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Surface Analysis Techniques in Forensic Science: Successes, Challenges, and Opportunities for Operational Deployment

Melanie J. Bailey,[1] Marcel de Puit,[2,3] and Francesco Saverio Romolo[4]

[1]Department of Chemistry, Stag Hill Campus, University of Surrey, Guildford, United Kingdom; email: M.Bailey@surrey.ac.uk

[2]Netherlands Forensic Institute, The Hague, The Netherlands

[3]Delft University of Technology, Delft, The Netherlands

[4]Dipartimento di Giurisprudenza, Università degli Studi di Bergamo, Bergamo, Italy

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Abstract

Surface analysis techniques have rapidly evolved in the last decade. Some of these are already routinely used in forensics, such as for the detection of gunshot residue or for glass analysis. Some surface analysis approaches are attractive for their portability to the crime scene. Others can be very helpful in forensic laboratories owing to their high spatial resolution, analyte coverage, speed, and specificity. Despite this, many proposed applications of the techniques have not yet led to operational deployment. Here, we explore the application of these techniques to the most important traces commonly found in forensic casework. We highlight where there is potential to add value and outline the progress that is needed to achieve operational deployment. We consider within the scope of this review surface mass spectrometry, surface spectroscopy, and surface X-ray spectrometry. We show how these tools show great promise for the analysis of fingerprints, hair, drugs, explosives, and microtraces.

INTRODUCTION

The aim of this article is to review the use and future potential of surface analysis techniques for providing useful information for forensic investigations. Here, we consider the scope of surface analysis to include tools that sample the top few microns (or less) of material, rather than the bulk. We consider within the scope of this article mass spectrometry [secondary ion mass spectrometry (SIMS), desorption electrospray ionization (DESI), matrix-assisted laser desorption ionization (MALDI), laser ablation inductively coupled mass spectrometry (LA-ICP-MS)]; surface spectroscopy [Fourier transform infrared (FTIR), Raman spectroscopy, laser-induced breakdown spectroscopy (LIBS)]; and X-ray spectrometry [scanning electron microscopy energy dispersive X-ray spectrometry (SEM-EDS), particle-induced X-ray emission (PIXE), X-ray fluorescence (XRF)]. We shall assume that the reader has a basic knowledge of surface analytical methods. For clarity, the current capabilities of these methods are summarized in **Table 1**, and the reader is referred to the literature to gain more detailed knowledge (1–4).

Surface analytical tools are rapidly developing and have much to offer to forensic investigation, for example, high-resolution imaging and rapid, portable, and/or nondestructive analysis. However, not all research efforts have led to adoption often due to a lack of understanding in the analytical community of some of the nuances and practices in forensic science. The forensic analysis community is necessarily conservative and unlikely to adopt a new method until it is fully validated. It is therefore vitally important that the surface analysis community gain a good understanding of forensic procedures and pathways to adoption when proposing a new method. A new method is unlikely to be adopted in forensic casework of the future unless it is compatible with current forensic practice. This article is written by forensic and analytical scientists in partnership and aims to communicate these issues for the benefit of the surface analysis community, thereby bridging the gap between technique development and operational deployment.

The nature of operational deployment is an important consideration in method development. Forensic deployment can be either at the scene of a crime or in laboratories. Instruments for crime scene analysis need to provide fast analytical answers to support investigations. Results with limited selectivity can be tolerated at the scene, but then the analysis must be repeated in the laboratory to provide results suitable for use in court proceedings. Deployment in forensic laboratories also has special requirements. For example, a single specimen may contain many possible traces [e.g., fingerprints, gunshot residue (GSR)]. Therefore, the forensic laboratory should consider the impact of performing a measurement on the viability of other traces. This leads to quite specific requirements; for example, scanning electron microscopes should have chambers that are capable of hosting large items.

The aim of forensic science is to provide scientific support to the judicial system with regard to the material evidence at hand. Bearing in mind that the purpose of forensic activity is legal, it is easy to understand that chemical information can be very useful, but it is not always needed. Moreover, words can have a different meaning if we compare chemistry, law, and forensic science. As an example, we consider it useful to preliminarily explain that the word identification plays an extremely important role in forensic science and has multiple meanings. From the forensic point of view, the comparison between the specimen to be analyzed and a reference sample (i.e., standard) of known origin to determine if they belong to the same class is called classification. Whenever a chemical report refers to the identification of a specific compound in a sample, a forensic scientist would use the word classification. There is a different connotation of the word identification in forensic science: When using information to infer toward a particular source, the process is referred to as individualization. This is used whenever it is possible to determine that two specimens come from the same unique source (5).

Table 1 Overview of surface analysis techniques considered in this review

Technique	Method	Probe	Image resolution	Analytes	Additional features
X-ray spectrometry	X-ray fluorescence (XRF)	X-rays (can be synchrotron, table-top, or portable)	0.1–1 micron	Na to U at ppm level	Nondestructive
	Scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDS)	Electron beam	Submicron level	C to U at >0.1 at%	High-resolution imaging of topography with secondary electrons
	Particle-induced X-ray emission (PIXE)	MeV ion beam from accelerator	0.1–1 micron	Full mass closure with total ion beam analysis (IBA) at ppm level	Quantitative (no need for matrix-matched standards)
Mass spectrometry	Laser ablation inductively coupled mass spectrometry (LA-ICP-MS)	Laser	2–100 microns	ppb level	Analysis of isotopes
	Matrix-assisted laser desorption ionization (MALDI)	Laser	1–100 microns	Drugs, metabolites, lipids, peptides, polymers	Typically requires addition of a matrix and is performed under vacuum
	Desorption electrospray ionization (DESI)	Electrospray	20–150 microns	Drugs, metabolites, lipids, explosives	Ambient analysis
	Secondary ion mass spectrometry (SIMS)	Ion beam	Submicron level	Elements, intact molecules and their fragments	Performed under ultrahigh vacuum
Spectroscopy	Laser-induced breakdown spectroscopy (LIBS)	Laser (handheld or benchtop)	10–50 microns	Elements down to ppm level	Can also provide chemical information
	Raman	Laser (visible, ultraviolet or near infrared)	500 nm	Vibrational frequencies of explosives and biomolecules	Surface-enhanced Raman spectroscopy (SERS) increases surface sensitivity
	Fourier transform infrared (FTIR)	Infrared light source	Submicron level	Absorption bands specific to chemical species	Attenuated total reflection Fourier transform infrared (ATR-FTIR) increases surface sensitivity

Abbreviations: ppb, parts per billion; ppm, parts per million.

Individualization is most often the first step of interpretation in forensic science. It is also known as the evaluation of a hypothesis at source level and is not the only aim of scientific investigation. Any information in forensic science is exploited to provide the maximum support to the reconstruction of something that happened in the past. A further step of interpretation in forensic science is therefore called interpretation at activity level (6). We can provide an example with GSR: When evaluating GSR at source level, we want to know whether the residue originated from the firearm that was used during the shooting or whether it was transferred during an event not related to the crime (e.g., during hunting or a shooting competition). If the GSR particles on a suspect are related to the crime, we want to know more about the activity: Were they deposited on the suspect because the suspect shot the victim or because he tried to help after shooting? The

victim is a rich source of GSR, and transfer on hands can occur after the shooting by touching the victim, the firearm, or the cartridge case.

We detail here the progress that has been made in applying surface analysis techniques to traces commonly found in forensic casework. We highlight where there is potential to add value to current forensic methods. We begin with fingerprints, the most important trace for individualization, followed by hair, which allows individualization in some cases, and can reveal drug use. We then move to forensic medicine. Later, we report on the opportunities for surface analysis tools in the detection and profiling of two particularly important chemical substances in forensic science: drugs and explosives. We then summarize the progress and opportunities for using surface analysis in the forensic analysis of three types of microtraces: GSR, paint, and glass.

FINGERPRINTS

The improved visualization and chemical imaging of fingerprints are excellent examples of the potential added value of the application of modern surface analysis technologies in forensic science (7). Fingerprints are regarded as the oldest single biometric feature used for individualization purposes (8) and can be of an incredibly high evidential value (9). Fingerprints normally must be developed to visualize them, but this is complicated by the fact that fingerprint chemistry is highly variable (10). The chemistry of a fingerprint varies between and within individuals but also due to environmental factors. Fingerprints at crime scenes can be deposited on any surface and can be exposed to a range of environmental conditions (e.g., heat, light, water) before being recovered. In many cases, conventional developers can fail to provide sufficient ridge detail for individualization (11).

Spectroscopic imaging techniques have been widely applied to fingerprints, and the work to date is summarized in a recent review by Amin et al. (12). Spectroscopic imaging has been proposed as an alternative method to enhance fingerprints. For example, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy has been used to construct chemical images of fingerprints using univariate and multivariate analyses (13), and surface-enhanced Raman spectroscopy (SERS) has been used to enhance fingerprints removed from surfaces by tape lifting (14). It is not yet fully clear how much improvement these methodologies give over conventional development processes, or whether they can be used in sequence with existing methodologies, which are likely to be used in the first instance in operational settings.

In the last few decades it has become apparent that the combination of fingerprint individualization, together with the chemical analysis of the fingerprint and other information, such as ink analysis (15–17), toxicology (18–20), drugs (21, 22), and explosives analysis (23), can be very powerful. Bulk analysis (mainly via extraction of the fingerprint and followed by separation and mass spectrometry) has shown that the chemical composition of fingerprints is relevant to the evaluation of hypotheses at source level, such as donor profiling (24–26), and activity level, such as determining whether someone has used or touched an illicit substance (27, 28), or their age estimation (11). However, bulk techniques are unlikely to be used in forensic casework because they are destructive, and the interpretation of results is doubtful. Therefore, surface analysis techniques, which do not destroy the fingerprint specimen, can play an important role.

Spectroscopic imaging has been used to establish changes in the chemical composition of a fingerprint over time (13, 29) to determine the age of a donor based on sebum composition (30) and to detect exogenous species such as explosives (31) and drugs (32). Similarly, multimodal synchrotron-XRF and infrared (IR) microscopy (**Figure 1*a***) have been used to image the distribution of inorganic residues incorporated in fingerprints through handling coins and cosmetics (33).

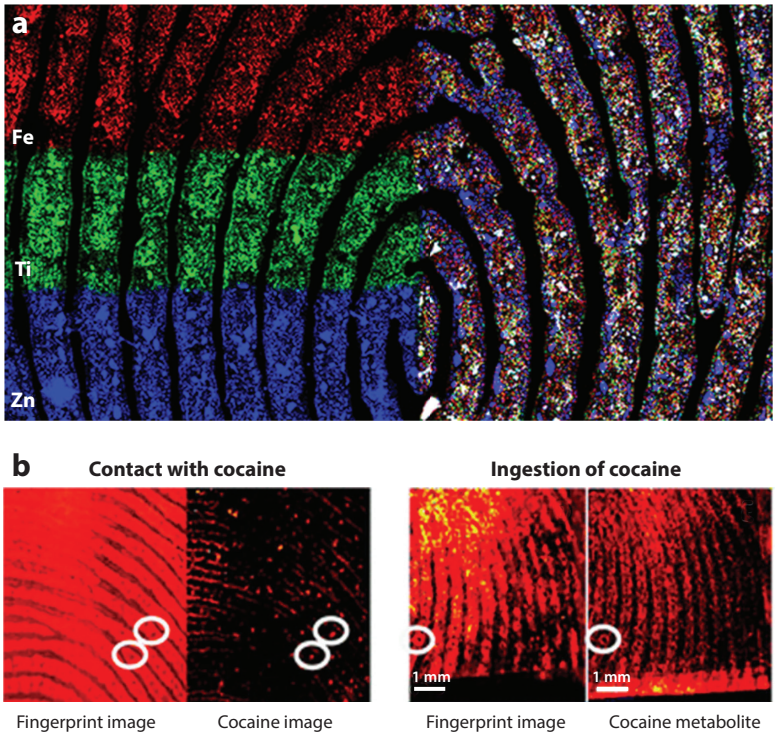

Figure 1

(*a*) Fingerprint sample imaged using synchrotron X-ray fluorescence (XRF) to show endogenous trace metals. Panel adapted with permission from Reference 33; copyright 2019 American Chemical Society. (*b*) Fingerprints from cocaine nonusers and users imaged using secondary ion mass spectrometry (SIMS) to show the difference between contact and ingestion of cocaine. Panel adapted with permission from Reference 39; copyright Royal Society of Chemistry.

While spectroscopic imaging techniques are relatively easy to use and can be available in portable equipment, mass spectrometry is more selective in terms of chemical identification. Surface mass spectrometry has also been widely applied for the imaging and analysis of contaminants in fingerprints, including time-of-flight secondary ion mass spectrometry (ToF-SIMS) (34), DESI (35) and MALDI (36, 37). There are some substantial differences between these three approaches in terms of analyte coverage, sampling depth, and destructive nature, which have an impact on the relevance of application to fingermark research. For example, although ToF-SIMS and MALDI techniques typically operate under high vacuum, DESI works under atmospheric conditions. Bright et al. (38) showed that fingerprint chemistry changes when placed in a vacuum system, making ambient analysis a more attractive proposition for researching certain applications (e.g., age estimation, donor profiling) where potential biomarkers may be affected by vacuum measurement. Conversely, vacuum analysis can be used for imaging of drug residues in fingerprints, and indeed, Costa et al. (39) showed that MALDI, DESI, or water cluster SIMS were appropriate for imaging the distribution of cocaine residues in fingerprints to distinguish between cocaine ingestion and dermal contact (**Figure 1*b***). Analyte coverage for MALDI, DESI, and SIMS is highly complementary. The inorganics detected by SIMS are useful for fingerprint visualization, and MALDI/DESI approaches provide superior sensitivity to metabolites, lipids, and drug molecules that may be used for offender profiling (21, 39–41). Similarly, the shallow information depth of

SIMS can be advantageous in revealing the chronology of deposition of fingerprints and other traces (15, 17).

In forensic casework, it is imperative that a new method does not interfere with other established methods and techniques in other disciplines, or is at least considered as the last analytical step of the forensic procedure. This mainly means that surface analysis techniques must be compatible with known fingerprint visualization reagents. ToF-SIMS can reveal fingerprints deposited on different surfaces that were not successfully visualized with conventional reagents (42). Following this study, it was also shown that the deposition order of fingerprints and inks on documents could also be established in sequence with the conventional developers used to enhance fingerprints in forensic laboratories (15). Similarly, MALDI and laser desorption ionization (LDI) protocols have been developed for the detection of drugs in predeveloped fingermarks (43, 44). These preliminary studies clearly show the applicability and the added value of surface analysis.

Surface analysis shows great promise for providing a new dimension to fingerprint evidence. However, despite these initial promising results, validation studies are needed to fully establish their use in forensic casework. For fingerprint enhancement, it is important to gain a more comprehensive understanding of the circumstances (e.g., donor, substrate, environment, prior development) under which an imaging technique can add value. For fingerprint chemical profiling (e.g., donor or sex), it is important to establish whether the procedures are robust enough to work after fingerprint aging and development and on all types of surfaces. For the detection of traces in fingerprints (e.g., drugs, explosives), more work is needed to establish the relevance of detecting that trace. Research to establish cutoff values can be done effectively using bulk analysis methods. However, in casework, surface analysis is needed to establish whether a trace is associated with a fingerprint or already present on a surface. Therefore, the surface analysis community should work closely with forensic providers and the bulk analysis community to provide robust results.

HAIR

Hair analysis is widely used in toxicology and forensics. In crime scene investigation, hair is one of the most common traces and can be used to provide investigative leads or associate a suspect with a location. In toxicology, hair is a useful sampling matrix owing to the long detection window and the ability to provide chronological information on substance misuse or exposure or poisoning. Surface analysis methods have the potential to contribute to all of these areas of investigation.

Hair can vary widely between individuals, making it an important tool in crime scene investigation. Microscopy applied to hair allows class characteristics (e.g., curly, wavy, straight, length, color) to be established. This information can be used to rapidly provide investigative leads. If the follicular tag is present, it can be possible to extract DNA to associate the trace evidence with an individual. Spectroscopy techniques carry the advantage of adding selectivity to optical microscopy, while preserving in most cases the follicular tag for more lengthy and costly DNA analysis. ATR-FTIR has been used to rapidly screen hair and classify different dyes in dark hairs, which can be particularly difficult to subclassify using microscopy (45). SERS has been used to identify and distinguish between hair dyes but has the disadvantage of requiring lengthy sample preparation (46). More recently, Esparza et al. (47) reported that SERS can be used to detect underlying colorants in hair that is redyed.

In toxicology, various surface analysis methods have been applied to explore drug uptake and consumption, using hair as a sampling matrix. Careful consideration of the analytical process and interpretation is needed because detection of a substance in hair can arise from environmental exposure, rather than from ingestion. Gerace et al. (48) used SEM to show that hair damaged by

cosmetic treatments can uptake more cocaine (from environmental exposure) than healthy hairs, giving insight into possible pitfalls in interpretation.

MALDI and ToF-SIMS have been applied by several groups to the longitudinal analysis of hair, giving measurements of drug concentration along the length of a hair that correspond to different consumption/exposure times (49–51). To mitigate signals from environmental exposure, it has been recommended that longitudinal sectioning of the hair should be performed prior to analysis to reveal the innermost section of a hair shaft for analysis. Flinders et al. (50) demonstrated that metal-assisted SIMS (meta-SIMS) can be used to measure the longitudinal distribution of cocaine and methadone in hair, with the potential to provide highly time-resolved measurements on the chronology of drug use (**Figure 2*a***). Likewise, Erne et al. (52) were able to locate a single dose of zolpidem in sectioned hair using MALDI (**Figure 2*b***).

An issue that has recently raised debate in the hair testing community is the validity of washing protocols that are used to remove surface contamination on hair. Mass spectrometry imaging has been used to show the limitations of certain hair decontamination protocols and how (in the case of cocaine) it can be possible to wash the analyte into the hair shaft using the very process that is designed to eliminate it (51). Mass spectrometry imaging has also played a useful role in establishing the validity of various alternative decontamination protocols to counter this problem (52, 53).

Surface analysis methods have also been proposed as a tool to monitor arsenic exposure. The interpretation of arsenic found in hair after burial has raised debate owing to the possibility that it may arise from the burial site rather than from exposure during life. Audinot et al. (54) proposed the use of nano-SIMS to image arsenic in cross sections of human hair to distinguish deliberate contamination from a suspected chronic arsenic exposure. Although this result needs validation (only a single image of a chronic exposure hair was presented), the images did highlight a clear difference between the two exposure routes. In 2009, Kempson et al. (55) used synchrotron techniques to measure arsenic exposure in ancient hair using synchrotron X-ray fluorescence (s-XRF) mapping, X-ray absorption spectroscopy, X-ray diffraction, and FTIR. This provided both information on the location of arsenic within the hair shaft and arsenic speciation analysis to determine the exposure route. Kučera et al. (56) later tested PIXE to provide the longitudinal distribution of Fe, As, Zn, Ag, Au, Hg, and Pb in Tycho Brahe's (sixteenth-century Danish astronomer) hair.

Clearly, surface analysis methods show promise for adding value in hair toxicology, in both the direct analysis of specimens and the evaluation of sample preparation methods. Vibrational spectroscopy can play a role in individualization through the detection of hair dyes. Initial results look promising, but the range of tested analytes, hair types, and scenarios is relatively small, providing room for further validation.

FORENSIC MEDICINE

We have seen how the analysis of hair and fingerprints can be used for individualization and also provides toxicological information. In forensic medicine, the inference about the cause and the time of a wound or an intoxication (regardless whether or not the victim survives) can be more important than individualization.

In forensic pathology, tissue specimens are collected and examined under a microscope to identify the cause of illness, wounding, or death. For example, a forensic pathologist may look for the presence or absence of natural disease and other microscopic findings, such as GSR around a gunshot wound. Conventional methods for analysis are based on histochemistry and immunohistochemistry or IR and ultraviolet (UV) imaging. As these are established methods and discussed comprehensively in the literature, we exclude them from this review. However, a recent overview

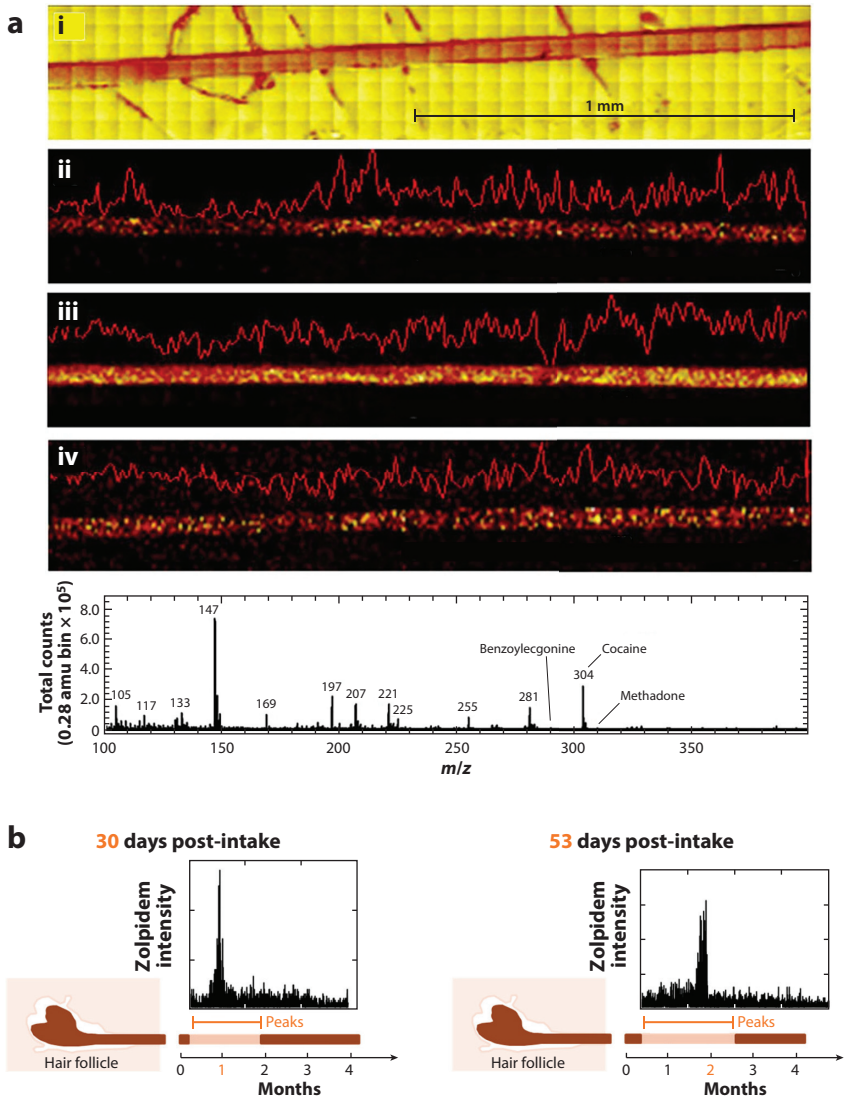

Figure 2

(*a*) Metal-assisted SIMS images of a longitudinally sectioned user hair sample showing (*i*) the total ion current, (*ii*) the distribution of benzoylecgonine at *m/z* 290, (*iii*) the distribution of cocaine at *m/z* 304, and (*iv*) the distribution of methadone at *m/z*. Panel adapted with permission from Reference 50; copyright 2015 John Wiley & Sons. (*b*) MALDI-MS measurements of single hairs sampled 30 and 53 days after the single administration of 10 mg of zolpidem. Zolpidem intensity (MS/MS transition 308.2/235.2) is depicted along the hairs. Location of zolpidem-positive peaks, to be found in longitudinally sectioned segments (*orange lines*), reflect a good agreement between the effectively elapsed time and the calculated time since intake (assuming 1 cm per month of hair growth). Panel adapted with permission from Reference 52; copyright 2019 American Chemical Society. Abbreviations: MALDI, matrix-assisted laser desorption ionization; MS/MS, tandem mass spectrometry; SIMS, secondary ion mass spectrometry.

of the perspectives and ethical considerations involved in forensic medicine called for a more comprehensive analysis during autopsies (57), demonstrating a place for new analytical approaches.

There is currently a dearth of literature on surface analysis methods in forensic pathology. Li et al. (58) described the use of MALDI-ToF as a tool to estimate the postmortem interval in liver tissue samples in 2017. In the same year, Lauer et al. (59) used LA-ICP-MS to identify metals in tissue sections extracted from wounds in postmortem investigation. This group observed metal accumulation at the site of a suspected electrocution, which they claimed was consistent with electrocution via an electrical panel. Both of these studies certainly highlight the potential of surface analysis to add value to forensic pathology, but the methods involved would require further validation for routine use.

In a criminal investigation, questions about the cause and time of death are quite common (60). The cause of death is especially important from a medicolegal standpoint. The use of advanced technologies to evaluate hypotheses on the cause of death would have a significant and positive impact on future criminal investigations. In mainstream medicine, surface analysis tools have also been shown to be of great benefit in biomarker discovery, for example, in cancer and infectious diseases (61–64). In forensic pathology, surface imaging might be used in a similar way to identify specific biomarkers to map degradation processes of the deceased. Future research should evaluate whether this information can be used to establish time or cause of death, the time or cause of a wound, or if the wound was antemortem or postmortem.

Surface analysis methods also allow metals, drugs, metabolites, lipids, and proteins to be imaged at scales ranging from tissue compartments to organelles. In drug discovery, mass spectrometry imaging is routinely used for the imaging of drugs and small-molecule biomarkers in tissue to probe the host response (65). Forensic toxicologists examine body tissues to determine the concentration of toxic chemical compounds and their metabolites. Therefore, being able to establish their distribution within tissue and the toxic (or otherwise) impact on the host tissue could allow specialists to infer the cause and time of death.

Surface analysis methods have also shown great potential to provide high-throughput screening of biofluid samples in forensic toxicology. Conventional analysis of biofluids is carried out by either liquid or gas chromatography coupled to mass spectrometry (66). However, vibrational spectroscopy (67), LDI (68), DESI (69), and liquid extraction surface analysis (LESA) (23) have been demonstrated to provide rapid analysis of illicit substances in biofluids, cutting run times by an order of magnitude in some cases. These techniques could be used to screen all samples to avoid more time-consuming, chromatographic analysis on negative samples. Although the loss of chromatographic separation removes a point of identification for forensic toxicologists, the advent of mass spectrometers with built-in ion mobility may help to overcome this obstacle.

DRUGS AND PHARMACEUTICAL PRODUCTS

The analysis of drugs is carried out not only on biological samples such as hair and tissues. Seized drugs must be analyzed as bulk materials during criminal investigations. Currently, in the illegal market there are traditional drugs of abuse such as cocaine and heroin as well as new psychoactive substances, which are a heterogeneous group of substances with the capacity to stimulate or depress the central nervous system (70). Moreover, nonmedical use of prescription drugs such as benzodiazepines, fentanyl analogs, and tramadol is a fast-emerging public health threat (71). Finally, counterfeit pharmaceuticals endanger lives worldwide (72).

Chemical analyses are carried out to identify the active ingredient in illegal products, to determine the percentage of the active compound in the seized material, and to profile impurities. There is also an interest in a timely and more complete analytical characterization, because the

early warning for the presence of other toxic chemical substances can protect public health. Sometimes laboratories are asked by law enforcement agencies to analyze new psychoactive substances that have never been encountered before, and they do not have standards or analytical results in their databases. In these cases, the analytical challenge is particularly difficult. The most difficult task in any forensic laboratory is the "characterization and impurity profiling of seized drugs. . .to classify material from different seizures into groups of related samples and to identify the origin of samples. Such information can be used for evidential (judicial, court) purposes or it can be used as a source of intelligence to identify samples that may have a common origin or history" (73, p. 1).

Forensic characterization of pills (e.g., drugs of abuse or counterfeit Viagra) can be carried out by optical image processing (74, 75). The size, shape, and color of a pill can be particularly useful to find links among seizures. Chemical analyses are generally conducted by chromatography coupled to mass spectrometry, but recent studies show that surface analysis tools have the potential to contribute to all of the abovementioned areas of forensic analysis.

One key advantage of surface spectroscopy approaches such as Raman spectroscopy and FTIR is that the analysis is much faster compared to traditional chromatographic approaches and does not require sample preparation. ATR-FTIR has been used to analyze standard mixtures of cocaine and cutting agents to obtain a profile of adulteration of cocaine seizures (76), to provide both qualitative and quantitative analysis of MDMA tablets (77), and to analyze counterfeit Viagra (78). Similarly, de Oliveira Penido et al. (79) reviewed the state-of-the-art use of Raman spectroscopy as a confirmatory method for rapid, inexpensive, and nondestructive analysis of cocaine and other drugs of abuse in seized samples.

Raman spectroscopy can also be used to analyze hidden compounds in legal materials, such as clothes and rugs, and used for illegal trafficking, providing not only qualitative results but also the drug concentrations in street samples (79). Raman spectroscopy has also been used for the rapid on-site analysis of drugs of abuse (80) and to analyze illegal pharmaceutical products (81). The signal amplification of SERS allows the use of portable Raman analyzers to detect trace amounts of opioids (codeine and fentanyl) on clothing and packages (82, 83).

Surface mass spectrometry approaches offer the possibility to rapidly profile drugs of abuse, giving similar peaks to traditionally used chromatography approaches. DESI has been used by a number of groups to profile drugs of abuse and medicinal products. Direct analysis in real time (DART) was recently used to detect organic impurities in cocaine samples seized in China, allowing discrimination between linked and unlinked seizures (84). DART was also used to provide semiquantitative data from drugs after sampling from a variety of porous and nonporous surfaces, including fabrics (85). While DESI and DART are (at best) minimally destructive to the sample, megaelectron volt secondary ion mass spectrometry (MeV-SIMS) is nondestructive and can provide molecular information on the samples under study with minimal sample handling (86).

Recent studies have shown that elemental surface analysis can also play a role in drug profiling. For example, PIXE has been reported to be effective at discriminating between authentic and illegal substances, for example, counterfeit versus authentic Viagra (86). In particular, PIXE is nondestructive, requires no sample preparation, and can identify suitable markers for different products in analytical windows of only a few minutes.

EXPLOSIVES

Another important class of chemical substances requiring bulk analysis in criminal investigations is explosives. Explosives are chemical substances posing a significant threat to the security of citizens, and their illegal use is severely punished under criminal law. Therefore, the capability to detect and identify explosives is critically important both in security applications and in support of criminal

investigations. It is easy to realize, based on the 2020 Annual List of Explosive Materials by the United States Bureau of Alcohol, Tobacco, Firearms and Explosives, that the general issue of the explosive threat is too complex to limit the analytical tools to one (87).

The detection of traces of explosives on a car's door handle can help prevent a bombing and today can be carried out remotely using a laser to scan the surface and a detector to analyze spectroscopic signals. This approach is called stand-off detection and allows remote detection of explosive traces from up to 100 m.

Raman spectroscopy is extremely appealing for stand-off (i.e., remote), on-site detection of explosives both airborne and on surfaces (88–90). Eye-safe Raman has been implemented in the research project called STANdoff Detection of EXplosives (STANDEX), carried out under the NATO Science for Peace and Security Programme (91). The new remote analytical system developed in STANDEX was called RADEX (RAman Detection of EXplosives). It allows for real-time analysis for proximal detection at 6–7 m (92) and was successfully operated in the BCT (Big City Trial) test in June 2013 in the Paris Métro station Bibliothèque François Mitterrand in Paris (93). The RADEX device allowed proximal stand-off detection of traces of explosives on fabrics with a target limit of detection of 100–1,000 $\mu g/cm^2$ (94).

It has been argued that the integration times required to obtain good signal to noise in stand-off Raman can be prohibitively long (95). LIBS allows an alternative ultrarapid stand-off detection approach, reportedly up to 130 m (96), and is also suited to on-site identification of explosives not requiring any sample preparation (97).

Raman techniques are also attractive for on-site (i.e., crime scene) analysis of airborne or buried explosive traces. SERS enhancement mechanisms allow for improved detection of explosive traces, allowing sensitive analysis with handheld Raman spectrometers (98). Wackerbarth et al. (99) studied airborne triacetone triperoxide (TATP) and TNT, sublimated onto a cooled nanostructured gold substrate, and compared signals of TNT with musk xylene and musk ketone, which can be mistaken for TNT, being nitroaromatic compounds (100). Huang et al. (101) recently introduced a new type of SERS substrate using retroreflective glass beads coated with silver nanoparticles with intrinsic Raman photon directing capability that compensates for the relatively low signal collection power of fiber-based Raman spectrometers. They reported detection of 100 pg 2,4-dinitrotoluene in field conditions (101) (**Figure 3**).

To screen large objects, the usual forensic practice is to wipe a surface with a swab and analyze the swab. This allows rapid surveillance of larger areas and preconcentrates the analytes. Screening analysis is conventionally carried out using thermal desorption ionization coupled to ion mobility spectrometry (TD-IMS), with confirmation by liquid chromatography mass spectrometry (LC-MS). However, TD-IMS is not suited to compounds that are thermally labile and lacks selectivity, whereas LC-MS requires lengthy sample preparation. Soparawalla et al. (102) showed that DESI is suitable for performing rapid analysis of explosives on swab materials.

Direct analysis from a surface offers several advantages over swabbing, including the possible preservation of other forensic traces (e.g., fingerprints, GSR) and reduces the possibility of contamination. Explosives such as RDX, HMX, TNT, PETN, and their plastic compositions (e.g., Composition C-4, Semtex-H, Detasheet) can be analyzed directly from a wide variety of surfaces (e.g., metal, plastic, paper, polymer) without sample preparation or pretreatment by DESI. Tandem mass spectrometry (MS/MS) can be carried out in very short time frames (<5 s), and selectivity can be increased by performing additional experiments with additives included in the spray solvent. Cotte-Rodríguez et al. (103) found that this approach provided absolute limits of detection for neat explosives at the subnanogram level in all cases and at subpicogram levels for TNT.

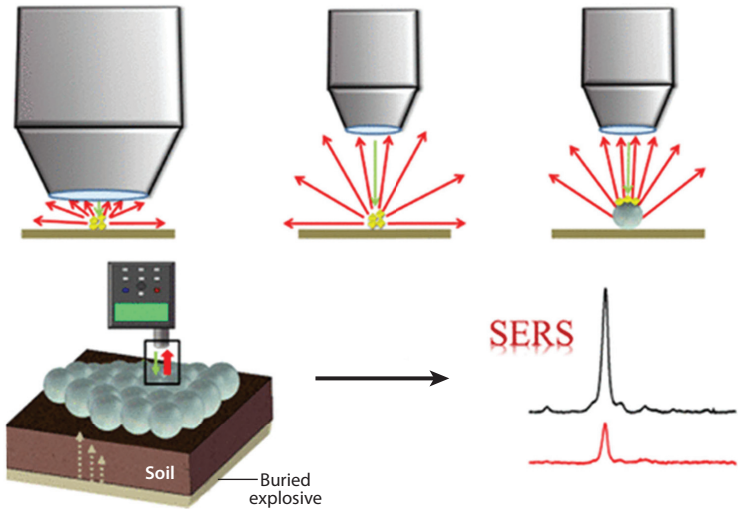

Figure 3

Detection of buried explosives using a surface-enhanced Raman scattering (SERS) substrate tailored for miniaturized spectrometers. Figure adapted with permission from Reference 101; copyright 2020 American Chemical Society.

Explosives have also been desorbed from solid surfaces by other emerging surface mass spectrometry methods. For example, Kauppila et al. (104) compared DESI with desorption atmospheric pressure photoionization (DAPPI) and found that DAPPI outperformed DESI for TNT but not for thermally labile compounds. Similarly, Ehlert et al. (105) investigated the detection of explosives in a wide range of samples and matrices using the ambient pressure laser desorption approach, which allowed detection in cases when a thermal desorber unit would decompose the analyte. It has been proposed that dielectric barrier discharge ionization is easier to integrate into a ruggedized portable system than DESI, allowing detection limits of 10 pg for TNT, 0.1 ng for RDX, and 1 ng for PETN (106).

Finally, multiphoton electron extraction spectroscopy has been shown to be one of the most sensitive detection methods for explosives on solid surfaces, giving detection limits in the subpicomole range. The method also allows for imaging of the examined surface. This analytical method is based on UV laser pulses used to scan the surface and to extract electrons from the excited material in multiphoton processes under ambient conditions (107).

It is not easy to envisage many cases of surface techniques making a noticeable difference in casework involving the bulk analysis of explosives in forensic laboratories, other than by increasing throughput through direct analysis or preserving other traces through the direct analysis of surfaces. Additionally, there are opportunities for on-site analysis of surfaces. Looking for traces of explosives is a promising field for the forensic application of surface analysis approaches. Moreover, remote sensing of explosives both airborne and on surfaces is expected to be a possible game changer in security applications.

As with the previous evidence types considered, it is likely that multiple surface analysis techniques can play a role in explosive detection. For example, MeV-SIMS is less portable than Raman spectroscopy and more expensive, but in forensic procedures the cheapest and fastest techniques are used first, possibly on-site. More-expensive and time-consuming approaches are used only in some cases, when more sensitivity is needed, resulting in a more comprehensive characterization of the trace or the bulk material seized.

GUNSHOT RESIDUE

The explosion of a cartridge for a firearm produces GSR due to the high temperature and pressure resulting from the explosion of the cartridge (108). The primary aim of searching GSR is the association of a suspect with a specific source during a specific shooting (both the cartridge and firearm contribute to the chemistry of GSR). The secondary aim is to contribute to the reconstruction of the sequence of activities carried out during the crime, providing information about not only the amount of GSR but also the shooting distance and time since discharge. In the last 40 years, a scanning electron microscope equipped with a detector for X-ray emission (SEM-EDS) became the accepted approach for automatic detection of particles followed by their chemical analysis by EDS. GSR particles are routinely sampled using a scanning electron microscope aluminum sample holder (stub) covered with an adhesive layer (an approach called tape lifting). The stubs are then scanned for heavy metal–containing particles in the scanning electron microscope that examines the signals from the backscattered electron detector.

Surface analysis techniques have the potential to rapidly screen for GSR directly from surfaces and without prior tape lifting. This approach could preserve the pattern of GSR on a surface for further forensic interpretation, preserve other traces, and/or accelerate the search for GSR particles on target surfaces. For example, Langstraat et al. (109) used macroscopic X-ray fluorescence (MA-XRF) for the chemical imaging and classification of GSR over large areas such as entire pieces of clothing and wall paneling. Khandasammy et al. (110) used Raman microspectroscopy to confirm GSR particles previously detected by a highly sensitive fluorescence hyperspectral imaging approach.

To both detect automatically and confirm manually the presence of individual GSR particle(s), an additional step is needed to exclude environmental particles and confirm the presence of GSR. The ASTM (American Society for Testing and Materials) standard currently requires that the analytical approach must be able to detect particles with diameters generally between 0.5 μm and 5.0 μm (111).

The most effective interpretative approach of forensic GSR traces is based on a case by case approach (112, 113): Traces found on the suspect are "compared to case-specific sources, such as cartridges or ammunition/firearm test fire deposits" (111). When this approach is followed, the evidence increases its strength in linking the suspect with a specific crime when unusual elements are found. An example is the presence in GSR of selenium (114) or molybdenum (115) due to the use of lubricants in firearms.

There have been various proposed improvements to the SEM-based analysis of GSR particles to facilitate case-by-case analysis. For example, a novel analytical approach based on the field emission gun scanning electron microscope (FEG-SEM) coupled with an X-flash energy dispersive X-ray detector allowed the characterization of GSR particles at the submicron level, providing previously unknown information about their structure and relationship to shooting distance (116). Additionally, Lucas et al. (117) sectioned particles using a focused ion beam, followed by SEM-EDS mapping of the internal surface. The internal morphology of the particles was found to vary with differing primer composition. Further validation of this approach is needed to verify the consistency of the features observed.

One key issue in GSR forensic analysis is the imaging capability with suitable spatial resolution. Ion beam analysis (IBA) has the capability to provide not only images of single GSR particles but also their analytical characterization (see **Figure 4**). The technology readiness level of IBA approaches in GSR forensic analysis has increased significantly in the last 12 years. For example, the IBA methods PIXE (118), backscattering spectrometry (119), and particle-induced gamma-ray emission (PIGE) (120) can be used to detect elements not shown by SEM-EDS.

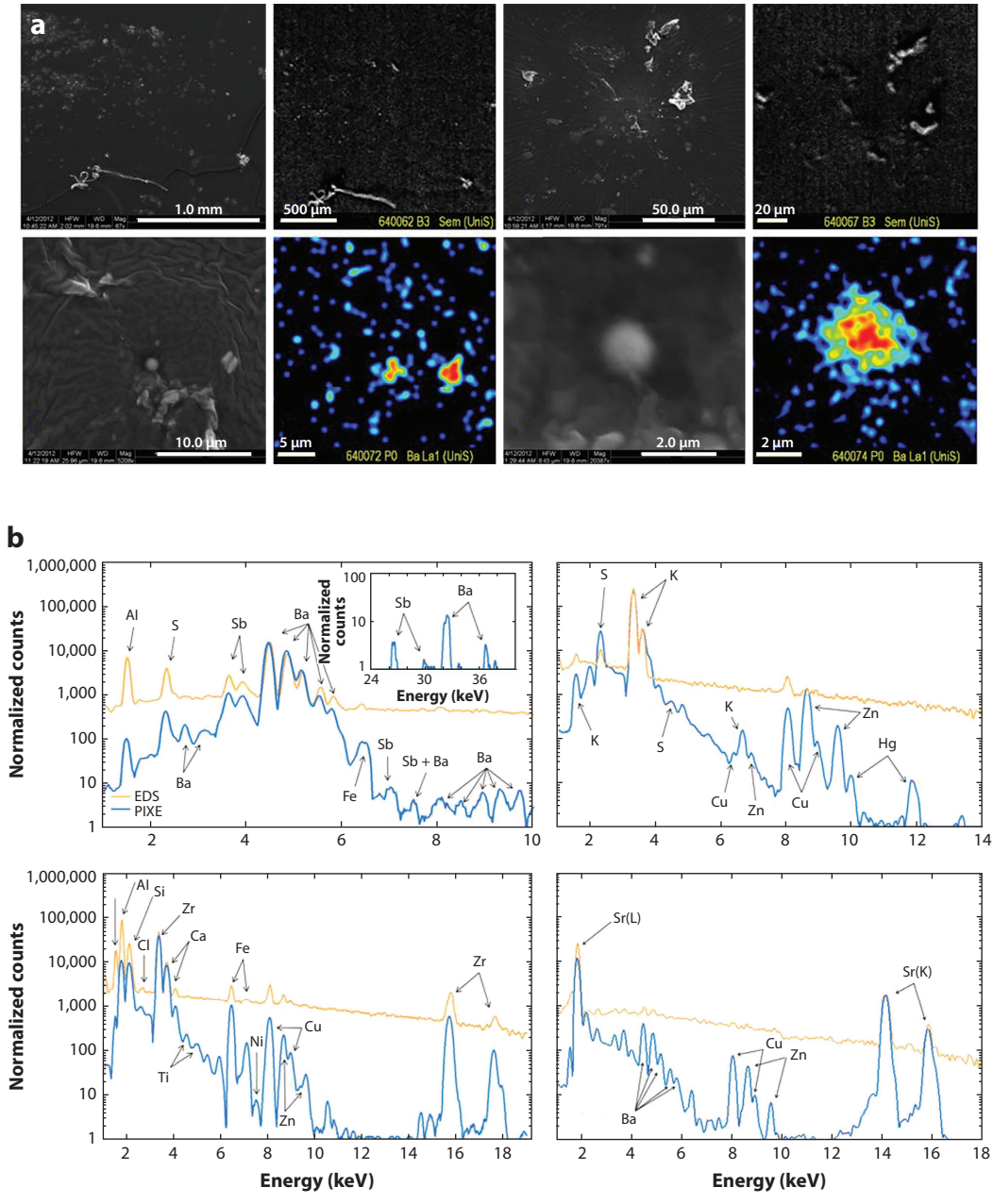

Figure 4

(*a*) The relocation of individual GSR particles from an SEM to a PIXE analysis system. (*b*) Comparison of SEM-EDS and PIXE spectra produced from the same single GSR particles. Abbreviations: GSR, gunshot residue; PIXE, particle-induced X-ray emission; SEM-EDS, scanning electron microscopy energy dispersive X-ray spectrometry. Figure adapted with permission from Reference 120; copyright 2013 Elsevier.

In 2013, Christopher et al. (121) reported for the first time chemometrics of GSR populations by IBA, yielding results that conventional SEM-EDS cannot provide. Later, Duarte et al. (122, 123) reported their IBA results from GSR particles produced after shooting tests and from all constituents of different cartridges. Romolo et al. (124) showed how to use PIXE to overcome the overlap ambiguity of Sb and Sn peaks in the X-ray spectra.

There are also mass spectrometry approaches capable of imaging single particles. In 2020, Aliste et al. (125) published a method to sample GSR in the nostrils using swab devices impregnated in ethylenediaminetetraacetic acid (EDTA) followed by scanning laser ablation and inductively coupled plasma mass spectrometry (SLA-ICPMS). While the proposed method, based on the ablation by a laser having a spot size of 160 mm, failed to provide the morphological information required for GSR identification and would be unsuitable for repeat testing, an interesting finding was that the GSRs persisted for longer periods in nasal mucus than on the hands of shooters.

In contrast, ToF-SIMS allowed Szynkowska et al. (126) to simultaneously visualize and analyze both inorganic and organic components in GSR particles. Secondary ion and electron mapping allowed both chemical and morphological characterization of GSR, providing information on elements and chemical substances at about 300-nm resolution (127).

Spectroscopic imaging can detect both inorganic GSR particles and organic residue on stubs and has been proposed as a rapid screening tool that could outperform SEM-EDS. For example, ATR-FTIR hyperspectral microscopy has been applied to the detection of organic GSR (128) and for inorganic GSR particles sized 4.7 μm or larger (129). Given the typical diameter of 0.5–5 μm, such an approach would be limited to only larger GSR particles. Bueno et al. (130) reported a validation study of a Raman mapping approach for organic GSR detection on adhesive tape, which was able to discriminate between GSR and automotive mechanics. Karahacane et al. (131) separated organic GSR from two different sources using Raman spectrometry and chemometrics.

The toxicity of heavy metals and their impact on the environment are progressively limiting the use of lead, antimony, and barium in the manufacturing of ammunition. SEM-EDS can be incapable of spotting the GSR particles produced by the latest ammunition among the many environmental particles collected by stubs in casework. Research is therefore looking for new analytical solutions. In 2019, Donghi et al. (132) proposed a cathodoluminescence detector coupled to a scanning electron microscope as a promising tool to both detect and characterize residues in forensic cases involving heavy metal free primers, with minor changes to the traditional SEM-EDS apparatus used for inorganic GSR analysis. Finding organic GSR with or without images of GSR is nonetheless expected to increase the probability that the trace comes from a shooting compared to the probability that the trace is not related to the use of firearms.

It has been shown that many surface analysis methods can detect individual GSR particles, and some surface techniques, in particular PIXE, PIGE and SIMS, are already mature enough to provide further information from particles already analyzed by the gold standard SEM-EDS. Forensic practitioners can already obtain analytical information about light elements such as boron and about organic GSR or distinguish elements producing overlapping signals, such as Sb and Sn. However, they will be able to avoid the SEM-EDS analysis only if the new analytical approach can automatically locate possible GSR particles having diameters down to at least 0.5 μm on stubs that are particularly rich in environmental particles if they aim to record images and analysis and to repeat the analysis of the same particle in a reasonable time and at a reasonable price.

PAINT

GSR is a type of microtrace related to the use of firearms, and paint is another type of microtrace capable of providing critical information during a criminal investigation. Paint fragments can be

recovered from incidents involving automotive tools, crowbars, and other painted tools. In investigations involving automobiles, paint can provide crucial information about the make, model, and year of a suspect's vehicle (133). Automotive paint can therefore form significant evidence in automotive incidents. The typical procedure employed by forensic practitioners is optical microscopy, followed by optical spectroscopy and then pyrolysis gas chromatography mass spectrometry (py-GC-MS) (134).

Automotive paint typically consists of four layers: electrocoat primer, primer surfacer, basecoat, and a clear coat. Optical microscopy is often sufficient to discriminate between paint layers, each with their own thickness and color (135). If the paint cannot be properly characterized using optical microscopy alone, FTIR spectroscopy is typically used because it can rapidly and nondestructively interrogate the paint system, for example, the binder/resin, the extender, and pigment components. Raman spectroscopy is also widely described in the literature for forensic paint analysis and provides information on organic and inorganic pigments and some extenders present in automotive paints (136). However, as multilayer paints become more chemically complex, so do the photon spectra. For multilayer paints, IR and Raman spectra can have convoluted spectra, with signal contributions from multiple layers due to the long information depths, which can necessitate further analysis. Py-GC-MS is therefore the next step in many operational workflows to profile organic compounds but is limited because it is destructive and requires long run times (134).

ToF-SIMS has been proposed as a method of mapping organic and inorganic components in the cross section of multilayer paint chips. To ensure that the signal was representative of the paint, and not simply contamination from the resin, it was necessary to first use the gas cluster ion beam in the SIMS system to clean the surface (137). Although this approach should not be expected to compete with existing techniques for throughput, it does offer the potential advantage of detecting organic and inorganic constituents simultaneously.

DART has been proposed as a high-throughput alternative to py-GC-MS for characterizing clear coat samples, requiring lower run times and less sample preparation. Initial results suggest similar discrimination power and detection of complementary species, giving a wider analyte coverage when DART and py-GC-MS are used together (138). Future work is needed to fully establish whether detection of these additional analytes is useful for discriminating between forensic paint traces.

SEM-EDS is found in many forensic laboratories, and one of its applications is forensic paint examination (139). A limitation of SEM-EDS is its low sensitivity to trace elements and lack of molecular information. However, when used in combination with spectroscopy, SEM-EDS can increase the selectivity of forensic paint examination (140). XRF has been shown to add value to FTIR and SEM-EDS analysis of forensic paint through the detection of trace elements from mineral species used in pigments (141).

For forensic paint analysis to provide evidence on the type of vehicle involved in an incident, databases are used. One example is the European Collection of Automotive Paints database, which has optical and spectroscopic characterization data on over 20,000 automotive paints. Use of a database is especially valuable when evidence is considered on a case-by-case basis. For example, if a technique returns a match between paint found at a crime scene and on a suspect's vehicle, a database provides context on the significance of that match, giving insight into whether the match was produced by chance. Many cars are produced with the same paint, but the paint of a repaired car can have unique features.

It is recommended that large sample populations are analyzed by any innovative technique prior to its widespread adoption, that analysis is benchmarked by conventional techniques, and that the analysis undergoes sufficient validation (134). The database should provide guidance on which paint layer(s) to analyze and which sample preparation tools to use. Therefore, proponents

of any new surface analysis methods should consider integrating their data into existing databases whenever possible to increase uptake by forensic practitioners, although it is recognized that analysis of large numbers of samples requires significant funding. Nonetheless, it is clear that surface analysis techniques already play an important role in forensic paint analysis and have the potential to expand on the suite of measurements available.

GLASS FRAGMENTS

Glass fragments are another type of evidentiary material belonging to the class of microtraces and are critically important to criminal investigation in cases such as car accidents, burgled homes, kidnappings, and bombings. Fragments are often found at the crime scene because glass is fragile. Fragments can be easily transferred onto suspects, and it is possible to measure their physical and chemical features thanks to their stability.

Glass analysis provides a case study of the adoption of surface analysis methods into the forensic workflow. There are three ASTM standards for the forensic analysis of glass fragments. These concern glass comparison using micro-XRF (μ-XRF) (142) and the determination of trace elements using ICP-MS (143) or LA-ICP-MS (144).

Interpretation of results is a key issue: Matching criteria, for example, based on a *t*-test or the overlap of confidence intervals, does not take into account the rarity of the glass composition. In 2017, van Es et al. (145) published the method used by the Netherlands Forensic Institute to compare glass fragments based on the concentration of 18 elements analyzed by LA-ICP-MS. The authors preferred the use of a likelihood ratio system to support expert opinion when the forensic question was about the origin of the glass trace. Additionally, Park & Tyner (146) published an article in 2019 criticizing the standard ASTM method. They believe that more data are required to determine a better comparison rule to infer about a source based on the chemical composition of float glass. In contrast, Akmeemana et al. (147) studied data sets of glass of known manufacturing history and found that the data supported both the ASTM match criteria and the possibility of using likelihood ratios.

LIBS is now commercially available as an add-on to LA-ICP-MS systems and can be used to expand upon the analyte coverage. El-Deftar et al. (148) evaluated accuracy, limits of detection, and precision of a commercially available LIBS instrument. They compared the discrimination potential of LIBS to that obtained using LA-ICP-MS, μ-XRF, and SEM-EDS. They concluded that LIBS offers advantages over LA-ICP-MS and μ-XRF and produces similar elemental information.

CONCLUSIONS

Surface analysis techniques can (and in some applications, currently do) offer significant value to forensic investigation, both at the crime scene and in the forensic laboratory. As we have discussed, some surface analysis approaches are now routinely used in forensic laboratories, for example, SEM-EDS for gunshot residue analysis, XRF and LA-ICP-MS for glass analysis, and SEM-EDS and vibrational spectroscopy for paint analysis.

In the future, other surface methods (and other applications of existing methods) could be added to the forensic scientist's toolbox. Stand-off detection of threat compounds by vibrational spectroscopy has reached a high-technology readiness level for on-site application. In the forensic laboratory, surface techniques could enable high-throughput screening and analysis of explosives and drug compounds in biofluids and on surfaces. We have shown how surface analysis methods may enhance the available source level information through enhanced characterization of traces such as GSRs and provide activity level information, for example, by providing information on the deposition sequence of fingerprints and inks on documents. We have also shown how

surface techniques can be used to strengthen hypotheses on drug use through hair testing. In forensic pathology analysis, surface analysis methods remain relatively unexploited but could play a significant future role.

Successful deployment of surface analytical methods will require collaboration between forensic scientists and surface analysts. For a new tool to be adopted in forensic case work, it should be benchmarked by techniques already available and undergo sufficient validation to be considered reliable. Surface analysts proposing a new approach should consult forensic scientists to ensure these benchmarking and validation exercises are appropriately designed. The proponents should also consider how destructive any sample preparation or analysis is to other traces and how their method would fit within current forensic workflows. Finally, the integration of data obtained by surface analysis methods into existing databases will be needed for full operational deployment of surface analysis methods in forensic science casework.

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