Significance

Two references regarding the interpretation of paint evidence were published that had been described in the previous Interpol report, though at the time were referenced as conference presentations. Edmondstone (126) reported on a study to assess the distinctiveness of automotive paints in order to determine their evidential value, and Buzzini (127) examined the interpretation of the results of examinations involving crowbar and household paints in burglary cases.

Case Reports

Zieba-Palus and Trzcinska (128) provide three case examples illustrating the usefulness of the applied methods and the difficulties that may occur in the interpretation of results. Multiple scientific techniques are mentioned (stereomicroscopy, polarization microscopy, fluorescence microscopy, IR, UV/Visible microspectrometry, and SEM/EDS); however, only microscopy and IR are specifically mentioned in the case examples. Case 1 described an automotive paint comparison, in which only the top layer was consistent between samples. The conclusion was that it could not be excluded as the striking vehicle. Several questions arose, which could only be addressed by undertaking a population study. Case 2 involved an analysis to determine whether a car had been repainted. Based on the examinations, it was concluded that the questioned vehicle had been repainted. The example emphasizes adequate sampling from multiple areas of a vehicle. Case 3 discussed how two vehicles' paints had been damaged: a paint stripper had been poured on them.

Giang et al. (129) reported on a case in which they were asked to compare red paint transfer found on a motorcycle to two different suspect trucks. Based on the limited amount of paint smear, the only techniques utilized were stereomicroscopy and micro-FTIR, in both transmission and attenuated total reflection (ATR) modes. Based on the examinations conducted, one suspect vehicle was eliminated as the source of the paint transfer whereas the other vehicle could not be eliminated. This case report provided an example of how limited sample size, and therefore, utilization of a reduced number of analytical techniques, can affect the overall strength of an association. Additionally, the usefulness of FTIR in such instances is demonstrated.

In a separate study, Buzzini and Massonnet collaborated with Sermier to report on forensic paint applications of Raman spectroscopy (130). In that paper, six case studies were presented: two automotive paint cross-transfer examples, architectural paint transfer to a burglar's tool, spray paint graffiti analysis, paint-to-fabric transfer, and paint transfer to leather shoes worn by a suspected vandal. Each example provides support to the author's claim that Raman and FTIR analysis are complementary techniques for non-destructive micro-analysis of suspected paint transfers.

Lawrence of the San Diego County (California, USA) Sheriff's Crime Laboratory reported on a case in which he was asked to determine if an unknown material was hull paint (40). In order to familiarize himself with marine coatings, Lawrence obtained a number of antifouling paints that contained 50% by weight cuprous oxide as their antifouling agent. In the article, the preparation and microscopic techniques used to confirm the presence of cuprous oxide are described. Additionally, the presence of copper was confirmed using a microchemical test and SEM/EDS.

Spectroscopic Methods

Ziuba-Palus (131) reported on the examination of spray paints on a variety of substrates by micro-ATR. The advantage of the ATR technique over transmission FTIR was that the paint could be examined in situ. The author analyzed spray paints on metal, glass, foil, fabric, and plaster, and consistently found that the thicker the applied spray paint, the better the ATR spectra. In instances where the spray paint layer was thinly applied, the substrate had an affect on the quality of the spectra, due to absorption, reflection, and scattering of the light by the sample. The best results were obtained on metal surfaces and the most difficulty was encountered on fabrics and various plaster surfaces. For those plaster surfaces, transmission FTIR was recommended.

FTIR and NMR were used by Ahmad et al. (132) to elucidate the structure of siloxane-modified epoxy resins they synthesized in an attempt to improve various properties of epoxies. Based on their study the authors recommended the use of siloxane-modified epoxies as anticorrosive paint systems for high-temperature applications. For forensic scientists this study provides an example of paint analysis via NMR spectroscopy, a technique that is not used routinely in forensic laboratories.

Suzuki (133) published the seventh article in his series on the IR analysis of pigments in automobile original finishes. In this article, he described the FTIR and XRF analysis of Nickel Titanate and Chrome Titanate, two inorganic pigments that can be used to formulate hues formerly produced by Chrome Yellow. Although the analysis was performed on automobile systems from the 1974 to 1989 era, the paint industry still utilizes these pigments in some yellow and orange-yellow topcoats. These titanate pigments are based on the rutile titanium dioxide structure, and only minor differences can be discerned between the infrared absorptions of the titanates with rutile, and even then only with extended-range FTIR. However, when analyzed with XRF for trace element content, identification is possible: elements comprising these pigments include nickel and antimony for Nickel Titanate and chromium and antimony for Chrome Titanate. Other elements detected included zirconium, niobium, and lead. Despite the information obtained from XRF, Suzuki acknowledged that the potential is not likely to be frequently seen. Reasons include the common use and availability in forensic science laboratories of SEM/EDS, which does not permit detection at these elemental levels, and sample sizes requirements for XRF that are much larger than normally encountered in casework.

In a second report on XRF analysis (134), the technique was used in an unconventional way, in that organic modifications in paints were detected. While XRF is traditionally used for inorganic applications, this study showed the possibility of evaluating organic information, due to other possible interactions between the incident X-ray beam and the sample. Applications included evaluation of the degradation of organic compounds for paint quality control purposes.

Buzzini and Massonnet conducted a paint analysis study of 40 commercially available green spray paints utilizing both FTIR and Raman spectroscopy (135). The FTIR data was used to discriminate the binders and some extender pigments while Raman provided identification of the primary organic pigments in the formulations. Eleven of the purchased paints were for automotive usage. The remaining 29 were designated for household applications, both indoor and outdoor use, for decorative applications, and appropriate for substrates ranging from wood to metal and plastics. The authors reported that both shaken and unshaken samples were analyzed in order to determine if differences could be detected between the two pre-application conditions. Given the low priority of proper application techniques during the commission of a crime, it is reassuring that the authors reported no differences between shaken and unshaken samples by either FTIR or Raman spectroscopy.

The main binder types identified by FTIR for these paints were acrylic, orthophthalic alkyd, isophthalic alkyd, and nitrocellulose- orthophthalic alkyd. Two sub-groups of six samples each could not be differentiated beyond classification as an orthophthalic alkyd with barium sulfate as the extender pigment or as a nitrocellulose-orthophthalic alkyd binder, respectively. The authors reported the discriminating power for this analysis as 0.95 for the 40 paints with 40 undifferentiated pairs remaining. Using a He-Ne laser at 632.8 nm, 15 groups were distinguished by Raman spectroscopy amongst the 40 analyzed samples. The discriminating power for this set was reported as 0.91 with 68 undifferentiated pairs. When an Argon laser set at 514.5 nm was used, Raman yielded eight groups with a discriminating power of 0.62, whereby 300 undifferentiated pairs remained for the 40 spray paints.

The authors then attempted to determine the extent to which further discrimination between groups could be achieved if the three reported methods were used in concert. Following the analytical sequence FTIR, then Raman He-Ne, then Raman Ar^+, 26 individual classes were obtained with a calculated discriminating power of 0.98 with 19 undifferentiated pairs for the 40 green spray paints.

Conclusions drawn from this work included the assertion that a combination of FTIR and Raman techniques provides the best discriminating capability for spray paint samples. Since the green Argon laser operated at 514.5 nm induced fluorescence for most of the samples in the study, Buzzini and Massonnet recommend use of a red He-Ne excitation source at 632.8 nm for green paints. In an ancillary pigment study within this paper, it was reported that the He-Ne laser identified primary green and blue phthalocyanine pigments within the spray paints. Moreover, despite fluorescence difficulties in many samples, use of the Argon laser did detect two yellow pigments in the paints studied. Thus, the combination of FTIR and Raman, particularly with different excitation sources, provides a robust analytical protocol for spray paint analysis.

Bell, Fido, Speers, and Armstrong have also published follow-up articles to their Raman work described in the previous review. The first study entailed the analysis of architectural finishes by Raman spectroscopy (136), in which 51 “lilac” colored paints were examined using three different excitation wavelengths. The authors note that the color choice was arbitrary in that it was based on availability of an extensive sample set. However, the decision to analyze single layer paints within a visually consistent color space was deliberate, since the importance of chemical discriminating ability is more critical in these types of comparative samples. Of the 51 paints in the sample set, the manufacturer, finish (e.g., gloss, matte, satin), and hue were all variables.

Raman spectra were collected on all 51 samples at an excitation wavelength of 785 nm. A smaller subset of the paints was also analyzed using visible excitations at 514 and 457.9 nm. However, discriminating features of the individual samples were masked at these wavelengths by the overwhelming bands produced by a component common to all of the paints. The use of the far red wavelength excitation energy at 785 nm allowed for both the pigments and non-resonance enhanced components to be evaluated using a conventional silicon-based charge-coupled device (CCD) detector.

A complicating factor in this discrimination study was the batch variation observed between nominally identical paint formulations. The authors concluded that further studies would be needed to address this issue. Nonetheless, PCA was able to provide good characterization and discrimination when major features of the spectra such as the presence of rutile and copper phthalocyanine pigments were used in conjunction with minor constituents. This approach allowed for the use of a library search methodology, since the analysis time was less than one minute and no sample preparation was needed. The authors further reported that when 20 samples were prepared and analyzed against a library created almost one year earlier, the “correct” sample was the top hit in 16 cases, the second top hit in two cases, and the fifth top hit in two additional cases. This work provided further validation of Raman spectroscopy as a forensic tool in architectural paint analyses.

Two subsequent publications by Bell et al. (137, 138) compared the merits of FTIR and Raman spectroscopic analyses on both the resinous binders and white paint formulations used in architectural finishes. In both papers, Raman spectroscopy was reported to provide slightly better discrimination capabilities with little sample preparation. In Part 1 of this series, 11 oxidizing resins, 20 modified alkyd resins, and 8 emulsion resins of varying manufacture, oil length, and modifier were analyzed. The authors noted that FTIR is commonly used to discriminate between resin types because it provides adequate comparative information in forensic casework. However, the ability to classify and further characterize resins within a given population is achievable with Raman spectroscopy particularly if background differences are corrected prior to measuring band intensities. While manual background subtraction is a simple exercise, the authors used a first derivative approach taking 11 points in a Savitzky Golay model in an attempt to eliminate bias and human error.

The study concluded that for the 39 resins studied, Raman and FTIR provided similar discrimination between resin classes. Further differentiation could not be achieved with the FTIR data, however, because within-group variation was comparable to the experimental uncertainty of the technique. Using Raman spectroscopy, the relative band intensity differences were small for a given resin type, yet were still greater than the experimental uncertainty of the technique.

In Part 2 of their study of architectural finishes by FTIR and Raman these authors examined samples classified as nominally “pure white.” Experimental conditions for the Raman analysis followed those of the lilac paint sample study described earlier. Fifty-one white paints of varying manufacture and finish were recorded at 785 nm, with additional attempts at analyzing a subset of 10 paints at both 514 and 532 nm. Fluorescence levels at the shorter wavelengths proved to be unacceptable, so this work was halted. The remaining analyses were all performed using the 785 nm experimental conditions. Of the 51 samples analyzed, Raman spectroscopy differentiated the paints into seven groups, where each spectrum within the group contained the same bands but not necessarily with the same intensity ratios. There were also six single samples that did not align with any other paint grouping. FTIR analysis yielded six distinct groups and four individual spectra. Additionally, the authors noted that twelve samples that comprised a single FTIR group were differentiated into three groups and two individual spectra by Raman. Both the binding media and inorganic pigments and extenders contributed to the discrimination capabilities in the study, but were more readily identified using Raman since there was little band overlap in these spectra.

The authors reported that approximately half of the white paints could be discriminated even within a given group. The other half of the samples were sufficiently consistent to be classified as a single group by both techniques. However, intensity differences in some bands provided a basis for concluding that the rutile-to-resin ratio had enough variability within this group to make it a discriminating parameter for further consideration. As a result of this series of papers, the authors make a strong case for complementing traditional FTIR paint analysis with Raman spectroscopy, particularly when more specific binder or pigment discrimination or identification is needed.

In a paper by DeGelder, Vandenabeele, Govaert, and Moens (139), Raman spectroscopy is augmented by FTIR in the analysis of cross-sectioned automotive paints. All layers (e.g., clearcoat, basecoat, primer surfacer, and primer electrocoat (e-coat)) of a typical OEM finish were analyzed in this study. Metallic finishes containing pearlescent and metallic effect pigments in the basecoat were chosen for analysis over non-metallic colorcoats. Both the clearcoat and e-coat were found to lack sufficient distinguishing chemistries by FTIR or Raman techniques to differentiate paints using either layer on its own. However, the primer surfacer was found to be a good discriminating layer with FTIR and Raman spectroscopy based on the presence or absence of calcium carbonate or barium sulfate. Raman could further discriminate paints by identifying the rutile form of titanium dioxide. Moreover, the basecoat was shown to be the most discriminating layer, particularly when Raman was used to characterize its organic pigments. Flakes of the individual topcoat layers were also analyzed by Raman spectroscopy with promising results that would further reduce the need for sample preparation on small samples.

In a similar study, Zi_ba-Palus and Borusiewicz (140) examined multilayer paint samples by IR, Raman, and XRF spectroscopies, where FTIR was used to determine the binder, Raman identified the pigments, and micro-XRF confirmed the Raman results.

Ito et al. (141) produced a paper describing the use of FT-Raman spectroscopy in conjunction with multivariate data analysis for rapid and quantitative determinations of the viscosity of waterborne automotive paint systems. This work is directed at on-line manufacturing processes but provides a foundation for consideration with respect to forensic analyses.

Color

Three separate articles written by Cramer (142), Nadal (143), and Takagi (144), respectively, address the importance of measuring the color of coatings containing pearlescent or interference pigments at different angles of reflection. Each author discussed that due to the presence of these pigments, the color measurement will differ depending on the angle of illumination and the aspecular angle. Although intended for quality control and assurance of manufactured products, the subject of these articles emphasize the importance of observing and comparing painted specimens under the same lighting conditions.

Kopchick and Bommarito (145) reported on the use of MSP on achromatic automotive paint samples. Samples whose colors are black, gray, or white are considered achromatic because they either reflect or absorb all wavelengths of visible light approximately equally, and therefore, achromatic samples are typically not analyzed via visible MSP in forensic laboratories. The authors, however, provided examples of black and gray/silver colorcoats in which MPS provided additional discrimination over that obtained via PLM. Such samples may contain secondary chromatic pigments added to the achromatic paint formulation resulting in MSP spectral variation. No spectral variation was found between white topcoat paints or in gray undercoats. Based on the results of this study, the authors recommended that when MPS is regularly included in the forensic analysis of automotive paints, it should be included in analytical schemes involving black and gray/silver topcoats.

Chemical Imaging

In chemical (hyperspectral) imaging, spatial and spectral information are gathered simultaneously. The technique combines macro/microscopic imaging with spectroscopy, resulting in a three-dimensional representation of a sample. A variety of spectroscopies can be applied, and two publications were found during the time period of this review for the technique's application to forensic paint samples.

Payne et al. (146) investigated the use of chemical imaging for a variety of materials but specifically evaluated multi-layered paint chips through visible and fluorescence chemical imaging. It was found that in comparison to traditional MSP, chemical imaging is more efficient, and that fluorescence chemical imaging can be performed on the same equipment without removing the sample. It was also found that the technique is powerful in presenting data to the layperson. However, traditional MPS is able to scan over a larger energy range.

Flynn et al. (147) analyzed multi-layered paints by infrared chemical imaging and, like Payne, found two key advantages of the technique: thousands of spectra are compared with thousands of spectra in a short time, and chemical imaging data can be displayed in ways that are easy for a layperson to visualize and understand. However, a main disadvantage was described in that the infrared spectral range is more restricted than for a conventional infrared microscope, specifically in the inorganic fingerprint range.

Elemental Analysis

Schreiner, Melcher, and Uhlir published a review on SEM/EDS and its applications in the field of cultural heritage (148). Although an analysis is performed on a multi-layered painting, the review is still quite relevant to forensic paint analysis, in that the authors discussed the potential, advantages, and disadvantages of SEM/EDS. An ESEM was used: the main advantage is the examination of non-conducting samples (e.g., paint) without application of a coating. Light microscope, UV-fluorescence, BSI, and X-ray mapping images were shown demonstrating the complementary pigment and layer structure information obtained from each. Despite the information available from such techniques, the authors stated that it should be kept in mind that many inorganic materials and pigments can occur in different crystalline structures, highlighting the use of XRD. Conventional XRD, however, is not suitable for the analysis of single layers in a multi-layered cross-section, but a recent study on synchrotron X-ray micro diffraction demonstrated the analysis of paint layers down to 1 or 2 microns (149).

Two articles were reviewed on the analysis of forensic paint samples by LA-ICP-MS. Deconinck et al. (150) performed depth profiling analysis of multi-layered automotive paints, which provided detailed information on the trace elemental composition of individual layers without the need for any separation from adjacent layers. The data was displayed in two ways: as depth profile plots (intensity versus time) and as bar graphs of elemental ratios, both of which allow for qualitative comparisons of samples. Quantitative analysis would potentially lead to a statistical evaluation of the results, which would be particularly important in comparing results of an unknown sample to a database. However, at this time quantitative analysis is still being developed. Also in this work, two mass spectrometers were used and compared (a quadrupole-based and a sector field instrument) and the advantages and disadvantages of both were discussed. It was demonstrated that LA-ICP-MS is very promising for layer-specific elemental characterization of multi-layered automotive paints but that further optimization is needed.

In a second LA-ICP-MS publication, Smith et al. (151) analyzed works of art for the detection of art forgeries. The work has potential applicability to the field of forensic paint analysis in that it includes an investigation into the possibility of identifying differences in elemental concentrations between brands, manufacturers, countries, and binders of artists' paints. In this work, the data was displayed in plots of intensity versus isotope, which as in Deconinck's study, showed visual differences between samples. It was also found that the binder could have an effect on the fit of a database search and should be taken into account.

A new procedure was proposed by Lopez-Molinero et al. (152) for the determination of metals in paint driers, which are catalysts used in paint formulations to accelerate drying effects and film formation. Common metals include barium, calcium, cobalt, lead, manganese, and zinc, but rare earth and transition metals can also be used. The procedure involved decomposition and mineralization of the organic matrix using microwave digestion and flame atomic absorption (FAAS) and/or emission (FAES) spectroscopy, resulting in no significant difference between concentrations calculated with these techniques and reference values. Although this study was for industry quality control purposes, it provides background information on paint driers to forensic scientists.

Jancik et al. (153) described the use of a miniaturized Mossbauer spectrometer for monitoring the color quality of copperas red pigments ($FeSO_4 \cdot 7H_20$) and as a control device in the manufacture of titanium dioxide from ilmenite. Although the target audience is the paint industry, the report demonstrated the potential of a unique technique for pigment analysis.

Pyrolysis

The pyrolysis technique is older than GC and MS, yet very little is published from practical or service laboratories. Therefore, in 2004 Wampler (154) wrote an editorial that provided examples of how pyrolysis is used in practical applications. Examples included forensics in general as well as the paint industry. Paint laboratories, for instance, use the technique to identify and measure the components in paint formulations and to analyze their competitors' products. The article noted that although paint may be marketed as polyurethane, it may only be present as a minor component. Pyrolysis is effective at characterizing these types of materials. The article also stressed that pyrolysis provides analytical information about a complex solid material, such as paint fragments submitted as items of evidence. Pyrogram libraries can be used to identify the components of an analyzed sample.

Wampler also published two short notes (155, 156) that show how Py-GC/MS was used to differentiate automotive paint samples. In both references, the two paint samples compared are primarily acrylic in composition and are discriminated by pyrolysis; however, it is not stated whether the paint samples could be differentiated by FTIR. Wampler reiterated that since inorganic fillers do not interfere with pyrolysis analysis, Py-GC/MS is a powerful tool for the analysis of complex filled and treated automotive paints. In the first publication, more detail is provided on paint formulations, which depending on the components identified, may allow one to establish the approximate age of the car.

Burns and Doolan (157), on the other hand, did examine automotive paints that had previously been found indistinguishable following FTIR analysis. These authors were approached by the European Paint Group (EPG, a group of scientists involved in paint analysis from multiple European forensic science laboratories) to collaborate in a study to evaluate the potential discrimination ability of Py-GC/MS for automotive paints. Approximately 75 automotive paint samples were analyzed by FTIR and Py-GC/MS to evaluate whether Py-GC/MS could discriminate samples that FTIR could not. In multiple instances, they did find that samples that could not be discriminated by FTIR were discriminated by pyrolysis, and on occasion, consideration of minor components was beneficial. Furthermore, they found that the reproducibility of the pyrograms was good for both the compounds detected and in the relative peak heights. However, it was not stated over what time frame the reproducibility was evaluated. However, reproducibility was further studied and discussed by the authors in a subsequent publication (158), in which the pyrograms showed excellent chromatographic reproducibility. The aforementioned article ends with a question: "what is the degree of discrimination that Py-GC/MS can provide between large numbers of samples of a particular class...all from within a single FTIR group?" The authors attempted to answer this question in a following article (159) involving the analysis of automotive paint clearcoats.

In that portion of their study, Burns and Doolan analyzed 300 clearcoats by Py-GC/MS to investigate the discriminating power of the technique. The 300 samples included groups of 4, 7, 9, 36, 49, 55, and 140 that could not be distinguished by FTIR analysis alone. The pyrolysis data was compared between groups, confirming the individuality of the FTIR groupings. In most cases, Py-GC/MS was able to further subdivide the groupings, substantiating an increased discrimination following the analysis.

White exterior paints were also analyzed by Py-GC/MS by Burns and Doolan (160). Since FTIR can identify classes of paint but it is not as good at differentiation within each class, 28 different white exterior paints were analyzed by Py-GC/MS to evaluate the technique's potential for discrimination. An evaluation of FTIR to discriminate the samples was not mentioned, but a majority of the samples could not be discriminated by Py-GC/MS analysis. Since the paints were mostly purchased locally, it is possible that despite the apparent variation in paint brands, many of the samples could still come from the same manufacturer. Also in this study, two of the samples were sampled twice: once before and once after stirring; no discernible differences were noted in the pyrograms. The authors mention developing a system for automating the acquisition and evaluation of data, in order to save time and to avoid problems in the subjective visual comparison of pyrograms, which is then reported on in a previously mentioned study (158).

Jansson et al. (161) described a Py-GC/MS technique for analyzing polymer additives, such as plasticizers, antioxidants, light stabilizers, flame retardants, and other modifiers, in which two or more low temperature (sub-pyrolysis) runs were performed prior to pyrolysis, a technique previously described by Wampler (162). This allowed for additional separation and further elucidation of components present in complex polymeric materials. Two light stabilizers found in paints (Tinuvin 622 and Chimassorb 944) were included in the discussion and were successfully identified and distinguished. For additives present in the parts-per-million range, selected or extracted ion mass spectrometry was the most informative.

Other Mass Spectrometry Techniques

Stachura et al. (163) reported on the laser desorption mass spectrometry (LDMS) analysis of automotive coatings in order to identify the organic pigments. LDMS has previously been demonstrated to be effective at analyzing colorants in inks and other matrices, but this study demonstrated the technique's utility for the analysis of automotive paints. LDMS has multiple advantages: it is fast and relatively nondestructive, is capable of analyzing small samples, has generally low detection limits, and can simultaneously detect inorganic and organic pigments at low concentrations in the presence of binders.

Reidy et al. (164) reported on a preliminary investigation into using ^{13}C-isotope ratio mass spectrometry (IRMS) for the forensic analysis of white architectural paints. Despite the promising applications of IRMS to other forensic materials (165) (refer to reference number 165 for a good synopsis of IRMS instrumentation and application), validation of the technique for paint analysis had not been attempted prior to this study. Since carbon is one of the most abundant elements in paint, this study investigated the influence that paint application, ageing, and homogeneity might have on the results obtained and the conclusions drawn from the technique. The authors warned that, at this point in the research, interpretation of the significance of the results should be approached with caution. Recommendations were also made about additional research that should be explored. However, the preliminary results are promising.

Updates on Databases

Since the last review, the Bundeskriminalamt (BKA) requested that the European Paint and Glass Group (EPG) of the European Network of Forensic Science Institutes (ENFSI) expand its activities to include the forensic analysis of tapes and security dyes. As a result, the EPG initiatives now include management of an adhesive tape database and establishment of a European database on security dyes. In 2007, the first collaborative exercise for sourcing adhesive tapes was administered, the purpose of which was to validate the utility of the adhesive tape database. The BKA and Gendarmerie nationale in France also continue to share responsibility for maintenance of the European Collection of Automotive Paints (EUCAP), which is the EPG's automotive paint database. EUCAP is available to non-ENSFI forensic laboratory partners upon request. Lastly, a new Raman database is being established for automotive paint samples, and an infrared database populated with a variety of routinely examined materials is also under development. Both the paint and glass sub-groups expect to establish best practice manuals for their individual disciplines before the end of 2007. These documents are likely to include discussion of the use of databases in casework.

The Paint Data Query (PDQ) database maintained by the Royal Canadian Mounted Police (RCMP) has continued to expand its partner laboratories during the past three years. Six laboratories have joined since the last review article and one inactive member has re-joined after several years of non-participation. In addition to a number of Canadian laboratory partners, PDQ has over 100 international participants. These include fifty-three American laboratories, thirty European laboratories, representing seventeen countries, eleven laboratories representing Australia or New Zealand, one in Japan, and one in Singapore. Approximately 500 samples continue to be added to PDQ annually with a new release of the software sent out to member laboratories each October. The version released in October 2006 contained 14853 samples which collectively were comprised of 54882 individual paint layers. The spectral libraries contain sixty-eight libraries containing 40893 individual spectra.

PDQ catalogs both the Munsell color and the chemistry of the primer layers. An article that addressed color variations of electrodeposition coatings (166) is of interest to the forensic paint examiner, particularly when relying on comparisons of e-coat colors to either a known or reference sample or to data compiled in a database. The author discussed a number of factors that have an effect on the resulting color of an electrodeposition coat. Factors included film build, improper mixing of the paint, iron or bacteria contamination in the tank, and less than optimal oven (curing) conditions. The author reported that the primary effect is yellowing of the dried film. Further, he stated that color shifts can occur with as little as 0.1 mil difference in dry film thickness, and lighter colors are generally affected to a greater extent than dark colors. The intent of the article is for someone in the paint industry to resolve problems they encounter regarding controlling color, but it is beneficial to the forensic paint examiner to understand the extent to which it occurs.

Glass

Overview

Several previous review papers and conference proceedings have covered some of the topics included within this review. Almirall and Trejos (167) published a *Forensic Science Review* paper concerning forensic analysis of glass fragments. This tutorial article emphasizes the basics of glass examination with acknowledgement of current methods and potential future improvements. The authors emphasize analytical methods, particularly elemental analysis, but also touch on other topics including sampling and recovery of glass fragments, optical and physical examination methods, and statistical interpretation of the results. This article is not a typical review of the literature in that a number of the recommendations, particularly in the areas of sampling and statistics, are made by the authors from their own experience with limited citation of references. Of the references listed, only about 10% are from the last three years and none are more recent than 2005.

The American Chemical Society publishes semiannual reviews covering a number of analytical fields in the journal, *Analytical Chemistry*. Of these, the most directly related to forensic glass analysis are the two on Forensic Science (168,169). These reviews provide a list of articles with little commentary. While the coverage of forensic science is extensive, only a single paragraph and a few references are devoted to glass. Other review articles in *Analytical Chemistry* concern specific analytical methods, some of which are applicable to glass. The Royal Society of Chemistry publishes similar analytical reviews both of analytical methods and materials analyzed in the *Journal of Analytical Atomic Spectrometry*. Their updates concerning Industrial Analysis: Metals, Chemicals and Advanced Materials (170,171) contain sections on glasses and ceramics. These reviews contain critical discussion as well as a summary of the published articles. Emphasis is on methods utilizing atomic spectrometric techniques. *Applied Spectroscopy Reviews* is a highly-rated journal containing instrumental developments of spectroscopic methods including applications. During the review period, articles appeared in this journal on the topics of TXRF, LA-ICP-MS, direct analysis of solids, and spectroscopic methods for cultural heritage conservation.

An overview article by Adriaens (172) presents the development of analytical methods associated with a European network COST Action G8 for the preservation and conservation of cultural heritage materials, including glasses and ceramics. Specific examples are discussed emphasizing instrument modifications utilized for specific studies. An interesting aspect of this review is a discussion of the need for collaboration between analytical scientists and those familiar with the cultural heritage materials.

Conference proceedings, although lacking the detail of published papers, may also serve as reviews of active research. Conferences focused on specific topics also provide the advantage of bringing many research papers together in a single source. Contact information for the presenters is provided in most conference programs, thereby giving a source for obtaining more detailed scientific information. Several conferences that may be of interest to glass examiners are the Winter Conferences on Plasma Spectrochemistry (2005 Budapest, 2006 Tucson, 2006 Bangkok, 2007 Taormina), American Academy of Forensic Sciences (AAFS 2005 New Orleans, 2006 Seattle, 2007 San Antonio), International Association of Forensic Sciences (IAFS 2005 Hong Kong), European Academy of Forensic Science (2006 Helsinki), Euro-Mediterranean Conference on LIBS (2007 Paris), and LIBS2006 (2006 Montreal). The programs and, in some cases, abstracts of the presentations can be found on the Internet.

The emphasis in this review is on the characterization of soda-lime glasses, since this class of glass is of most interest to the forensic examiner. However, some glasses of other compositions are included when they are of historical interest or the methodology utilized represents a significant advance. There are a large number of additional papers not included in this review concerning topics such as the physics and chemistry of glass production or the characterization of specialty materials, such as glass used for storage of radioactive waste.

Manufacturing Trends

The production of glass for architectural, automotive and specialty uses is a continually evolving process. The chemical composition of both float and container glass has been fairly consistent over the past 30 years or more. However, manufacturers are constantly making small changes to the generic formulas of glass to effect desirable end-use properties at the lowest production costs. Although these changes appear to be relatively minor, they may result in significant changes in measured properties that are forensically important in that they may affect both analytical measurement methodologies and interpretation of the significance of the resulting data. Another significant trend is the increasing globalization of production. A number of new float glass plants are under construction, several of them in Russia, India, and China. The utilization of new sources of raw materials and updated production processes, as well as the production of new product lines by these plants may result in novel materials presented to the glass examiner.

There is a large body of literature concerning the relationships between the composition and the properties of float glasses. Although the process of glass production is well-understood, a number of minor alterations have taken place to improve the quality of the glass or decrease the cost of production. For example, Arbab *et al*. (173) reported that the Fe content of automobile glass is being increased in order to produce a thinner glass without reducing its strength or ability to block UV radiation. The resulting weight reduction improves automobile fuel efficiency. They report that current average window thickness is approximately 4 mm, compared with 6.5 mm 30 years ago. A similar effect can also be accomplished by altering the glass redox ratio while decreasing the Fe content. A shift in the redox ratio produces glass with a more bluish tint. Another example, reported by van Mol *et al*. (174) is the vapor phase addition of tin oxide coatings to the “non-float” side of glass while in the float chamber. These coatings impart high transparency to visible light, high hardness, decreased electrical resistivity, increased reflectivity of IR light, and improved environmental stability. An important aspect of this practice for forensic glass examiners is that Sn coatings will occur on both sides of a float glass treated by this process. In another study, Hoffmann *et al*. (175) studied the diffusion of ions from glass into sol-gel dip-coatings of SiO_2 and Na_2O-SiO_2. They report that Ca and Mg diffuse into the films to satisfy electroneutrality requirements, while several other ions do not migrate. Processes such as these may provide additional points of comparison for glass examination.

These points are only given as a few examples. Many other changes occurring in the flat glass industry are documented on several web sites. A couple of most interest include:

www.glasswebsite.com – the web site of the GANA, the Glass Association of North America provides links to many other sites.
www.glass.org – the web site of NGA, the National Glass Association (mainly U.S.).
www.glassonweb.com – industry news concerning flat glass.
www.glassfiles.com – forum for exchange of information in the international glass industry.

A similar situation exists within the container glass industry. Although the chemical composition of container glass is quite consistent, modifications in this composition are occurring because of the increased incidence of recycling and the desire to reduce melting temperatures to save heating costs and to meet increasingly stringent environmental regulations concerning gaseous emissions. In a research laboratory environment, Bingham and Marshall (176) measured the effects of relatively small changes in the composition of a benchmark soda-lime-silicate glass (UK average composition) on its physical properties. They believe that a 20% to 40% decrease in nitrous oxide emissions can be obtained through fairly minor reformulations. Decreases in sulfur oxides, particulates, and heavy metals could also result from these reformulations. Although additional work is needed before these changes become economically practical in a production line environment, the glass examiner should be aware that compositional changes and the associated changes in physical and optical measurements are a continuing possibility. Ercole (177) puts these considerations into perspective by discussing the complicated relationships between composition and the workability of container glass melts. Another aspect of container glass production is the recycling of other waste materials as cullet in glass making. In one example from Russia, Vlasova and Brylina (178) indicate that a ferrochromium industrial slag can be used in the production of green container glass. In a final example, container glass may be strengthened by dip-coating in a halide base Li solution. An optimum thickness of the exchange layer needed to counteract surface flaws in the glass is 20 to 70 μm. Surface layers produced by dip coating and other processes should be observable using several of the methods discussed further in this review.

Glass Examinations

Physical and Optical Measurements

Fracture matching

The unique morphology of a fracture surface and the ability to match adjoining fracture surfaces unambiguously have long been a well-accepted principle of glass examination. Several studies were conducted that reinforce the idea of uniqueness of fracture matching by studying the mechanisms of crack formation and propagation under a variety of conditions. Guin and Wiederhorn (179) studied cavity formation during crack growth in silicate glasses using atomic force microscopy (AFM). There is no evidence of cavity formation, making it so that fracture surfaces matched to a resolution of better than 0.3 nm normal to the surface and 5 nm parallel to the surface. They conclude that glass fracture is completely brittle. In another study Guin *et al*. (180) found that when cracking of a soda-lime glass occurred under water, some corrosion of the crack tip occurs due to hydroxyl ion exchange along the crack surface. However, fracture surfaces still matched to an accuracy of much better than can be observed by optical microscopy. Wang (181) explains crack propagation and many other properties of silica glasses in terms of long-range density fluctuations (on a nm scale) that arise in the glass-forming liquid. According to this theory, cracks propagate around areas of high density, thereby giving each fracture a unique path.

Refractive index (RI)

There are presentations at nearly every AAFS and IAFS meeting concerning the variations in physical or optical properties, particularly RI, both within and among glass objects. In one such presentation, Roux *et al*. (182) reported the discrimination capability of thickness, RI, microspectrophotometry, and visible fluorescence for differentiating among 86 new and 104 used wine bottles, including several from the same product line. Using all of the tests, they found 99.2% of the bottles could be discriminated, including all bottles of the same type.

Newton *et al*. (183) verify the utility of laboratory annealing as a technique in forensic glass examination. Differing from previous studies that observed complete separation of toughened and laminated samples, they found a continuum of _RI values across their set of 356 glass samples. Rather than attribute the results of older studies to sampling errors as they do, an alternative explanation for the continuum of results observed by Newton *et al*. results from the fact that they considered all laminated glasses to be untoughened. However, they failed to note that some of these glasses are likely made by newer processes, such as press-bending and chemical strengthening, which result in partial strengthening of the glass products. Thus, the changes observed during laboratory annealing, particularly with the short schedule used in their study, take on a more continuous range than those reported in previous studies. The authors' recommendation that _RI values should be treated as continuous in attempts to classify glass seems to be a good one when considering all glasses made by current and older processes.

Becker and Dücking (184) presented the results of a study of changes in RI caused by laser heating (at 213 nm) of glass fragments when they are subjected to laser ablation (LA) for elemental analysis. They only provided preliminary results, but did report that in the immediate crater region, the laser interacts with the glass to produce an edge for which RI cannot readily be measured. For edges near the crater, the variability in RI increases, but the mean is unaffected. Outside of the immediate vicinity of the crater, changes in RI are too small to be considered significant within the precision of measurement.

Elemental composition

It is now widely accepted that quantitative chemical analysis is a powerful tool for both the classification and discrimination of small glass fragments in forensic and archaeometric investigations. Continuing the trend reported in previous reviews, the use of elemental composition has been shown to supplement other more traditional measurements and is taking on increasing importance. The number of publications concerning development and evaluation of analytical methods for elemental determination far exceeds those concerning other forms of glass examination.

In a series of papers, Smrcek (185-187) presented and discussed the changes in major element composition of flat, container, and pressed glasses over the period 1830 to 1990. He utilized data culled from the published literature and manufacturer's archives to assess differences in composition related to manufacturing processes, countries of production (U.S. and Europe only), and production dates. Although some of the trends are partially obscured by opportunistic sampling and variations in data quality over the 160 year time period and large portions of the world are not included in the compilation, Smrcek's papers present much information that is useful to the glass examiner. The general compositional variations noted provide some insight into the interpretation of compositional data, particularly as it relates to attempts to source a glass fragment. The examiner is well reminded to consider that potential sources for a recovered glass fragment may be an object produced by one of these older production methods. Jackson *et al*. (188) discussed attempts to link the compositions of ancient and historic glasses to the birch, oak, and bracken ash used as the alkali source in their production. The variability in the compositions of these ashes and changes in the element distribution that occur during manufacture add to the complexity of classification of historic glasses to specific geographic locations or manufacturing methods.

Papers concerning development of methods for measurement of and forensic interpretation of major, minor, and trace element concentrations in glass have been divided into four categories based on the general type of instrumentation used.

X-ray methods

Methods based on measurement of x-rays continue to be popular for forensic applications, primarily because of their nondestructive nature, minimal sample handling, ability to provide multielemental data on small, irregularly shaped fragments, and relative speed. X-rays can be induced by electron beams (e.g., SEM-EDX), particle beams (e.g., PIXE), and x-rays (e.g., XRF). Traditional x-ray methods for glass analysis are well-developed and accepted and, as a result, few recent papers have been written concerning their use. However, there have been many publications concerning applications in the archaeology and art fields where nondestructive analysis is most important. X-ray methods, particularly XRF, remain routine methods for monitoring glass chemistry for industrial glass formulation studies and during float glass production. Publications dealing with glass production are, for the most part, not included in this review because the utilization of large sheets of glass is not pertinent to most forensic applications.

Comparative studies

Falcone *et al*. (189) compare the analytical sensitivity and accuracy of WDXRF, EPMA, and SEM/EDX for the analysis of small irregularly shaped fragments using a single commercial container glass standard. Their aim was to determine which method provided the best data for source classification of fragments of various sizes. With their instrumental setup, they concluded that WDXRF provides accurate results for most major and minor elements and some trace elements using beads made from a heated mixture of $Li_2B_4O_7$ flux and powdered glass having a mass greater than 50 to 100 mg. At lower masses, the accuracy becomes "unacceptable", but classification is still possible. EPMA was performed only on embedded polished samples down to 0.3 mm in size, for which major and minor elements could be reliably detected. The accuracy was too poor when using nonembedded particles. SEM/EDX gave good accuracy for the main elements and Fe and Cr for embedded samples, but could not reliably measure elements present at concentrations lower than 500-1000 ppm of oxides. Nonembedded particles were analyzed by SEM/EDX, requiring 20 repeat analyses to correct for variations in surface geometry. The accuracy is quite poor, but still allowed a glass fragment of 100 μm in size to be recognized as belonging to a "class" that contains the green soda-lime glass used in this study. These results appear to be fairly typical of those routinely achieved by forensic laboratories that have used these techniques.

In a similar study, Gomez-Morilla *et al*. (190) compared the precision and accuracy of PIXE (2 methods), μ-SRXRF, and EPMA using a BCR-126A glass reference material. They used normal operating parameters for the four instrumental setups, but with similar beam spot sizes of 25 μm^2 except for the EPMA which had to be defocused to avoid alkali element migration in the samples. Each technique provided its own challenges that could be addressed by adjusting operating parameters. Overall, the four methods gave similar results in that the precision based on multiple area measurements on the glass was typically better than 3.5% for most elements. The various deviations can be accounted for by the operating principles of each method. The authors conclude that the four techniques each have advantages and disadvantages, but they complement each other.

X-ray fluorescence

As stated in the 2004 review, recent commercial introduction of micro XRF spectrometers (μ-XRF) has spurred interest in their use for forensic characterization of small particles. Continuing this trend, Miller *et al*. (191) used a polychromator μ-XRF instrument with a spot size set at a nominal 60 μm to characterize single glass reference spheres of various sizes and a defocused beam of approximately 360 μm to characterize bulk samples. By monitoring the Si intensity from borosilicate microspheres of various sizes, they determined that if individual particles are separated by a distance larger than the beam diameter, particles can be detected down to a mass of 0.04 ng and a mean particle diameter of 0.06 μm. With this instrument, they were able to observe the presence of Mg, Al, Si, Ca, Ti, and Fe in larger particles and bulk samples of several reference glasses.

Most μ-XRF studies to date have utilized qualitative data, because quantitation is made difficult by the lack of knowledge of the energy distribution of the excitation spectrum resulting from the use of capillary x-ray focusing lenses. Padilla *et al*. (192) attempted to solve this problem by using a standardless calculation based on a fundamental parameters calculation. They demonstrated the application of their program using glass certified reference materials. Lankosz *et al*. (193) also used a fundamental parameter calculation with an x-ray microbeam of 30 μm to quantify elements in polished slabs of glass standard reference materials. The results of these studies and others presented at forensic conferences indicate that benchtop μ-XRF systems based on capillary optics provide some opportunity to use x-ray spectra qualitatively for forensic glass comparison, but quantitative results have large errors in accuracy and to a lesser degree precision.

There is a strong interest in developing portable μ-XRF systems for field use in the analysis of materials of interest in the cultural heritage and forensic fields. A prototype portable polycapillary-based system capable of focusing the primary x-ray beam down to 70 μm is described by Vittiglio *et al*. (194). This instrument is capable of detecting the presence of a number of elements present at above the 10-100 ppm level in glass matrices. Another portable XRF was developed and utilized for classification of Islamic glasses in Egypt (195,196). This instrument utilizes two x-ray sources and operates with an air path limiting it to detection of elements heavier than Na. Using this instrument the researchers were able to classify the alkali sources of a number of glass objects using intensities and their ratios, including Sr, Ti, Sr/Zr and K/Ca.

Total reflection x-ray fluorescence spectrometry (TXRF) has been found to be effective for discriminating among similar glasses. Nishiwaki, *et al*. (197) utilized a TXRF instrument with a Mo target x-ray tube operated at 40 kV and collimated to a

1 cm beam width for x-ray excitation. They followed the interesting protocol of dissolving a fragment weighing less than 0.5 mg and condensing it to 10 L, which was then dried onto a quartz disk for analysis. They detected 13 elements in most glasses with relative standard deviations of less than 8.1%. Using the ratios of five elements to Sr, they were able to differentiate several glass samples having indistinguishable RIs. One drawback to traditional TXRF instruments is that they are expensive large-scale systems. Rosnach (198) demonstrated the potential utility of a benchtop TXRF system by analysis of soils and sediments and hypothesized that it should be effective for trace element measurements in glass.

In a forensic application, synchrotron radiation XRF (SRXRF) was assessed to determine the level of additional discrimination among sheet glasses that could be obtained over RI alone (199). In this study, triplicate fragments smaller than 1 mm in maximum dimension from 11 sheets were compared in a pairwise manner using cluster analysis of Ca, Fe, Sr, Zr, Ba, and Ce measurements by SRXRF. Using the combined procedure, 515 of 528 pairs could be correctly discriminated. Implementation of this technology in forensic laboratories is limited by the accessibility of synchrotron sources.

An interesting new development during the period covered by this review is the introduction of new instrumentation for performing XRF using the energy-dispersive x-ray detector in a scanning electron microscope. In one development paper, Bjeoumikhov *et al*. (200) describe a microfocus x-ray source that is directed through capillary optics to provide x-ray excitation in the same region of a sample as that impacted by the electron beam used for imaging in an SEM. Because of the large reduction in Bremsstrahlung background with x-rays compared to electron beam excitation, a two order of magnitude improvement in detection limits is realized. With a motorized stage, elemental maps can be generated that coincide with scanning e-beam images. Two commercial applications of this technology have recently been introduced (201). Since most forensic laboratories already have SEMs with existing x-ray detectors, this approach offers the simultaneous capabilities of high resolution imaging and improved sensitivity for minor element detection without the requirement of acquiring a separate XRF instrument.

Electron beam excitation

Scanning electron microscopy, particularly combined with energy dispersive x-ray microanalysis (SEM/EDX) is widely used in forensic laboratories for elemental comparison of evidentiary materials including glass fragments. This is a previously well-characterized technique, so little new literature has appeared on improvements in methodology or application to forensic glass comparisons. A review article by Schreiner *et al*. (202) describes the use of SEM/EDX for the characterization of cultural artifacts within several European programs designed to utilize science and technology to improve the preservation and conservation of their cultural heritage. Examples are given of the use of SEM/EDX measurements for the classification of ancient archaeological glass fragments from Ephesos/Turkey and for investigation of the chemical processes that occurring during the weathering of glass window panels and Medieval glass paintings.

SEM/EDX analysis of glass in controlled studies has been used to determine chemical/physical models for weathering and contamination of glasses in Europe.

Melcher and Schreiner (203) studied two K_2O-CaO-SiO_2 model glasses exposed at 26 test sites throughout Europe. Using SEM/EDX and other methods, they were able to relate the degree of weathering product formation on the surface of the samples with weathering factors, such as the temperature, the relative humidity, and the amounts and composition of acidifying gases in the environment. Carbo *et al*. (204) studied the degradation of buried glass from different archaeological sites in the Valencian region of Spain using a combination of SEM/EDX and square wave voltammetry. Lombardo *et al*. (205,206) exposed soda-lime-silica float glass samples to a polluted urban environment (Paris) for up to two years and studied leaching of alkalis and deposit of soot and soluble salts on the tin bath and top surfaces of the glass. Each of these studies took advantage of the spatial imaging capability of SEM combined with the analytical evaluation of multiple layers of varying thickness and composition using EDX. For the forensic glass examiner, these studies introduce the possibility that analysis of the surfaces of glass objects, including modern float glass, may provide data that could be used to form opinions as to their potential sources.

Researchers in Belgium used electron probe x-ray microanalysis (EPMA) in several archaeological studies of glasses obtained from archaeological sites throughout Europe to determine the origin of glass fragments from the 15th through 17th centuries (207-209). They were able to measure elements present at the percent level in the glasses with enough accuracy to allow classification into production groups or manufacturing methods.

Particle induced x-ray emission

A number of studies have been conducted using proton induced x-ray emission (PIXE), either alone or in combination with other analytical methods, for the analysis of glass of archaeological interest. The principal advantage of PIXE is that it is nondestructive. Weber *et al*. (210) review a number of applications of PIXE and proton induced -ray emission (PIGE) under variable ion beam incident angles. By tilting the sample, they were able to eliminate the integration effect of x-rays or --rays produced at different positions in the beam path and resolve layers in multilayer structures. They applied this approach to measuring silver yellow on a stained glass window with PIXE and measuring the degree of sodium migration in the first 50 m of glass thickness resulting from surface corrosion on a Roman glass sample with PIXE and PIGE. In another study, Weber *et al*. (211) used PIXE to measure the Na concentration near the surface and PIGE to measure the Na concentration in the bulk of stained glass pieces. The age of the glass could be correlated with the two concentration measurements. Mäder and Neelmeijer (212) reviewed the use of PIXE, PIGE, and Rutherford backscattering spectrometry (RBS) to study the atmospheric degradation of historic glass objects. By analyzing the bulk composition of a glass object through a thin surface corrosion coating, they were able to determine museum storage conditions required to prevent further degradation.

Zhang *et al*. (213) studied early glasses unearthed from tombs in south China dating from 475 BC to 220 AD. Using external beam PIXE results and cluster analysis, they were able to attribute the glasses to two systems, PbO-BaO-SiO_2 and K_2O-SiO_2. In a follow-up study (214), they combined PIXE and ICP-AES to expand upon the number of systems that could be characterized and also used the combined data to hypothesize as to sources of some of the raw materials used to make glass in the south of ancient China. Combinations of PIXE, PIGE, and RBS were also used for analysis and partial source classification of 5th century AD Roman glass fragments (215) and 20th century AD U.S. and Austrian Art Nouveau glasses (216). In both cases, the information obtained is used to compare glasses of widely different types and to observe layering structures and weathering features. These studies take good advantage of the nondestructive nature of PIXE, but also demonstrate the interpretive limitations imposed by relatively low sensitivity and quantitative inaccuracy that characterizes PIXE compared to other analytical methods.

mit, *et al*. (217) provide an excellent demonstration of the comparative and combined sourcing power of PIXE/PIGE and laser ablation-inductively coupled-mass spectrometry (LA-ICP-MS) in a study of glasses that had been recovered from Ljubljana and Slovenian castles. PIXE with a 2 MeV proton beam in air was used to determine elements Si and heavier; PIGE at 3.2 MeV was used for Na, Mg, Al, and Si; and the results were normalized using Si. The LA-ICP-MS provided quantitative results for Zr, Hf, and the rare earth elements (REE). The PIXE and PIGE results are used to demonstrate that the glasses were made according to the Venetian style. The REE fingerprinting indicated that different local sources of silica were likely used for the various glasses.

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)

Background Studies

Solution-based ICP methods utilizing either optical emission spectrometry (OES) or MS detection have been utilized by crime labs for the analysis of glass fragments for over 25 years. Recently, ICP-MS coupled with laser ablation (LA-ICP-MS) has received great interest as a method for analysis of glass fragments. Appealing features of LA-ICP-MS include its quantitative multielement capability, its wide linear dynamic ranges, its good accuracy and precision, and its ability to analyze small glass fragments without dissolution or other sample pretreatment. Very few publications concerning solution-based ICP methods for glass analysis have appeared in the recent literature. In contrast, several hundred publications and presentations during the review period present results of fundamental studies and applications of LA-ICP-MS to the analysis of glass.

Despite the growing appeal and current utilization of LA-ICP-MS in forensic laboratories, there remain some fundamental questions concerning processes collectively referred to as elemental fractionation. Fractionation refers to differences in behavior among the various elements and ions resulting from the collective processes of matrix-dependent ablation efficiencies, efficiency of aerosol transport, vaporization and ionization properties of particles within the ICP, and ion extraction yield into the MS. The significance of fractionation is that it can have a significant influence on matrix-matching requirements of standards for calibration (i.e., accuracy) and also on measurement precision and detection limits. Most researchers who are studying the fundamental properties of LA-ICP-MS utilize glass reference materials, such as U.S. National Institute of Standards (NIST) Standard Reference Material, SRM 610 for their work. Glass SRMs are appropriate for these studies because they contain known concentrations of many trace elements and are relatively homogeneous even on the cubic micrometer scale of ablation volumes.

While these studies are not designed for the development of forensic protocols, per se, the fact that glass is used makes the results applicable to the forensic interpretation of LA-ICP-MS data. Therefore, a few examples selected from the many papers published during the review period are briefly mentioned.

G_nther and his coworkers continued their studies into the causes of elemental fractionation in LA-ICP-MS. Of particular pertinence to glass analysis is the doctoral dissertation work of Kuhn. Kuhn and G_nther (218,219) collected aerosol particles produced by LA of various materials including SRM 610 glass and examined them by SEM imaging. Using laser wavelengths of 193nm and 266nm and helium and argon transport gases, nano-particles were formed and condensed during aerosol transport, reaching the plasma as micrometer sized clusters. The size and structure of the clusters is matrix dependent, thereby supporting the need for using matrix-matched standards or making mass transport corrections for analysis of unknown materials. In the case of glass, the availability of nominally matrix-matched standards having a wide range of compositions simplifies the analysis. Kuhn and G_nther (220) further developed this approach into an analytical protocol in which 1% of the particle stream is separated for particle size measurements, which are used to form correction factors for mass measurements. The remainder of the aerosol was used for ICP-MS analysis with NIST SRM 610 glass as an external calibration standard. Using this method, they obtain results agreeing within 10% of those obtained by internal standardization across a variety of matrices including SRM 612 and 614 glasses.

Wang, Hattendorf, and Günther (221) measured the distribution of 36 atoms and 2 oxide ions across and along the main axis of the ICP in a LA-ICP-MS as functions of laser wavelength (193nm and 266nm) using helium and argon transport gases. They produced spatial intensity maps that provide information that can be used to define optimal operating conditions for the use of internal standards in making matrix corrections. For example, He produced lower variability in elemental intensity ratios than Ar, but measured signals were lower because of a wider radial spread of the ions.

Tunheng and Hirata (222) describe two devices that when placed between the LA chamber and the ICP, serve to smooth the measured MS signal. They claim that these devices improve precision and lessen fractionation effects for small crater sizes and low laser firing rates. They attribute this signal improvement to the removal of large particles from the ablation aerosol stream.

Koch *et al*. (223) used near-infrared femtosecond laser ablation of NIST 1412 glass to study the fractionation of Ca, Sr, Ba, and Pb relative to Zn (all present at nominally 4.5 oxide percent in this material). They showed using their LA setup that elemental fractionation is most significant for laser fluxes below 5 J-cm^{-2}. At higher fluxes, particle sizes were more tightly grouped in the 10 – 100nm range. They also observed conglomerates similar to those reported by Kuhn and Günther.

Gonzalez *et al*. (224) studied the temporal response of the MS signal using 213nm laser ablation in LA-ICP-MS. Their central conclusion, which has been widely replicated and has been implemented into most forensic protocols, was that single spot sampling provided better accuracy and precision than a scanning strategy, particularly when the first 15 seconds of sampling time is eliminated from the data analysis. Gonzalez *et al*. (225) showed that precision can be improved using double pulse ablation. The first pulse removes a mass of particles from the sample. After a variable time delay, a second pulse breaks the particle mass into a finer aerosol. The intent of this approach is to minimize matrix-induced fractionation. The use of double pulse ablation has not found widespread use in glass analysis because the consistency of glass matrices minimizes the problems associated with matrix matching seen with other materials. Gonzalez *et al*. (226) measured precision of measurements within a spot and between spots on SRM 610 and 612 samples using repetitive fs and ns 266nm laser ablation. Femtosecond laser sampling provided improved precision because it generated more consistent particle size distributions. They attribute the primary errors in LA to systematic effects (i.e., particle sizes) rather than random counting statistics.

Luo *et al*. (227) attempted to follow the EURACHEM/CITAC Guide for estimation of a budget for the sources of uncertainty for measured Co, La, and Th in NIST and USGS glasses. They utilized commercial LA-ICP-MS systems operating at 193nm with a 60 μm spot size at a 10 Hz rep rate. They conclude that overall uncertainty is dominated by reference value errors, providing good support for the use of this method for forensic glass comparison.

Forensic Applications

The NITE-CRIME Thematic Network completed their interlaboratory studies for development and evaluation of a LA-ICP-MS protocol for determination of 41 elements in a glass fragment (228). They presented the first compositional data for the FGS1 and FGS2 standards that were produced by Schott Glas under the guidance of the BKA for their use in instrument calibration. Results obtained by most labs and elements presented for the BKA's FG10-1 float glass agreed to within 10% of their accepted values. A similar protocol was also published by Smith *et al*. (229). Both protocols recommend use of ^{29}Si as an internal standard and the use of single spot ablation made with a spot size of approximately 50 μm. The NITECRIME study utilized fragments imbedded in a resin and polished, while the Smith procedure merely required placing the cleaned fragments in an ablation cell and the use of helium as a transport gas. Neufeld (230) demonstrated the application of a similar procedure to the determination of 20 elements in 4 SRMs and 3 glass headlamp lenses.

The NFI was the first crime laboratory to validate a LA-ICP-MS protocol according to the ISO/IEC 17025 standards. Berends-Montero, *et al*. (231) reported the results of their validation including measurements of the variation of measured element concentrations as a function of fragment size and across a large pane of glass. The NFI protocol consists of measuring the concentration of 10 elements (others were considered to be less forensically useful) in embedded glass fragments (unless fragments were too small, then they were not embedded) using a 213nm laser in the spot mode and helium carrier gas. A full validation report authored by Montero is available on the NFI website (232). Additional laboratories, including the BKA are in the process of completing validation studies for protocols that are very similar to those already published. As these methods have become more widely accepted, several researchers have begun to look at the distributions of measured element concentrations in a variety of glass objects with the goal of establishing match criteria. Some of these studies are discussed later in this report under the heading of Interpretation.

Previous studies by ICP-OES lead to the general conclusion that glass was homogeneous enough that real variations in element concentrations could not be detected using the mg-sized samples for dissolution techniques. It has been hypothesized that the smaller sample sizes from crater pits in LS methods could reveal heterogeneity not previously seen, thereby leading to a need for new match criteria in glass fragment comparisons. Trejos and Almirall (233,234) utilized LA-ICP-MS to evaluate the microheterogeneity of element concentrations in common containers and automobile and architectural windows. They could not detect spatial heterogeneity in float sheets using a 266nm laser at a spot size of 50 m. They also could detect no particle size effects for free standing particles of a homogeneous standard reference glass from the size of a bulk sample down to a particle size of 0.2mm. However, bottle glass exhibited heterogeneity that was measurable under their analytical conditions.

Umpierrez *et al*. (235) provided data to support the widely-advertised advantage of use of a collision cell to diminish the mass spectral interferences on Fe isotopes. They reported roughly a 100-fold improvement in the detection limits for Fe in glass, down to 0.03 mg-kg^{-1}.using LA-ICP-collision cell MS with methane as the collision gas.

LA-ICP-MS for the determination of lead isotopic composition of several glasses was also reported. Ehrlich *et al*. (236) used a multiple collector MS to make high precision Pb isotope measurements in NIST SRM 610 glass. Schultheis *et al*. (237) used a similar LA-ICP-MS with a high resolution sector field MS to determine Pb isotope ratios in several art nouveau glass samples. The glasses were high lead-borosilicate glasses produced by the U.S. manufacturer, Tiffany. The three samples were readily distinguished by both ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb ratios. No mention was made as to whether the glasses were distinguishable by other methods, although, at least one pair was of different colors.

Laser induced breakdown spectroscopy (LIBS)

LIBS has emerged in the past ten years or so as a promising technique for elemental and molecular characterization of a wide variety of materials, including glass. LIBS is a method based on collection of optical spectra emitted by a material following excitation by a high intensity pulsed laser. The potential advantages of LIBS that have stimulated interest in the forensic community are that it is quick, is practically nondestructive (at least, less so than laser ablation), is capable of measurement of both organic molecules as well as elements, can be constructed in a portable package, and is less expensive and complicated than LA-ICP methods. Studies of LIBS have demonstrated the ability to detect the presence of major constituent elements in several glass types. Almirall *et al*. (238) presented some preliminary data comparing the discrimination capability of LIBS with those of SEM-EDS, XRF, and LA-ICP-MS and they conclude that LIBS has potential utility of in forensic analysis of glass samples. In a review article, Giakoumaki *et al*. (239) discuss the prospects for use of LIBS in archaeological applications and provide several examples involving glass and pottery. Commercial LIBS systems are advertised as applicable to both laboratory and in-line manufacturing plant environments for characterization of defects in glass as well as sorting and quality control applications (240,241).

Bridge *et al*. (242) compare the use of LIBS to that of LA-ICP-MS for discrimination of glass sources in a crime laboratory. Unfortunately, in part because of MS stability problems, they utilize intensity ratio measurements rather than providing element concentrations. The only data provided are the discrimination percentages. They compared pairs of 23 separate glass sources and found that using LIBS alone 82 to 93 percent of sample pairs could be discriminated depending upon the level of significance compared with 83 to 87 percent for RI and 100% for LA-ICP-MS at all significance levels. In combination, LIBS and RI were capable of discriminating between 96 to 99 percent of the pairs.

A number of studies reported the results of exploratory studies of application of LIBS to glass and comparison with other techniques. Galiova *et al*. (243) compare the use of LIBS with LA-ICP-OES using a 266nm laser for both glass and soil samples. They obtained good calibration responses for Si, Na, Mg, and K in glass. Carmona *et al*. (244) explored the possibility of using LIBS to study the surfaces of unweathered and artificially corroded glasses. The soft ablation of the laser allowed successive analyses of the corrosion layers, to include major elements and chromophores, such as Co, Cr, Cu, Fe, and Mn. In their study, they highlighted the advantages of LIBS ablation by comparing results with those obtained by SEM-EDX, XRF, and UV-Vis spectroscopy. In a more recent study, Carmona *et al*. (245) demonstrated the use of LIBS with a 266nm laser to differentiate among three types of leaded glass (10 to 30 wt% PbO) both before and after acid and alkaline attack. Melessanaki *et al*. (246) demonstrated the use of a transportable LIBS instrument to characterize glass beads and similar samples of archaeological interest. Lal *et al*. (247) reported the effects of various setup parameters on the results obtained using LIBS for analysis of pelletized powders of glasses used for vitrification of radioactive wastes.

Despite its relative simplicity and ease of use, LIBS has not yet attained the same level of interest as LA-ICP-MS for forensic comparison of small glass fragments. The reasons generally cited for this are the historical problem of poor accuracy, particularly for small, irregularly shaped particles, and the poor sensitivity, which limits coverage to major elements. Novel approaches, such as the use of double pulsed laser systems as reported by Gautier *et al*. (248) may have the potential to improve the analytical capabilities of LIBS. In the Gautier study and others, it has been observed that two laser pulses with optimized time delay and energy levels result in a significant increase in emission intensities, however accurate quantitation remains problematic.

Other Methods

ICP-OES has been used successfully for forensic analysis of dissolved glass fragments for over 20 years. However, because it is such an established method, few publications using it have appeared recently. Zachariadis *et al*. (249) optimized the acid composition and other digestion parameters for microwave assisted dissolution of glass for ICP-OES analysis. Their protocol was optimized for ancient

Byzantine glass samples, but can also be applied to modern glass. They report good analytical results for 7 elements using 12 wavelengths for NIST SRM 621 and 12 elements at 20 wavelengths in archaeological glass. Wang *et al*. (250) report an ICP-OES method for determination of sulfur at 181.972 nm and phosphorous at 177.434 nm in glass following dissolution. Their reported detection limits and analytical precisions are good enough that the method could be applied to characterization of glass fragments. However, the forensic utility of these elements for glass source comparison is not known. Bian *et al*. (251) coupled a near-IR femtosecond laser with ICP-OES for analysis of glass without dissolution. They found that this arrangement reduces the level of fractionation to the extent that accurate quantitative results could be obtained without the need for matrix-matched standards. Most of their work was for Cu and Zn measurements in brass, but in one worst-case example, they showed linearity of calibration curves for Zn/Cu ratios across the brass and glass matrices.

Pisonero *et al*. (252) describe the development of a radiofrequency glow-discharge source that they coupled to a time-of-flight mass spectrometer (TOFMS) for direct analysis of nonconducting samples such as thick glass shards. They compared two instrumental configurations using homogeneous glasses to determine optimum design and operational characteristics. They detect major and minor elements and isotope ratios within approximately 1% accuracy using a TOFMS with a moderate mass resolving power of 700.

Secondary ion MS (SIMS) continues to show promise in studies of glass of archaeological interest. Dowsett and Adriaens (253) review the application of SIMS to solution of a variety of problems in the area of cultural heritage. Advantages of SIMS are its ppm to ppb sensitivity using very small sample volumes. SIMS can provide surface specific information when used in the static mode and depth profile analysis in the dynamic mode. These authors discuss specific glass applications including source authentication, determination of origin and provenance, and evaluation of weathering processes. In a nontechnical overview, Rutten *et al*. (254) describe the advantages of TOF-SIMS for characterization of several glass samples of historical interest. Of particular interest is the advantage of using SIMS to characterize small opacifying inclusions in glass beads and a decorated vessel from the 10th and 14th centuries. It is hypothesized that the data obtained in these studies will provide new insight into whether Egypt made glass from local materials or imported ready-made raw glass from Mesopotamia. Fearn *et al*. (255) used low-energy SIMS to study the corrosion of glass in a museum environment in an attempt to optimize the storage environment to prevent deterioration of glass objects on display.

In a comprehensive review article, Johnson and Johnson (256) summarize the large number of studies utilizing Mossbauer spectroscopy to measure tin and iron distributions in float glass and relate these distributions to the chemistry occurring during the float process. In addition to an overview of the Mossbauer principle and its application to silicate glasses, they also provide convincing data to show that Sn^{2+} and Fe^{3+} act as conditional glass formers, while Sn^{4+} and Fe^{2+} act as modifiers. The oxidation of Sn from the +2 to +4 state as a function of depth from the float surface at different temperatures allows calculation of the oxygen diffusion coefficient. In tinted glasses containing percent levels of iron, the Fe^{3+} oxidizes the Sn^{2+} to Sn^{4+}.

Colomban *et al*. (257) established a Raman procedure for on-site evaluation of the degree of weathering of stained glass windows. They divided stained glass into four categories based on the Na-K-Ca distributions. Using ion exchange in the laboratory and confirmation of the Raman results with those obtained by IR spectroscopy, optical microscopy, and SEM/EDX, they correlated different weathering rates with the glass type and the changes occurring in the microstructure. The potential demonstrated for measuring the degree of weathering of glass *in situ* may have application in a few forensic situations.

Interpretation, Statistics, And Significance

Transfer and persistence

The number of studies concerning transfer and persistence of glass fragments on the clothing of participants in crime scenarios and the number of particles in the noncriminal environment has dropped from past reporting periods. However, this information is needed for determination of the significance of recovering indistinguishable fragments. Therefore, these studies are being conducted in a few forensic laboratories under case-specific circumstances. Zadora (258) presented the results of such a study in which the number of fragments were measured in a repeated simulated break-in scenario. In this study, the number of fragments recovered depended upon the breaking scenario and the time between breaking and recovery of fragments as expected. Generally, a greater number of fragments were recovered from upper garments of the breaker than on other garments, regardless of the retention ability of the fabrics. This result indicates that distance from the window is the most significant factor in determining number of fragments retained. In another part of this study, the researchers found that 14% of a population of garments not intentionally exposed to glass fragments contain one or two fragments of glass. The authors offer no explanation as to why this result is higher than those reported in most of the previous studies.

One difficulty that has plagued studies of glass transfer is the extreme variability observed in particle recovery under any dynamic test that represents a realistic crime scenario. Hicks *et al*. (259) attempted to minimize this variability by performing a study to develop models for predicting the number of particles transferred to the upper garments of persons in the vicinity of the breaking window by correlation with the number of fragments recovered from a cardboard square of fixed size on an area on the floor at their position. The controlled variables included glass thickness, glass type, method of breaking, and ammunition type for breaking by shooting. Despite the inherent variation in the breaking process, they were able to show at least within the limited range of their variables, that they could make a reasonable estimate of the number of particles transferred to a shooter at a fixed location at time=0 using linear regression models. This study has many limitations, such as not taking into account the variability of collecting fragments from the ground in a fixed area around the breaker's suspected position. However, it is a good first step in attempting to generalize the calculation of the number of recovered fragments, information that is needed for assessing activity level propositions in some approaches for interpretation of evidence. Further work is needed and anticipated by the authors to consider a wider range of breaking parameters, the effects of garment type, and the effects of post-breaking activity.

Statistical studies

David Lucy's book entitled "Introduction to Statistics for Forensic Scientists" (260) provides an excellent introduction to the concepts related to forensic comparison of samples, presented in a readily understandable manner. Lucy presents the advantages of various approaches for evaluating the value of specimens having similar characteristics, as well as the often difficult requirements placed on the examiner as to selection of databases and number of measurements required. Near the end of the book, Lucy gives a good, but brief, summary of how to treat the continuous, multidimensional data that results from modern methods of glass examination.

As in prior reviews, statistical studies can be readily divided into two categories, those based on traditional hypothesis testing and those based on calculation of likelihood ratios (LR). The use of a full Bayesian analysis with calculation of likelihood ratios has been criticized when applied to multivariate data (element concentrations) because of the unavailability of appropriate databases and the large sampling requirements of a multivariate problem. In response, Aitken and his colleagues have produced several papers describing approaches to diminish the complexity of the multivariate problem. Aitken and Lucy (261) used XRF data from 62 windows taken from a single house (5 measurements from each window) to compare five methods of assessment of the value of the evidence. Their data consisted of the log ratios of Ca/Fe, Ca/K, and Ca/Si. The five tests were a multiple *t*-test, a multivariate significance test based on Hotelling's T^2, and three LR tests. The three LRs consist of the ratio of a Hotelling's T^2 statistic to a univariate kernel density estimate, the convolution of two multivariate normal densities, and a within group probability density function to a between group multivariate kernel density estimate. Of the five approaches, the one using the multivariate kernel density estimate of the between group variation is recommended. One consideration in this result is that different window panes are considered to be "different groups" although, since taken from a single house (even from a single window, in some instances), they could have a single origin.

Aitken, *et al*. (262) attempted to reduce the parameterization of a full LR model for multivariate elemental data while still retaining much of the dependence structure. They evaluated the derived models using log ratios of Na, Mg, Al, Si, and Ca to oxygen as determined by SEM/EDX on 130 sheets of float glass. The three-level model that they used resulted in a large proportion of false negatives (nearly 50%) and what they termed a small proportion of false positives (8%), both much worse than the two-level approach of Aitken and Lucy.

Aitken, *et al*. (263) continued their study of the two-level model. Their data consisted of the log concentration ratios of 7 elements to oxygen as determined by SEM/EDX in replicate measurements from 200 glass objects. Because the number of elements exceeded the number of measurements, they used a graphical method of estimating the dependency structure among the variables, thereby reducing the dimensionality of the problem. They showed improved performance of this two-level model compared with previous models, giving 15.2% false positive and 5.5% false negative rates. These three studies demonstrate the need to reduce the dimensionality that results from measurement of element concentrations in order to calculate LRs.

For multiple pairwise comparisons, Pawluk-Kolk *et al*. (264) propose the use of a false discovery rate (FDR) procedure to set significance levels in order to minimize both Type I and Type II errors. Using RI measurements for 72 automobile window glasses, they claim that the Welch modification to the t-test with the FDR correction to the significance level results in fewer total errors than do more traditional hypothesis tests. Their approach may not be applicable in most case work glass comparisons because the number of pairs is typically small, but nevertheless, they present another method of setting match criteria that may distribute Type I and II errors in an acceptable manner.

The increasing interest in measurement of element concentrations in glass, particularly by LA-ICP-MS has also lead to consideration of match criteria for multivariate comparison of glass fragments. Montero (232) used the variations measured in a sheet glass to establish match criteria in the NFI validation study. The NFI match criteria are that 9 or more of 10 measured elements must have ranges that overlap or are have end members that are within two times a standard deviation measure. Becker and Weis (265) reported that the BKA studied various match criteria and found that the best success is obtained when the mean values of 6 measurements for each of 19 elements must agree to within four times an instrumental standard deviation determined by long-term analysis of a standard reference material.

Aeschliman *et al*. (266) used principal components analysis (PCA) of 32 elements in spectra of glass samples obtained by LA-ICP-MS to differentiate 4 “similar” glass samples. They did not utilize concentration measurements made using standards, but instead performed a 2-dimensional PCA plot of the multivariate results. They used 266nm ablation in a line scan at a rate of 50 m-sec^{-1} across a fairly large sample surface and low resolution sector field mass spectrometry (SFMS). Bajic *et al*. (267) used the PCA procedure for comparison of groups of samples having indistinguishable refractive indices. They used a 193nm laser and argon carrier gas with a SFMS instrument in the low resolution mode. They used the full spectrum without calibration for the PCA. All sample pairs were discriminated at a very high level of significance. In both of these studies, no element concentration data are given, so one cannot assess how different the compared samples are. However, the high discriminating power of LA-ICP-MS is strongly indicated and the simplicity of PCA is touted.

International Activities

SWGMAT published its guidelines for glass examinations in Forensic Science Communications (268). The seven published guidelines provide a general overview of glass collection and examination, but only limited protocol details. Notably missing from the SWGMAT glass guidelines is one concerning interpretation of results.

ASTM Method E2330-04, Standard Test Method for Determination of Trace Elements in Glass Samples Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was approved and published (269). This method is applicable to determination of 15 elements in glass, but can readily be modified to include additional elements. It is applicable to measurement of element concentrations in solution following dissolution of small irregularly shaped glass fragments as small as 200 μg.

As discussed previously, several LA-ICP-MS protocols for analysis of glass fragments were produced by international organizations or were validated under international guidelines. The NITE-CRIME committee published the results of their interlaboratory studies and recommended a method for LA-ICP-MS of glass fragments (228). The NFI completed the validation of their LA-ICP-MS protocol under ISO 17025 guidelines and published the results on their website (232).

As this review is being written, the ENFSI EPG best practice guidelines for glass examination are being voted on at their meeting in September 2007. These guidelines consist of six documents concerning the topics: general introduction to glass, determination of refractive index, microscopic techniques for glass examiners, elemental analysis by XRF, elemental analysis by SEM/EDX, and elemental analysis by LA-ICP-MS. As with SWGMAT, the EPG guidelines for evaluation of analytical data and statistical treatment of source level questions is not ready for a group vote at this time.

Acknowledgements

The assistance of Jane Garrison and Yvette Trozzi in performing literature searches and acquiring references is gratefully acknowledged. Appreciation is also expressed to Maureen Bottrell and JoAnn Buscaglia for assistance in reviewing the manuscript.

References

1 Ford Earns EPA Award. Coatings World 2007; (April):16.
2 Spielman S. 2005 Automotive Report. Industrial Paint & Powder 2005; 16(9):81-87.
3 Schoff CK. Organic coatings: the paradoxical materials. Progress in Organic Coatings 2005; 52:21-27.
4 Pianoforte K. Automotive Coatings Market. Coatings World 2007; (March):30-32.
5 BASF Introduces 1K Cathodic Electrodeposition Coating. Coatings World 2007; (May):28.
6 Giles TR. Emerging Technologies in Pretreatment. Coatings World 2006; (October):52-61.

7 Gichuhi T, Novelli W, Erbsloh C, Adams A, DeGroot M, Sapp M, Thorn A. High Performance Organic and Inorganic Zinc-Free Corrosion Inhibitors. European Coatings Journal 2005; 17:47-56.

8 Chouinard T. Changing The Way We Color Our World. Paint and Coatings Industry 2006; (June):26-30.

9 Whitfield K. Who Needs Paint? Automotive Design & Production 2004; (October).

10 Challener C. Pigment Market Sill Performing but Challenges May Impact Intensity of Growth. Journal of Coatings Technology 2006; (October):96-101.

11 Wright T. Metallic Pigments. Coatings World 2007; (June):30-33.

12 Venturini M, Liu W, Sullivan W. Aluminum Effect Pigment Blends. US Patent Appl. US 2005/0252416 A1, Nov. 17, 2005.

13 Yates MJ, Mitchell, J. Optimising formulations. Polymers Paint Colour Journal 2006; (December):24-26.

14 Pianoforte K. High Performance Pigments. Coatings World 2007; (August):28-31.

15 Cooper RJ, Camp PJ, Henderson DK, Lovatt PA, Nation DA, Richards S, Tasker PA. The binding of phosphonic acids at aluminium oxide surfaces and correlation with passivation of aluminum flake. Dalton Trans. 2007:1300-1308.

16 Kerr S. Surface-Treated Metallic Pigments. Paint and Coatings Industry 2006; (August):72-78.

17 Brussaard Y, Genn B. High-Performance Titanium Color Pigments. Paint and Coatings Industry 2004; (October):34-40.

18 Frischmann L, Klose S. Does Yellow Beat White? Paint and Coatings Industry 2007; (July):106-108.

19 Wilker G. Progress in the Field of Yellow Organic Pigments. Paint and Coatings Industry 2004; (May):76-80.

20 Schmid R, Mronga N. A New Generation of Sparkling Effect Pigments. Paint and Coatings Industry 2004; (October):118-122.

21 Parker B. Pigments Exhibiting Diffractive Light Interference. Paint and Coatings Industry 2004; (September):60-67.

22 Balber F. Black Pigment Compositions. US Patent Appl. US 2005/0014863 A1, Jan. 20, 2005.

23 BASF Offers Functional Black Pigments for Solar Heat Management. Coatings World 2006; (October):50.

24 Hope M. IR-technology-based additives keep surfaces cool. Plastics Engineering, 2006; 1:8.

25 Milmo S. Smart paints are not catching on easily. Coatings World 2006; (October):24-25.

26 Hogan J. Smog-busting paint will be a breath of fresh air. New Scientist 2004; 2433.

27 Yadav T. Nanotechnology Enables Breakthrough Coatings. Paint and Coatings Industry 2004; (May):56-58.

28 Cayton RH. Nanoparticle Composites for Coating Applications. Paint and Coatings Industry 2004; (May):48-54.

29 Blanco A. Microspheres aid coating formulations. Plastics Engineering 2005; 61:6-7.

30 Shinkareva EV, Safonova, AM. Conducting and Heat-Insulating Paintwork Materials Based on Nickel-Plated Glass Spheres. Glass and Ceramics 2006; 63(1-2):32-33.

31 Rogers J, Moyer B, Kalscheur G. Advanced Light Stabilizers for the Next Century's Needs. Journal of Coatings Technology 2007; (February):82-86.
32 Bradford CJ. The Innovation of Hyper-Dispersible Hectorite Clays for Automotive Applications. Paint and Coatings Industry 2004; (May):66-75.
33 Koleske JV, Springate R, Brezinski D. 2005 Additives Guide. Paint and Coatings Industry 2005; (May):34-110.
34 Milmo S. New pigment technologies help drive growth in use of color in Europe. Ink World 2004; 10(1):21-22.
35 Silver Continues its Reign Among Automotive Colors. Journal of Coatings Technology 2007; (February):19.
36 Silver Starts to Shift, but Remains Top North American Vehicle Color in 2006, According to PPG Industries. Paint and Coatings Industry 2007; (June):36-38.
37 BASF Coatings' Color Trend Forecast. Paint and Coatings Industry 2007; (June):32-33.
38 Wright T. Marine Coatings Market. Coatings World 2007; (May):40-44.
39 Srinivasan M, Swain GW. Managing the Use of Copper-Based Antifouling Paints. Environmental Management 2007; 39(3):423-441.
40 Lawrence G. Marine Coatings:Components and Analysis. Microscope 2005; 53 (2):69-72.
41 PPG Industries Patents Anti-Fouling Coatings Containing Silica-Coated Copper. Coatings World 2007; (June):14.
42 Tadros AB. Application of natural materials in marine paint formulations. Pigment & Resin Technology 2005; 34(6):340-346.
43 Borst S, Laubender T, Snyder S, Greene J. Adding Value to Industrial Coatings by Using Epoxy Functional Silicone Resins. Paint and Coatings Industry 2004; (October):132-147.
44 Procopio LJ, Larson GR, Rosano, WJ. Low-VOC Waterborne Coatings for Use in Industrial Maintenance Painting. Journal of Coatings Technology 2007; (February):50-59.
45 Kukackova A. Using the Si-O strength. European Coatings Journal 2007; (6):54-59.
46 Skelton HA. History of Pigment Use in Western Art Part 1. Paint and Coatings Industry 2004; (January).
47 Skelton HA. History of Pigment Use in Western Art Part 2. Paint and Coatings Industry 2004; (October):82-107.
48 Adriaens A. Non-destructive analysis and testing of museum objects: An overview of 5 years of research. Spectrochimica Acta Part B 2005; 60B(1):1503-1516.
49 Cultural Heritage Conservation and Environmental Impact Assessment by Non-Destructive Testing and Micro-Analysis. Leiden, Netherlands: A.A. Balkema Publishers, 2005.
50 Ambers J. Raman analysis of pigments from the Egyptian Old Kingdom. Journal of Raman Spectroscopy 2004; 35:768-773.
51 Andrikopoulos KS, Daniilia S, Roussel B, Janssens K. In-vitro validation of a mobile Raman-XRF micro-analytical instrument's capabilities on the diagnosis of Byzantine icons. Journal of Raman Spectroscopy 2006; 37:1026-1034.
52 Brysbaert A, Vandenabeele P. Bronze Age painted plaster in Mycenaean Greece: a pilot study of the testing and application of micro-Raman spectroscopy. Journal of Raman Spectroscopy 2004; 35:686-693.

53 Burgio L, Clark RJH, Sheldon L, Smith GD. Pigment identification by spectroscopic means: evidence consistent with the attribution of the painting "Young Woman Seated at a Virginal" to Vermeer. Anal. Chem. 2005; 77(5):1261-1267.

54 Castro K, Sarmiento A, Princi E, Pérez-Alonso M, Rodríguez-Laso MD, Vicini S, Madariaga JM, Pedemonte E. Vibrational spectroscopy at the service of industrial archaeology: Nineteenth-century wallpaper. Trends in Analytical Chemistry 2007; 26(5):347-359.

55 Castro K, Perez-Alonso M, Rodriguez-Laso MD, Fernandez LA, Madariaga JM. On-line FT-Raman and dispersive Raman spectra database of artists' materials (e-VISART database). Anal. Bioanal. Chem. 2005; 382(2):248-258.

56 Centeno SA, Mahon D, Wypyski MT. Examination of a Spanish medieval processional crucifix substantially reworked in the 20th century. Journal of Raman Spectroscopy 2004; 35:774-780.

57 Chen K, Leona M, Vo-Dinh KC, Yan F, Wabuyele MB, Vo-Dinh T. Application of surface-enhanced Raman scattering (SERS) for the identification of anthraquinone dyes used in works of art. Journal of Raman Spectroscopy 2006; 37:520-527.

58 Raman Spectroscopy in Archaeology and Art History. Cambridge, United Kingdom: The Royal Society of Chemistry, 2005.

59 Edwards HG, Wolstenholme R, Wilkinson, DS, Brooke C, Pepper M. Raman spectroscopic analysis of the enigmatic Comper pigments. Anal. Bioanal. Chem. 2007; 387(6):2255-2262.

60 Edwards HG, Nik Hassan NF, Middleton, PS. Anatase--a pigment in ancient artwork or a modern usurper? Anal. Bioanal. Chem. 2006; 384(6):1356-1365.

61 Edwards H, Benoy TJ. The de Brécy Madonna and Child tondo painting: a Raman spectroscopic analysis. Anal. Bioanal. Chem. 2007; 387(3):837-846.

62 Hernanz A, Gavira-Vallejo JM, Ruiz-López JF. Introduction to Raman microscopy of prehistoric rock paintings from the Sierra de las Duerdas, Cuenca, Spain. Journal of Raman Spectroscopy 2006; 37:1054-1062.

63 Villar S, Edwards, H, Medina J, Perez FR. Raman spectroscopic analysis of mediaeval wall paintings in the Palencia region, Spain. Journal of Raman Spectroscopy 2006; 37:1078-1085.

64 Middleton AP, Edwards H, Middleton PS, Ambers J. Identification of anatase in archaeological materials by Raman spectroscopy: implications and interpretations. Journal of Raman Spectroscopy 2005; 36:984-987.

65 Ortega-Avilés M, Vandenabeele P, Tenorio, D, Murillo G, Jiménez-Reyes M, Gutiérrez N. Spectroscopic investigation of a 'Virgin of Sorrows' canvas painting: A multi-method approach. Analytica Chimica Acta 2005; 550:164-172.

66 Pagès-Camagna S, Calligaro T. Micro-PIXE and micro-Raman spectrometry applied to a polychrome wooden altarpiece from the 16th century. Journal of Raman Spectroscopy 2004; 35:633-639.

67 Vandenabeele P, Weis TL, Grant ER, Moens LJ. A new instrument adapted to in situ Raman analysis of objects of art. Anal. Bioanal. Chem. 2004; 379(1):137-142.

68 Vandenabeele P, Lambert K, Matthys S, Schudel W, Bergmans A, Moens L. In situ analysis of mediaeval wall paintings: a challenge for mobile Raman spectroscopy. Anal. Bioanal. Chem. 2005; 383(4):707-712.

69 Vandenabeele P, Tate J, Moens L. Non-destructive analysis of museum objects by fibre-optic Raman spectroscopy. Anal. Bioanal. Chem. 2007; 387(3):813-819.

70 van der Weerd J, Smith GD, Firth S, Clark RJH. Identification of black pigments on prehistoric Southwest American potsherds by infrared and Raman microscopy. Journal of Archaeological Science 2004; 31:1429-1437.

71 Wang X, Wang C, Yang J, Chen L, Feng J, Shi M. Study of wall-painting pigments from Feng Hui Tomb by Raman spectroscopy and high-resolution electron microscopy. Journal of Raman Spectroscopy 2004; 35:274-278.

72 Weis TL, Jiang Y, Grant ER. Toward the comprehensive spectrochemical imaging of painted works of art: a new instrumental approach. Journal of Raman Spectroscopy 2004; 35:813-818.

73 Angelini E, Grassini S, Corbellini S, Ingo GM, de Caro T, Plescia P, Riccucci C, Bianco A, Agostini S. Potentialities of XRF and EIS portable instruments for the characterisation of ancient artefacts. Applied Physics A 2006; 83:643-649.

74 Ardid M, Ferrero JL, Juanes D, Lluch JL, Roldán C. Comparison of total-reflection X-ray fluorescence, static and portable energy dispersive X-ray fluorescence spectrometers for art and archeometry studies. Spectrochimica Acta Part B 2004; 59:1581-1586.

75 Bonizzoni L, Galli A, Poldi G, Milazzo M. In situ non-invasive EDXRF analysis to reconstruct stratigraphy and thickness of Renaissance pictorial multilayers. X-Ray Spectrometry 2007; 36:55-61.

76 Cesareo R, Castellano A, Buccolieri G, Quarta S, Marabelli M. Giotto in the Chapel of the Scrovegni: EDXRF analysis of the golden haloes with portable equipment. X-Ray Spectrometry 2004; 33:289-293.

77 Green RL,Watling RJ. Trace element fingerprinting of Australian ocher using laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) for the provenance establishment and authentication of indigenous art. J. Forensic Sci. 2007; 52(4):851-859.

78 Ida H, Kawai J. Portable x-ray fluorescence spectrometer with a pyroelectic x-ray generator. X-Ray Spectrometry 2005; 34:225-229.

79 Kanngießer B, Malzer W, Rodriguez AF, Reiche, I. Three-dimensional micro-XRF investigations of paint layers with a tabletop setup. Spectrochimica Acta Part B 2005; 60:41-47.

80 Krug K, Dik J, Den Leeuw M, Whitson A, Tortora J, Coan P, Nemoz C, Bravin, A. Visualization of pigment distributions in paintings using synchrotron K-edge imaging. Applied Physics A 2006: 83:247-251.

81 Miliani C, Rosi F, Borgia I, Benedetti P, Brunetti BG, Sgamellotti A. Fiber-optic Fourier Transform Mid-Infrared Reflectance Spectroscopy: A Suitable Technique for in Situ Studies of Mural Paintings. Applied Spectroscopy 2007; 61(3):293-299.

82 Nobuyuki, K. Analytical Study of Paintings by X-ray Radiography and Spectroscopy. In: Uda M. et al., editors. X-rays for Archaeology. Springer, 2005: 253-258.

83 Pavlidou E, Arapi M, Zorba T, Anastasiou M, Civici N, Stamati F, Paraskevopoulos KM. Onoufrios, the famous XVI's century iconographer, creator of the "Berati School": studying the technique and materials used in wall paintings of inscribed churches. Applied Physics A 2006; 83:709-717.

84 Sanchez del Río M, Martinetto P, Somogyi A, Reyes-Valerio C, Dooryhée E, Peltier N, Alianelli L, Moignard B, Pichon L, Calligaro T, Dran, JC.

Microanalysis study of archaeological mural samples containing Maya blue pigment. Spectrochimica Acta Part B 2004; 59:1619-1625.

85 Szökefalvi-Nagy Z, Demeter I, Kocsonya A, Kovács I. Non-destructive XRF analysis of paintings. Nuclear Instruments and Methods in Physics Research B 2004; 226:53-59.

86 Carretti E, Dei L, Macherelli A, Weiss RG. Rheoreversible polymeric organogels: the art of science for art conservation. Langmuir 2004; 20(20):8414-8418.

87 Genestar C, Pons C. Earth pigments in painting: characterization and differentiation by means of FTIR spectroscopy and SEM-EDS microanalysis. Anal Bioanal Chem 2005; 382:269-274.

88 Haswell R, Carlyle L, Mensch K. Van Gogh's Painting Grounds: Quantitative Determination of Bulking Agents (Extenders) Using SEM/EDX. Microchimica Acta 2006; 155:163-167.

89 Higgitt C, Plater J. Old masters in the spotlight. Chemistry World 2004; 76:40-45.

90 Katsibiri O, Boon JJ. Investigation of the gilding technique in two port-Byzantine wall paintings using micro-analytical techniques. Spectrochimica Acta Part B 2004; 59:1593-1599.

91 Keune K, Boon J. Analytical imaging studies clarifying the process of the darkening of vermilion in paintings. Anal. Chem. 2005; 77(15): 4742-4750.

92 Mazzeo R, Cam D, Chiavari G, Fabbri D, Ling H, Prati S. Analytical study of traditional decorative materials and techniques used in Ming Dynasty wooden architecture. The case of the Drum Tower in Xi-an, P.R. of China. Journal of Cultural Heritage 2004; 5:273-283.

93 van Loon A, Boon, JJ. Characterization of the deterioration of bone black in the 17th century Oranjezaal paintings using electron-microscopic and micro-spectroscopic imaging techniques. Spectrochimica Acta Part B 2004; 59:1601-1609.

94 White R, Phillips MR, Thomas P, Wuhrer R. In-Situ Investigation of Discolouration Processes Between Historic Oil Paint Pigments. Microchimica Acta 2006; 155:319-322.

95 Grassi N, Migliori A, Mandò PA, del Castillo HC. Differential PIXE measurements for the stratigraphic analysis of the painting Madonna dei fusi by Leonardo da Vinci. X-Ray Spectrometry 2005; 34:306-309.

96 Reiche I, Britzke R, Bukalis G, Reinholz U, Weise H-P, Gadebusch, RD. An external PIXE study: Mughal painting pigments. X-Ray Spectrometry 2005; 34:42-45.

97 Duwe S, Neff H. Glaze and slip pigment analyses of Pueblo IV period ceramics from east-central Arizona using time of flight-laser ablation-inductively coupled plasma-mass spectrometry (TOF-LA-ICP-MS). Journal of Archaeological Science 2007; 34:403-414.

98 Dupuis G, Menu M. Quantitative characterisation of pigment mixtures used in art by fibre-optics diffuse-reflectance spectroscopy. Applied Physics A 2006; 83:469-474.

99 Burakov V, Kiris V, Klyachkovskaya A, Kozhukh N, Raikov S. Application of emission spectrometer with laser sampler to microanalysis of pigments from Hubert Robert's canvas painting. Microchimica Acta 2007; 156:337-342.

100 Chiavari G, Fabbri D, Prati S, Zoppi A. Identification of Indigo Dyes in Painting Layers by Pyrolysis Methylation and Silylation. A Case Study: "The Dinner of Emmaus" by G. Preti. Chromatographia 2005; 61(7/8):403-408.

101 Altavilla C, Ciliberto E. Copper resinate: an XPS study of degradation. Applied Physics A 2006; 83:699-703.

102 Kouloumpi E, Lawson G, Pavlidis V. The contribution of gas chromatography to the resynthesis of the post-Byzantine artist's technique. Anal. Bioanal. Chem. 2007; 387(3):803-812.

103 Pitthard V, Finch P, Bayerova T. Direct chemolysis-gas chromatography-mass spectrometry for analysis of paint materials. J. Sep. Sci. 2004; 27(3):200-208.

104 Pitthard V, Stanek S, Griesser M, Muxeneder T. Gas Chromatography-Mass Spectrometry of Binding Media from Early 20th Century Paint Samples from Arnold Schonberg's Pallete. Chromatographia 2005; 62(3/4):175-182.

105 Pitthard V, Griesser M, Stanek S. Methodology and application of GC/MS to study altered organic binding media from objects of the Kunsthistorisches Museum, Vienna. Ann. Chim. 2006; 96(9-10):561-573.

106 P_ikryl P, Havlícková L, Pacáková V, Hradilová J, _tulik K, Hofta P. An evaluation of GC-MS and HPLC-FD methods for analysis of protein binders in paintings. J. Sep. Sci. 2006; 29(17):2653-2663.

107 Cappitelli F. THM-GCMS and FTIR for the study of binding media in Yellow Islands by Jackson Pollock and Break Point by Fiona Banner. Journal of Analytical and Applied Pyrolysis 2004; 71:405-415.

108 Cappitelli F, Koussiaki F. THM-GCMS and FTIR for the investigation of paints in Picasso's Still Life, Weeping Woman and Nude Woman in a Red Armchair from the Tate Collection, London. Journal of Analytical and Applied Pyrolysis 2006; 75:200-204.

109 Scalarone D, Chiantore O. Separation techniques for the analysis of artists' acrylic emulsion paints. J. Sep. Sci. 2004; 27(4):263-274.

110 van Ham R, van Vaeck L, Adams F, Adriaens A. Feasibility of analyzing molecular pigments in paint layers using TOF S-SIMS. Journal of Analytical and Bioanalytical Chemistry 2005; 383:991-997.

111 Baglioni P, Giorgi R. Soft and hard nanomaterials for restoration and conservation of cultural heritage. Soft Matter 2006; 2:293-303.

112 Spyros A, Anglos D. Studies of aging in oil paintings by 1D and 2D NMR spectroscopy. Anal. Chem. 2004; 76(17):4929-4936.

113 Chiavari G, Fabbri D, Prati S. Effect of pigments on the analysis of fatty acids in siccative oils by pyrolysis methylation and silylation. Journal of Analytical and Applied Pyrolysis 2005; 74:39-44

114 De la Cruz-Cañizares J, Doménech-Carbó MT, Gimeno-Adelantado JV, Mateo-Castro R, Bosch-Reig, F. Study of Burseraceae resins used in binding media and varnishes from artworks by gas chromatography-mass spectrometry and pyrolysis-gas chromatography-mass spectrometry. Journal of Chromatography A 2005; 1093:177-194.

115 Andreotti A, Bonaduce I, Colombini MP, Gautier G, Modugno F, Ribechini E. Combined GC/MS analytical procedure for the characterization of glycerolipid, waxy, resinous, and proteinaceous materials in a unique paint microsample. Anal. Chem. 2006; 78(13):4490-4500.

116 Erhardt D. Materials science: the art of restoration. Nature 2004; 431(7007):410-411.

117 Harrison SM, Kaml I, Rainer F, Kenndler E. Identification of drying oils in mixtures of natural binding media used for artistic and historic works by capillary electrophoresis. Journal of Separation Science 2005; 28:1587-1594.

118 Hynek R, Kuckova S, Hradilova J, Kodicek M. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry as a tool for fast identification of protein binders in color layers of paintings. Rapid Communications in Mass Spectrometry 2004; 18:1896-1900.

119 Schnell A, Goretzki L, Kaps C. IR-Laser Effects on Pigments and Paint Layers. In: Dickmann K, Fotakis C, Asmus J F., editors. Lasers in the Conservation of Artworks, Volume 100:291-296.

120 Kendix E, Nielsen OF, Christensen MC. The use of micro-Raman spectroscopy in architectural paint analysis. Journal of Raman Spectroscopy 2004; 35:796-799.

121 Ariese F. Book review: Raman spectroscopy in archeology and art history. Trends in Analytical Chemistry 2005; 24(10):894-895.

122 Ryland SG, Jergovich TA, Kirkbride, KP. Current Trends in Forensic Paint Examination. Forensic Science Review 2006: 18(97):98-117.

123 Saferstein R. Hairs, Fibers, and Paint. In Criminalistics: An Introduction to Forensic Science, 8th ed. Upper Saddle River, NJ: Pearson Prentice Hall, 2004:194-232.

124 Saferstein R. Hairs, Fibers, and Paint. In Criminalistics: An Introduction to Forensic Science, 9th ed. Upper Saddle River, NJ: Pearson Prentice Hall, 2007:206-245.

125 Kubic TA, Petraco N. Microanalysis and Examination of Trace Evidence. In: James SH, Nordby JJ., editors. Forensic Science: An Introduction to Scientific and Investigative Techniques, 2nd ed. Boca Raton, FL: CRC Press, 2005:315-340.

126 Edmondstone G, Hellman J, Legate K, Vardy G, Lindsay E. An Assessment of the Evidential Value of Automotive Paint Comparisons. Canadian Society of Forensic Science Journal 2004; 37(3):147-153.

127 Buzzini P, Massonnet G, Birrer S, Egli NM, Mazzella W, Fortini, A. Survey of crowbar and household paints in burglary cases-population studies, transfer and interpretation. Forensic Sci. Int. 2005; 152(2-3):221-234.

128 Zieba-Palus J, Trzcinska BM. Paint as Evidence - Selected Cases. Problems of Forensic Sciences 2004; LVII:124-138.

129 Giang Y-S, Cho L-L, Wang S-M, Chiu L-Y. Identification of a tiny, thin and smeared dot of red paint in a fatal traffic accident case by Fourier transform-infrared microspectroscopy. Forensic Science Journal 2005; 4:47-54.

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

131 Zieba-Palus J. Examination of spray paints by the use of reflection technique of microinfrared spectroscopy. Journal of Molecular Structure 2005; 744-747:229-234.

132 Ahmad S, Ashraf SM, Sharmin E, Mohomad A, Alam M. Synthesis, Formulation, and Characterization of Siloxane-Modified Epoxy-Based Anticorrosive Paints. Journal of Applied Polymer Science 2006; 100:4981-4991.

133 Suzuki EM, McDermot MX. Infrared spectra of U.S. automobile original finishes. VII. Extended range FT-IR and XRF analyses of inorganic pigments in situ--nickel titanate and chrome titanate. J. Forensic Sci. 2006; 51(3):532-547.

134 Verbi FM, Pereira-Filho ER, Bueno M. Use of X-Ray Scattering for Studies with Organic Compounds: a Case Study Using Paints. Microchimica Acta 2005; 150:131-136.

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

136 Bell SE, Fido LA, Speers SJ, Armstrong WJ. Rapid forensic analysis and identification of "lilac" architectural finishes using Raman spectroscopy. Appl. Spectrosc. 2005; 59(1):100-108.

137 Bell SE, Fido LA, Speers SJ, Armstrong WJ, Spratt S. Forensic analysis of architectural finishes using fourier transform infrared and Raman spectroscopy, part I: the resin bases. Appl. Spectrosc. 2005; 59(11):1333-1339.

138 Bell SE, Fido LA, Speers SJ, Armstrong WJ, Spratt S. Forensic analysis of architectural finishes using fourier transform infrared and Raman spectroscopy, part II: white paint. Appl. Spectrosc. 2005; 59(11):1340-1346.

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

140 Zieba-Palus J, Borusiewicz R. Examination of multilayer paint coats by the use of infrared, Raman and XRF spectroscopy for forensic purposes. Journal of Molecular Structure 2006; 792-793:286-292.

141 Ito K, Kato T, Ona T. Rapid viscosity determination of waterborne automotive paint emulsion system by FT-Raman spectroscopy. Vibrational Spectroscopy 2004; 35:159-163.

142 Cramer, WR. Interference Pigments- Description and Characterization. Paint and Coatings Industry 2007; (January):42-51.

143 Nadal, ME, Early, EA Color Measurements for Pearlescent Coatings. Color Research and Application 2004; 29(1):38-42.

144 Takagi A, Watanabe A, Baba G. Prediction of Spectral Reflectance Factor Distribution of Automotive Paint Finishes. Color Research and Application 2005; 30(4):275-282.

145 Kopchick KA, Bommarito CR. Color analysis of apparently achromatic automotive paints by visible microspectrophotometry. J. Forensic Sci. 2006; 51(2):340-343.

146 Payne G, Wallace C, Reedy B, Lennard C, Schuler R, Exline D, Roux C. Visible and near-infrared chemical imaging for the analysis of selected forensic samples. Talanta 2005; 67:334-344.

147 Flynn K, O'Leary R, Lennard C, Roux C, Reedy B. Forensic applications of infrared chemical imaging: multi-layered paint chips. J. Forensic Sci. 2005; 50(4):832-841.

148 Schreiner M, Melcher M, Uhlir K. Scanning electron microscopy and energy dispersive analysis: applications in the field of cultural heritage. Anal. Bioanal. Chem. 2007; 387(3):737-747.

149 Hochleitner B, Schreiner M, Drakopoulos M, Snugureva I, Snigirev A. Analysis of paint layers by light microscopy, scanning electron microscopy and synchrotron induced x-ray micro-diffraction. In: Van Grieken R, Janssens K., editors. Cultural Heritage Conservation and Environmental Impact Assessment

by Non-Destructive Testing and Micro-Analysis. London: Taylor & Francis, 2005: 171-182.

150 Deconinck I, Latkoczy C, Günther D, Govaert F, Vanhaecke F. Capabilities of laser ablation-inductively coupled plasma mass spectrometry for (trace) element analysis of car paints for forensic purposes. Journal of Analytical Atomic Spectrometry 2006; 21:279-287.

151 Smith K, Horton K, Watling R, Scoullar N. Detecting art forgeries using LA-ICP-MS incorporating the in situ application of laser-based collection technology. Talanta 2005; 67:402-413.

152 Lopez-Molinero A, Cebrian MA, Castillo JR. FAAS Determination of Metals in Complex Paint Driers using Microwave Sample Mineralization. Atomic Spectroscopy 2004; 25(1):44-51.

153 Jancik D, Mashlan M, Zboril R, Adetunji J, Nomura K. A new fast type of Mössbauer spectrometer for the rapid determination of iron-bearing minerals used in the paint industry. Czechoslovak Journal of Physics 2005; 55(7):803-811.

154 Wampler T. Practical applications of analytical pyrolysis. Journal of Analytical and Applied Pyrolysis 2004; 71:1-12.

155 Wampler T. Analysis of Automobile Paints by Pyrolysis-GC-MS. LC-GC North America 2005; 23(1):579.

156 Wampler T. Analysis of Automobile Paints Using Pyrolysis-GC/MS; Field Application report, Perkin Elmer:www.perkinelmer.com

157 Burns DT, Doolan K. A comparison of pyrolysis-gas chromatography-mass spectrometry and fourier transform infrared spectroscopy for the characterisation of automotive paint samples. Analytica Chimica Acta 2005; 539:145-155.

158 Burns DT, Doolan K. The automation of the acquisition and evaluation of pyrolysis-gas chromatography-mass spectrometry data for paint samples. Analytica Chimica Acta 2006; 571:25-29.

159 Burns DT, Doolan K. The discrimination of automotive clear coat paints indistinguishable by Fourier transform infrared spectroscopy via pyrolysis-gas chromatography-mass spectrometry. Analytica Chimica Acta 2005; 539:157-164.

160 Burns DT, Doolan K. The Discrimination of White Exterior Paints by Pyrolysis-Gas Chromatography-Mass Spectrometry. Chemia Analityczna (Warsaw) 2006; 51:541-550.

161 Jansson KD, Zawodny CP, Wampler T. Determination of polymer additives using analytical pyrolysis. Journal of Analytical and Applied Pyrolysis 2007; 79:353-361.

162 Wampler T. Polymer additive analysis using multi-step thermal sampling-GC/MS. Lab Plus International 2004; 6-9.

163 Stachura S, Desiderio VJ, Allison J. Identification of organic pigments in automotive coatings using laser desorption mass spectrometry. J. Forensic Sci. 2007; 52(3):595-603.

164 Reidy LJ, Meier-Augenstein W, Kalin RM. 13C-Isotope ratio mass spectrometry as a potential tool for the forensic analysis of white architectural paint: a preliminary study. Rapid Commun. Mass Spectrom. 2005; 19(13):1899-1905.

165 Benson S, Lennard C, Maynard P, Roux C. Forensic applications of isotope ratio mass spectrometry--a review. Forensic Sci. Int. 2006; 157(1):1-22.

166 Lemons, WC. Color Control in Electrocoat. Coatings World 2006; (October):80-87.

167 Almirall JR, Trejos T. Advances in the Forensic Analysis of Glass Fragments with a Focus on Refractive Index and Elemental Analysis. Forensic Science Review 2006; 18(2):73-96.

168 Brettell TA, Butler JM, Saferstein R. Review in Forensic Science. Analytical Chemistry 2005; 77(12):3839-3860.

169 Brettell TA, Butler JM, Almirall JR. Forensic Science. Analytical Chemistry 2007; 79(12):4365-4384.

170 Fisher A, Goodall P, Hinds MW, Nelms SN, Penny, DM. Atomic spectrometry update. Industrial analysis: metals, chemicals, and advanced materials. Journal of Analytical Atomic Spectrometry 2004; 19(12):1567-1595.

171 Charlton B, Fisher AS, Goodall PS, Hinds MW, Lancaster S, Salisbury M. Atomic spectrometry update. Industrial analysis:metals, chemicals and advanced materials. Journal of Analytical Atomic Spectrometry 2006; 21(12):1431-1471.

172 Adriaens A. Non-destructive analysis and testing of museum objects:An overview of 5 years of research. Spectrochimica Acta, Part B 2005; 60(12):1503-1516.

173 Arbab M, Shelestak LJ, Harris CS. Value-added flat-glass products for the building, transportation markets, part 1. American Ceramic Society Bulletin 2005; 84(1):30-35.

174 Van Mol AMB, Alcott GR, Allendorf MO. Tin oxide precursor chemistry and its link to coating properties. American Ceramic Society Bulletin 2005; 84(1):37-41.

175 Hoffmann U, Heide G, Frischat GH. Reactions between sol-gel coatings and some technical glass substrates during consolidation. Journal of Non-crystalline Solids 2004; 351(43-45):3562-3569.

176 Bingham PA,Marshall M. Reformulation of container glasses for environmental benefit through lower melting termperatures. Glass Technology 2005; 46(1):11-19.

177 Ercole P. Workability of soda-lime glass in the production of containers. International glass journal 2004; 130:18-29.

178 Vlasova SG, Brylina TE. Green container glass based on ferrochromium industrial slag. Class and ceramics 2005; 62(9-10): 276-278.

179 Guin J-P, Wiederhorn SM. Fracture of silicate glasses: ductile or brittle? Physical Review Letters 2004; 9221:5502.

180 Guin J-P, Wiederhorn SM, Fett T. Crack-tip structure in soda-lime-silicate glass. Journal of the American Ceramic Society 2005; 8(3):652-659.

181 Wang C. Long-range granular feature of silicate glasses and its relation to glass properties. Glass Science and Technology 2005; 78(6):279-286.

182 Roux C, Catt L-E, Spikmans V, Maynard P, Doble P, Woods, B. The evidential value of wine bottle glass. Presentation T120 at 4th European Academy of Forensic Science Conference (EAFS2006), Helsinki Finland.

183 Newton AWN, Kitto L, Buckleton JS. A study of the performance and utility of annealing in forensic glass analysis. Forensic Science International 2005; 155:119-125.

184 Becker S, Dücking M. Laser ablation ICP-MS in forensic glass analysis:wavelength dependent changes of refractive index of glass fragments

after laser ablation. in European Winter Plasma Conference. 2005:ICP Information Newsletter.

185 Smrcek A. Evolution of the compositions of commercial glasses 1830 to 1990. Part I. Flat glass. Glass Science and Technology 2005; 78:173-184.

186 Smrcek A. Evolution of the compositions of commercial glasses 1830 to 1990. Part II. Container glass. Glass Science and Technology 2005; 78:230-244.

187 Smrcek A. Evolution of the compositions of commercial glasses 1830 to 1990. Part III. Pressed glass. Glass Science and Technology 2005; 78:287-294.

188 Jackson CM, Booth CA, Smedley JW. Glass by design? Raw materials, recipes and copositional data. Archaeometry 2005; 47(4):781-795.

189 Falcone R, Sommariva G, Verita M. WDXRF, EPMA, and SEM/EDX quantitative chemical analyses of small glass samples. Mikrochimica Acta 2006; 155(1-2):137-140.

190 Gomez-Morilla I, Simon A, Simon R, Williams CT, Kiss AZ, Grime GW. An evaluation of the accuracy and precision of X-ray microanalysis techniques using BCR-126A glass reference material. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2006; 249(1-2):897-902.

191 Miller TC, DeWitt HL, Havrilla GJ. Characterization of small particles by micro x-ray fluorescence. Spectrochimica Acta Part B: Atomic Spectroscopy 2005; 60:1458-1467.

192 Padilla R, Van Espen P, Abrahantes A, Janssens K. Semiempirical approach for standardless calibration in _-XRF spectrometry using capillary lenses. X-Ray Spectrometry 2005; 34(1):19-27.

193 Lankosz M, Szczerbowska-Boruchowska M, Chwiej J, Ostachowicz J, Simionovici A, Bohic S. Research in quantitative microscopic X-ray fluorescence analysis. Spectrochimica Acta Part B: Atomic Spectroscopy 2004; 59B(10-11):1517-1521.

194 Vittiglio G, Bichlmeier S, Klinger P, Heckel J, Fuzhong W, Vincze L, Janssens K, Engström P, Rindby A, Dietrich K, Jembrih-Simburger D, Schreiner M, Denis D, Lakdar A, Lamotte A. A compact -XRF spectrometer for (in situ) analyses of cultural heritage and forensic materials. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms Origins 2004; 213(1):693-698.

195 Nakai I, Yamada S, Terada Y, Shindo Y, Utaka T. Development of a portable X-ray fluorescence spectrometer equipped with two monochromatic X-ray sources and silicon drift detector and field analysis of Islamic glasses at an excavation site in Egypt. X Ray Spectrometry 2005; 34(1):46-51.

196 Sawada T, Hokura A, Yamada S, Nakai I, Shindo Y. On-site analysis of Islamic glass excavated in the Sinai Peninsula by a portable X-ray fluorescence spectrometer for classification of glasses based on their chemical compositions. Bunseki Kagaku 2004; 53(3):153-160.

197 Nishiwaki Y, Shimoyama M, Nakanishi T, Ninomiya T, Nakai I. Application of total reflection X-ray fluorescence spectrometry to small glass fragments. Analytical Sciences 2006; 22(10):1297-1300.

198 Rosnach H. Environmental trace-element analysis using a benchtop total reflection x-ray fluorescence spectrometer. Analytical Sciences 2005; 21(7):873-876.

199 Suzuki Y, Kasamatsu M, Suzuki S, Nakanishi T, Takatsu M, Muratsu S, Shimoda O, Watanabe S, Nishiwaki Y, Miyamoto N. Forensic discrimination of

sheet glass by a refractive-index measurement and elemental analysis with synchrotron radiation X-ray fluorescence spectrometry. Analytical Sciences 2005; 21(7):855-859.
200 Bjeoumikhov A, Arkadiev V, Eggert F, Hodoroaba V-D, Langhoff N, Procop M, Rabe J, Wedell R. A new microfocus x-ray source, iMOXS, for highly sensitive XRF analysis in scanning electron microscopes. X-ray Spectrometry 2005; 34:493-497.
201 www.ixrfsystems.com
202 Schreiner M, Melcher M, Uhlir K. Scanning electron microscopy and energy dispersive analysis: applications in the field of cultural heritage. Analytical and Bioanalytical Chemistry 2007; 387:737-747.
203 Melcher M, Schreiner M. Statistical evaluation of potash-lime-silica glass weathering. Analytical and Bioanalytical Chemistry 2004; 379(4):628-639.
204 Doménech-Carbó M-T, Doménech-Carbó A, Osete-Cortina L, Sauri-Peris, M-C. A study on corrosion processes of archaeological glass from the Valencian region (Spain) and its consolidation treatment. Mikrochimica Acta 2006; 154(1-2):123-142.
205 Lombardo T, Chabas A, Lefevre RA, Ionescue A. Modelling the soiling of float glass in a polluted atmosphere. Glass Technology 2005; 46(2):192-196.
206 Lombardo T, Chabas A, Lefevre RA, Verita M, Geotti-Bianchini F. Weathering of float glass exposed outdoors in an urban area. Glass Technology 2005; 46(3):271-276.
207 Van der Linden V, Bultinck E, De Ruytter J, Schalm O, Janssens K, Devos W, Titi W. Compositional analysis of 17-18th century archaeological glass fragments, excavated in Mechelen, Belgium: Comparison with data from neighboring cities in the Low Countries. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2005; 239(1-2):100-106.
208 Smit Z, Janssens K, Schalm O, Kos M. Trace element fingerprinting of facon-de-Venise glass. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2005; 239(1-2):94-99.
209 Schalm O, Caluwé D, Wouteres H, Janssens K, Verhaeghe F, Pieters M. Chemical composition and deterioration of glass excavated in the 15th-16th century fishermen town of Raversijde (Belgium). Spectrochimica Acta Part B: Atomic Spectroscopy 2004; 59B(10-11):1647-1656.
210 Weber G, Martinot L, Strivay D, Garnir HP, George P. Application of PIXE and PIGE under variable ion beam incident angle to several fields of archaeometry. X Ray Spectrometry 2005; 34(4):297-300.
211 Weber G, Vanden Bemden Y, Pirotte M, Gilbert B. Study of stained glass window using PIXE-PIGE. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2005; 240(1-2):512-519.
212 Mäder M, Neelmeijer C. Proton beam examination of glass - an analytical contribution for preventive conservation.. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2004; 226(1-2):110-118.
213 Zhang, B, Li YH, Li QH, Ma B, Gan FX, Zhang ZQ, Cheng HS, Yang FJ. Non-destructive analysis of early glass unearthed in south China by external-beam PIXE. Journal of Radioanalytical and Nuclear Chemistry 2004; 261(2):387-392.

214 Zhang, B, Cheng HS, Ma B, Li QH, Zhang P, Gan FX, Yang FJ. PIXE and ICP-AES analysis of early glass unearthed from Xinjiang (China). Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2005; 240(1-2):559-564.
215 Gómez-Tubio B, Ontalba Salamanca MÁ, Ortega-Fellu I, Respaldiza MÁ, Amores Carredano F, González-Acuña D. PIXE-PIGE analysis of late Roman glass fragments. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2006; 249(1-2):616-621.
216 Mäder M, Jembrih-Simbürger D, Neelmeijer C, Schreiner M. IBA of iridescent Art Nouveau glass - comparative studies. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2005; 239(1-2):107-113.
217 _mit _, Janssens K, Bulska E, Wagner B, Kos M, Lazar I. Trace element fingerprinting of facon-de-Venise glass. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2005; 239(1-2):94-99.
218 Kuhn, H-R, Guenther D. Laser ablation-ICP-MS:particle size dependent elemental composition studies on filter-collected and online measured aerosols from glass. Journal of Analytical Atomic Spectrometry 2004; 19(9):1158-1164.
219 Kuhn, H-R, Guenther D. The agglomeration state of nanosecond laser-generated aerosol particles entering the ICP. Analytical and Bioanalytical Chemistry 2005; 383(3):434-441.
220 Kuhn, H-R, Guenther D. A quantification strategy in laser ablation ICP-MS based on the transported aerosol particle volume determined by optical particle size measurement. Journal of Analytical Atomic Spectrometry 2006; 21(11):1209-1213.
221 Wang ZK, Hattendorf B, Günther D. Vaporization and ionization of laser ablation generated aerosols in an inductively coupled plasma mass spectrometer - implications from ion distribution maps. Journal of Analytical Atomic Spectrometry 2006; 21(11):1143-1151.
222 Tunheng A, Hirata T. Development of signal smoothing device for precise elemental analysis using laser ablation-ICP-mass spectrometry. Journal of Analytical Atomic Spectrometry 2004; 19(7):932-934.
223 Koch J, Lindner H, von Bohlen A, Hergenröder R, Niemax K. Elemental fractionation of dielectric aerosols produced by near-infrared femtosecond laser ablation of silicate glasses. Journal of Analytical Atomic Spectrometry 2005; 20:901-906.
224 González JJ, Fernández A, Mao, X, Russo RE. Scanning vs. single spot laser ablation (_=213 nm) inductively coupled plasma spectrometry. Spectrochimica Acta Part B: Atomic Spectroscopy 2004; 59:369-374.
225 González J, Liu, C, Yoo J, Mao X, Russo RE. Double-pulse laser ablation inductively coupled plasma mass spectrometry. Spectrochimica Acta Part B:Atomic Spectroscopy 2005; 60(1):27-31.
226 González J, Dundas SH, Liu, CY, Mao X, Russo RE. UV-femtosecond and nanosecond laser ablation-ICP-MS:internal and external repeatability. Journal of Analytical Atomic Spectrometry 2006; 21(8):778-784.
227 Luo Y, Gao, S, Longerich HP, Günther D, Wunderli S, Yuan H-L, Liu X-M. The uncertainty budget of the multi-element analysis of glasses using LA-ICP-MS. Journal of Analytical Atomic Spectrometry 2007; 22(2):122-130.

228 Latkoczy C, et al. Development and evaluation of a standard method for the quantitative determination of elements in float glass samples by LA-ICP-MS. Journal of Forensic Sciences 2005; 50(6):1327-1341.

229 Smith K, et al. A guide for the quantitative elemental analysis of glass using laser ablation inductively coupled plasma mass spectrometry. Atomic Spectroscopy 2006; 27(3):69-75.

230 Neufeld LM. Application of laser ablation ICP-MS to the analysis of forensic glass samples. Spectroscopy (Springfield, Or.) 2005; 20(7):31-36.

231 Berends-Montero S, et al.. Forensic analysis of float glass using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS):validation of a method. Journal of Analytical Atomic Spectrometry 2006; 21(11):1185-1193.

232 Montero S. Forensic float-glass analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), method validation. 2005, NFI: Den Haag. http://www.forensicinstitute.nl/NFI/en/Publications/DFefaulr?year=2005.

233 Trejos T, Almirall JR. Sampling strategies for the analysis of glass fragments by LA-ICP-MS. Part I:Micro-homogeneity study of glass and its application to the interpretation of forensic evidence. Talanta 2005; 67(2):388-395.

234 Trejos T, Almirall JR. Sampling strategies for the analysis of glass fragments by LA-ICP-MS. Part II:Sample size and sample shape considerations. Talanta 2005; 67(2):396-401.

235 Umpierrez S, et al. Determination of iron in glass by solution and laser ablation DRC-ICP-MS. Atomic Spectroscopy 2006; 27(3):76-79.

236 Ehrlich S, Ben-Dor L, Halicz L, Precise isotope ratio measurement by multicollector-ICP-MS without matrix separation. Canadian Journal of Analytical Science and Spectroscopy 2004; 49(3):136-147.

237 Schultheis G, et al. Characterisation of ancient and art nouveau glass samples by Pb isotopic analysis using laser ablation coupled to a magnetic sector field inductively coupled plasma mass spectrometer (LA-ICP-SF-MS). Journal of Analytical Atomic Spectrometry 2004; 19(7):838-843.

238 Almirall J, et al. Forensic elemental analysis of materials by laser induced breakdown spectroscopy (LIBS). in Sensors and Command, Control, Communications, and Intelligence (C3I) Technologies for Homeland Security and Homeland Defense IV. 2005:Proceedings of the International Society for Optical Engineering (SPIE).

239 Giakoumaki A, Melessanaki K, Anglos D, Laser-induced breakdown spectroscopy (LIBS) in archaeological science-:applications and prospects:archaeometry. Analytical and Bioanalytical Chemistry 2007; 387(3):749-760.

240 http://www.lla.de/en/index.php/content/view/20/48/

241 Craparo JC, Weisberg A, DeSaro R, New technique developed to measure glass batch, sort cullet. American Ceramic Society Bulletin 2006; 85(3):33-37.

242 Bridge CM, et al. Characterization of automobile float glass with laser-induced breakdown spectroscopy and laser ablation inductively coupled plasma mass spectrometry. Applied Spectroscopy 2006; 60(10):1181-1187.

243 Galiova M, et al. Study of laser-sample interactions of glasses and soils using laser-induced breakdown spectrocopy and optical emission spectroscopy with inductively coupled plasma. Chemicke Listy 2006; 100(3):204-209.

244 Carmona N, et al. Analysis of corroded glasses by laser induced breakdown spectroscopy. Spectrochimica Acta Part B:Atomic Spectroscopy 2005; 60B(7-8):1155-1162.

245 Carmona N, et al. Lead determination in glasses by laser-induced breakdown spectroscopy. Spectrochimica Acta Part B:Atomic Spectroscopy 2007; 62(2):92-100.

246 Melessanaki K, et al. Analysis of archaeological objects with LMNTI, a new transportable LIBS instrument. Springer Proceedings in Physics 2005; 100:443-449.

247 Lal et al.

248 Gautier C, et al. Applications of the double-pulse laser-induced breakdown spectroscopy (LIBS) in the collinear beam geometry to the elemental analysis of different materials. Spectrochimica Acta Part B:Atomic Spectroscopy 2006; 61B(2):210-219.

249 Zachariadis G, et al. Optimized microwave-assisted decomposition method for multi-element analysis of glass standard reference material and ancient glass specimens by inductively coupled plasma atomic emission spectrometry. Talanta 2006; 68(5):1448-1456.

250 Wang H, et al. Determination of sulfur and phosphorus in glass by inductively coupled plasma emission spectrometry. Fenxi shiyanshi 2007; 26(1):112-115.

251 Bian QZ, et al. Non-matrix matched calibration of major and minor concentrations of Zn and Cu in brass, aluminium and silicate glass using NIR femtosecond laser ablation inductively coupled plasma mass spectrometry. Journal of Analytical Atomic Spectrometry 2006; 21(2):187-191.

252 Pisonero J, et al. A radiofrequency glow-discharge-time-of-flight mass spectrometer for direct analysis of glasses. Analytical and Bioanalytical Chemistry 2004; 379(4):658-667.

253 Dowsett M, Adriaens A. The role of SIMS in cultural heritage studies. Nuclear Instruments and Methods in Physics Research Section B:Beam Interactions with Materials and 2004; 226(1-2):38-52.

254 Rutten F, Henderson J, Briggs D. Unlocking the secrets of ancient glass technology using TOF-SIMS. Spectroscopy Europe. 2005; 17(1):24-30

255 Fearn S, McPhail DS, Oakley V. Room termprature corrosion of museum glass: an investigation using low-energy SIMS. Applied Surface Science 2004; 231-1:510-514.

256 Johnson JA, Johnson CE. Mossbauer spectroscopy as a probe of silicate glasses. Journal of Physics-Condensed Matter 2005; 17(8):R381-R412.

257 Colomban P, Etcheverry M-P, Asquier M, Bounichou M, Tournié A. Raman identification of ancient stained glasses and their degree of deterioration. Journal of Raman Spectrocopy 2006; 37(5):614-626.

258 Brozek-Mucha Z, Zadora G, Zidba-Paulus J, Parczewski A. Persistence of glass fragments after break-in through multiply glazed windows. Presentation T115 at 4th European Academy of Forensic Science Conference (EAFS2006), Helsinki Finland.

259 Hicks T, Schutz F, Curran JM, Triggs CM. A model for estimating the number of glass fragments transferred when breaking a pane: experiments with firearms and hammer. Science and Justice 2005; 45(2):65-74.

260 Lucy D. Introduction to statistics for forensic scientists. 2005, Chichester, West Sussex, England:John Wiley & Sons Ltd., 251 pp.

261 Aitken CGG, Lucy D. Evaluation of trace evidence in the form of multivariate data. Applied Statistics 2004; 53(1):109-122.

262 Aitken CGG, Lucy D, Zadora G, Curran JM. Evaluation of transfer evidence for three-level multivariate data with the use of graphical models. Computational Statistics & Data Analysis 2006; 50(10):2571-2588.

263 Aitken CGG, Zadora G, Lucy D. A two-level model for evidence evaluation. Journal of Forensic Sciences 2007. 52(2):412-419.

264 Pawluk-Ko_c M, Zi_ba-Palus J, Parczewski A. Application of false discovery rate procedure to pairwise comparisons of refractive index of glass fragments. Forensic Science International 2006; 160(1):53-58.

265 Becker S, Weis P. Laser ablation ICP-MS in forensic glass analysis: a decade of experience. Presented at Trace Evidence Symposium, Clearwater Beach, Florida, August 16, 2007.

266 Aeschliman DB, et al. Multivariate pattern matching of trace elements in solids by laser-ablation inductively coupled plasma mass spectrometry:source attribution and preliminary diagnosis of fractionation. Analytical Chemistry 2004; 76(11):3119-3125.

267 Bajic SJ, et al. Analysis of glass fragments by laser ablation-inductively coupled plasma-mass spectrometry and principal component analysis. Journal of Forensic Sciences 2005; 50(5):1123-1127.

268 http://www.fbi.gov/hq/lab/fsc/backissu/jan2005/index.htm

269 www.astm.org