Recent advances in micro-sample preparation with forensic applications

Abuzar Kabir, Howard Holness, Kenneth G. Furton, José R. Almirall

Sample preparation in forensic science offers special challenges in that the sample matrix and the analytes change depending on the circumstances of the case. It is difficult to standardize the sample preparation step for many types of cases due to sample and matrix complexity and the total unknown nature of the target analytes present within the matrix. Secondly, the analytical results obtained from forensic samples often undergo rigorous legal scrutiny and challenges. As such, maintaining the integrity of the sample chain of custody should be considered during the sampling and sample preparation prior to analysis. Finally, for those sample matrices where the sample preparation can be standardized (i.e., fire debris analysis and toxicology), utmost care should be taken to minimize the possible interferents and maximize the analyte concentration to meet the analytical requirements.

In this article, we discuss the nature and the types of forensic samples of interest, and recent developments and innovations in micro-sample preparation techniques in different disciplines within forensic science. We also discuss the future outlook of forensic sample preparation.

Keywords: Environmental forensics; Explosive; Forensic toxicology; Gunshot residue; Human decomposition product; Human odor; Ignitable liquid residue; Micro-sample; Sample preparation; Trace analysis

Abuzar Kabir*, Howard Holness, Kenneth G. Furton, José R. Almirall, International Forensic Research Institute, Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, Florida 33199, USA

*Corresponding author. Tel.: +1 305 348 2396. E-mail: akabir@fiu.edu

1. Introduction

The application of scientific values and practices for legal purposes defines the basics of forensic science. Chemists in the field not only examine a wide variety of samples of forensic interest, but also interpret data acquired from the analytical investigation to present in civil and/or criminal judicial proceedings. Continual advances in the area of forensic analysis are essential because applications of forensic chemistry have broad implications in the establishment of evidential value of the analyzed sample to the court of law with a superior level of quality assurance.

An important first step in forensic chemical analysis is sampling and sample preparation, especially when working with trace and ultra-trace levels of the target analyte(s) present in various complex matrices (e.g., soil, biological, environmental, drug, and fire-debris), and the amount of the sample available to the investigator is limited, as in most cases. Considering the complex nature of the sample matrix in which the desired analyte(s) is present, the samples cannot be introduced directly into the analytical instrument for qualitative/quantitative chemical analyses. This is because the complex sample matrix can damage the performance of the analytical instrument if introduced without prior sample treatment/clean-up procedures and the concentration of the analyte of interest in the sample matrix may be lower than minimum limits of detection (LOD) of the instrument. Unlike with other disciplines, it is difficult to standardize the analytical approach to sampling and sample preparation, as every forensic case is unique. Although conventional sample preparation techniques [e.g., liquid-liquid extraction (LLE), solid-phase extraction (SPE), purge-and-trap and their different modifications] are still being used in handling almost all types of forensic samples, recent trends clearly attest that embracing micro-sample preparation techniques [e.g., solid-phase microextraction (SPME) and liquid-phase microextraction (LPME)] in forensic samples is continually rising.

0165-9936/$ - see front matter © 2013 Elsevier Ltd. All rights reserved. doi:http://dx.doi.org/10.1016/j.trac.2012.11.013

This review article discusses the variety of new sample-preparation techniques being applied to analyze forensic samples and focuses on the present best practices and the newest developments in sampling and sample preparation techniques for forensic samples with special emphasis on emerging micro-sample preparation techniques. Considering the complexity, limited availability, and the legal implications of forensic samples, micro-sample preparation techniques seem more appropriate than their conventional counterparts because of their superior attributes, which include:

- simplicity in operation;
- relatively short extraction time;
- comparatively low matrix interferences;
- equilibrium based non-exhaustive extraction allowing multiple extraction from the same sample;
- solvent-less or solvent-minimized extraction;
- easy to interface with many analytical instruments;
- potential of automation;
- due to the possibility of non-invasive sampling, integrity of the sample can be maintained if required as forensic evidence; and,
- portable and therefore convenient for field sampling.

Fig. 1 demonstrates major sample preparation techniques currently used in different areas of forensic chemistry. Although it is very challenging to cover such a broad topic in a single article, we have given our best effort to include as much information as possible. Interested readers are encouraged to read the references cited in the article for additional, more comprehensive information.

2. Sampling and sample preparation of trace evidence

Trace evidence may be defined as materials that normally require a microscope to observe them, prior to forensic analysis. Sampling and sample preparation of ''trace evidence'' is important for forensic samples due to the nature of the samples of interest, the matrix from which they are collected at the crime scene and the manner that these are received into the laboratory. Trace evidence originates from transfer of man-made and natural materials, and it can be used to associate objects to a person, persons to a location or to another person or objects to each other, through contact. The more violent the contact (e.g., a vehicle crash), the greater the opportunity for trace evidence transfer. The category of trace evidence normally includes glass, fiber, tapes, adhesives and paint evidence, but, because of the small quantity of the material analyzed, other substrates (e.g., paper, ink on paper, and other materials) can also be categorized as trace evidence and are therefore included here.

2.1. Characterization of glass, paint, fibers and hairs

The use of laser-induced breakdown spectroscopy (LIBS) is gaining popularity amongst forensic scientists as a fast, simple technique that does not require much sample preparation. The use of LIBS and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) for the elemental analysis of white cotton fibers [1,2] has been reported. The more expensive, more complex method of LA-ICP-MS for the elemental analysis of glass continues to be used {e.g., the recent publication on sampling ancient glass [3]}. When combined with refractive index, LA-ICP-MS was reported to provide excellent discrimination between different sources of container glass samples [4]. Although LIBS is a relatively new sampling/analysis method, it was reported as providing excellent discrimination between glass samples thought to have originated from different float-glass manufacturing sources [5,6].

The use of Fourier transform infrared-attenuated total reflectance (FTIR-ATR) imaging of paint cross sections was reported as a useful method for paint characterization [7,8], and laser-desorption MS was used to analyze synthetic organic pigments in works of art [9]. A novel application of Fourier transform photoacoustic infrared (PAIR) spectroscopy was used in the forensic analysis of inorganic pigments [10].

LIBS was also used by McIntee et al. for the elemental analysis of automotive paints [6,11], as was scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) for elemental analysis (but with ~100 times worse sensitivity) [12]. The organic components of car paint samples were differentiated using microspectrophotometry in the visible range [13], and pyrolysis-gas chromatography-MS (Pyr-GC-MS) was used for the analysis of spray paints [14]. The plasticizer content in polyvinyl acetate polymer (PVA) binders in the paint medium [15] was also analyzed using microspectrophotometry.

An FTIR-ATR sampling method was recently reported for the examination of hair-keratin fibers [16] that could be of interest to hair and fiber examiners. Characterization and interpretation of dyed hair was reported using two-dimensional infrared correlation spectroscopy [17]. Sampling and sample preparation techniques that facilitate the coupling of chromatographic methods to MS for the analysis of drugs and other organic compounds of interest to forensic scientists in hair were also recently reported [18–20]. A recent publication reported sample preparation prior to elemental analysis of hair using inductively coupled plasma optical emission spectrometry (ICP-OES) [21], as was the direct solid sampling of hair for elemental analysis using electrothermal atomic absorption spectrometry (ET-AAS) [22], capillary electrophoresis (CE) coupled to a chemiluminescence detector [23] and ICP-MS [24]. Kirkbride et al. recently

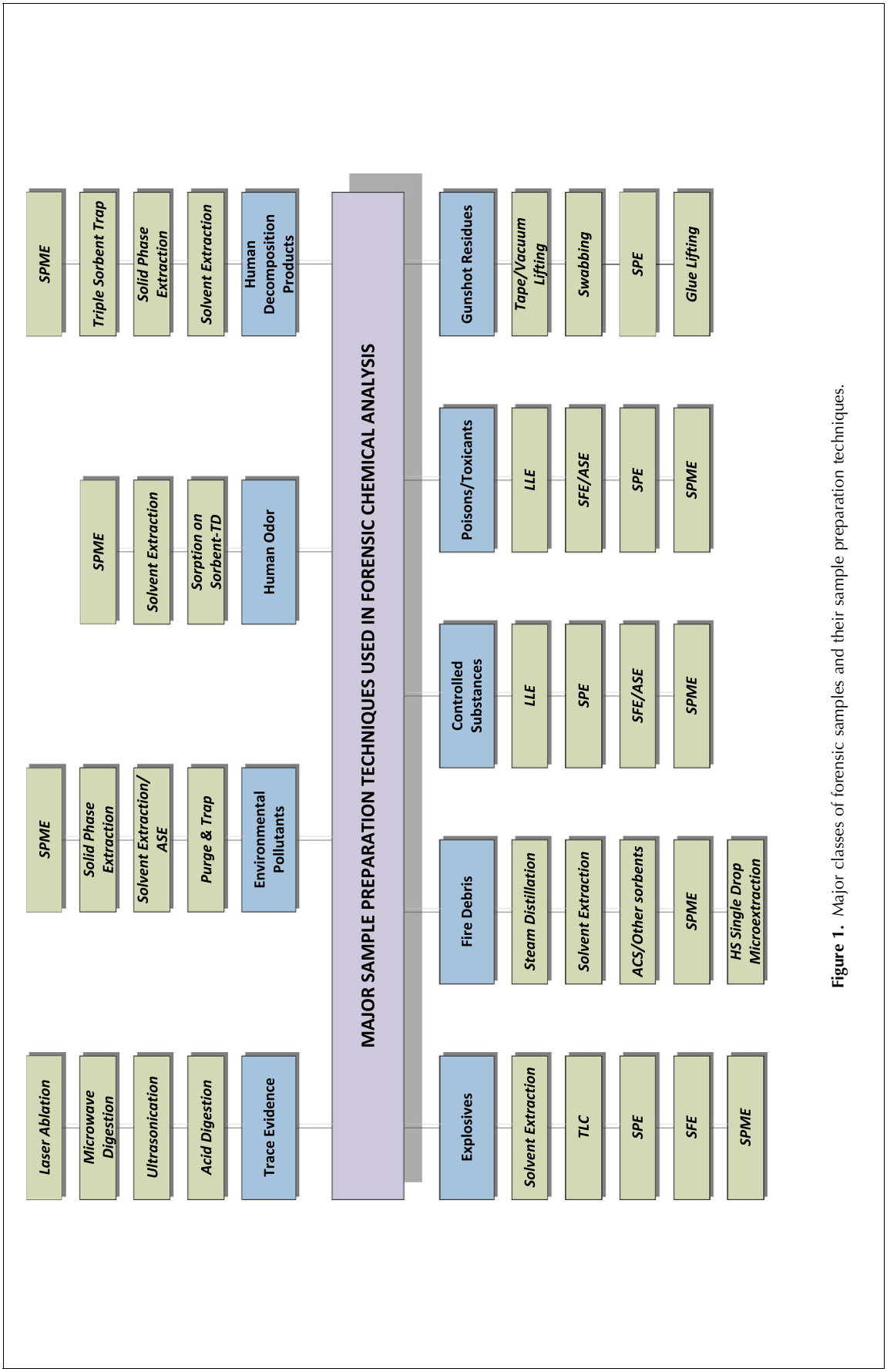

Figure 1. Major classes of forensic samples and their sample preparation techniques.

reported the use of scanning confocal microscopy (SCM) for the examination of hairs and textile fibers [25] and a chemical microextraction of dyes from fibers followed by CE coupled to MS (CE-MS) was also reported [26].

Thermal hydrolysis of trace quantities of natural fibers (wood and vegetable sources) was followed by methylation and pyrolysis GC-MS [27]. Black textile fibers were also discriminated from each other with a combination of Raman and UV-visible spectroscopy [28]. A more general fiber characterization using UV-visible microspectrophotometry was reported [29], and the sampling and analysis of a single PET fiber for the elemental composition of the fiber was reported using laser ablation (LA) coupled to an ICP-MS [30].

2.2. Paper analysis and analysis of ink on paper

The usefulness of micro-Raman for the identification of the organic components of inks has been reported by several groups [31,32]. Desorption electrospray ionization (DESI) has been used to characterize the organic composition of the inks by Allison [33] and reported separately by Weyermann et al. [34,35], Adams et al. [36], Donnelly et al.[37] and others using a variety of methods of surface desorption methods followed by ionization including UV-laser desorption ionization MS (LDI-MS) [37] and direct analysis in real time MS (DART-MS) [36]. These researchers reported >85% discrimination between different inks including printer inks [37] when combining the collection of negative and positive ions of the molecular spectra. The characterization of naturally and artificially aged inks and papers was conducted using pyrolysis GC-MS [38]. Micro-attenuated total reflectance sampling coupled to FTIR was also reported for the study of documents containing red seal inks [39] and Coumbaros et al. reported the use of time-of-flight secondary ion MS (ToF-SIMS) for the *in situ* analysis of ballpoint-pen inks on paper [40]. ToF-SIMS was also reported for the simultaneous analysis of organic and inorganic components from ballpoint-pen inks [41].

The inorganic components of toner inks were reported using direct solid sampling for chemical characterization using LA-ICP-ToF-MS [42] and the elemental characterization of historical documents (paper) was reported with the use of SEM-EDS [43]. Paper was also characterized with the more laborious acid-digestion sample preparation followed by ICP-MS analysis [44,45] in order to discriminate between paper sources. A comparison of different methods [e.g., X-ray fluorescence (XRF), LA-ICP-MS and isotope ratio MS (IRMS)] for the analysis of paper was also recently reported [46]. The use of LA-ICP-MS and LIBS for the elemental characterization of both paper and gel inks was reported to provide >95% discrimination [47] and the elemental composition of blue ballpoint-pen ink was determined by LA-ICP-MS by other groups [48]. Finally, the use of total reflectance XRF was also reported for the elemental characterization of ink samples [49] and the use of graphite furnace atomic absorption spectroscopy (GF-AAS) was reported for the determination of metals in iron gall ink [50].

3. Micro-sampling applications in forensic toxicology

Forensic toxicology may be defined as the analysis of substances from human body fluids and tissues. The target analytes are often controlled substances that cause high mortality at relatively low doses (toxins) [51]. As a result, these substances require extraction from a matrix and analyte enrichment (pre-concentration) prior to being analyzed. Both LLE and SPE have been the *de facto* extraction and pre-concentration methods of choice for forensic toxicology for over 40 years [52]. However, these methods, though reliable, need improvement due to their requirements for relatively large samples, which are limited in forensic applications, and large amounts of solvent for extraction.

Several techniques have emerged to overcome these hurdles while providing comparable extraction efficiencies. These techniques are termed micro-sampling or microextraction techniques, as they remove only a portion of the analyte of interest and are based on equilibrium between the analyte and the extraction phase [53]. The most popular micro-sampling technique has been SPME, which has been reworked into several other adaptations [53] [e.g., electrochemically enhanced SPME (EE-SPME) which was developed by applying electrical potentials to a SPME fiber while it was immersed in a biological matrix]. EE-SPME was reported to extract 11 times more analyte from urine than conventional direct immersion-SPME and eliminated the need for analyte derivatization [54].

For even higher extraction efficiencies than EE-SPME, stir-bar sorptive extraction (SBSE) has been developed. SBSE utilizes a magnetic stir bar coated with polydimethylsiloxane (PDMS), which stirs in the matrix of interest to extract a target analyte [55,56]. This method has yielded analyte-recovery values of 45.7–99.9% for analytes dissolved in urine allowing for detection in the parts per trillion (ppt) range [55].

Conventional SPME, though widely used, is limited in its ability to extract non-volatile analytes. To overcome this limitation, SPME membrane (SPMEM) was introduced in 2004 [57]. The SPMEM device is immersed directly into the matrix of interest. The analyte is then desorbed using a solvent and sonication. The extract is then subjected to chromatographic analysis, extracting less volatile compounds than headspace-SPME and using far less solvent than conventional SPE [57].

Thin-film microextraction (TFME) was also developed and used to perform direct extraction of analytes from

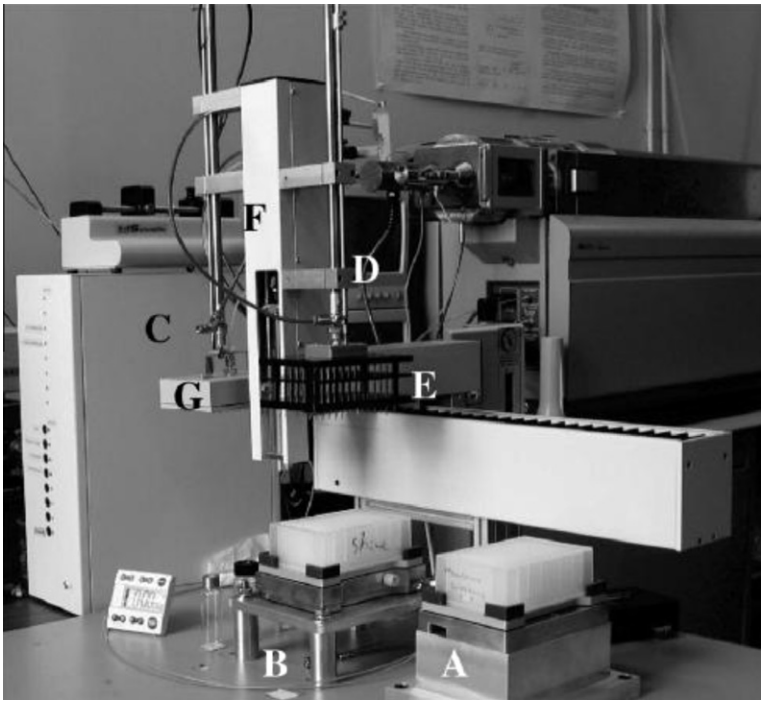

Figure 2. Image of high-throughput automated SPME sampler. (A, B) Orbital agitators for extraction and desorption; (C) system controller; (D) arm used to manipulate the SPME multifiber device; (E) SPME multifiber device; (F) syringe arm; and, (G) arm used for simultaneous nitrogen evaporation from all wells. (Reprinted with permission from [60], ©2008, American Chemical Society).

whole blood without requiring any prior sample preparation [58].

Restricted access materials (RAMs) have been extensively developed and used for the on-line extraction of plasma samples. RAM combines tedious SPE or LLE and protein precipitation into a single step providing a faster sample purification process for the analysis of analytes in blood samples [59]. A high-throughput automated system utilizing SPME has also been developed to mimic the automated SPE systems traditionally used in toxicology and other areas of analytical chemistry. This has allowed the extraction of 96 samples in as little as 100 min utilizing SPME (Fig. 2) [60].

Other non-SPME based micro-sampling techniques have also emerged. A new format of SPE termed microextraction by packed sorbents (MEPS) has been successfully used to extract analytes from whole blood and plasma utilizing much smaller volumes than traditional SPE. A review highlighting this technique has been published by Rehim [61].

Another non-SPME based micro-sampling technique is Spin columns, which utilize conventional SPE packing particles (e.g., C_{18}), but are more compact than conventional SPE and so require less solvent and smaller sample sizes for extraction [62]. These columns are used in conjunction with a centrifuge in order to perform the extraction steps of conditioning, elution and washing.

Disposable pipette extraction (DPX) or tip-based microextraction (TBME) is a variation of Spin columns that utilizes packing particles in a pipette tip. This eliminates the need for centrifugation as all extractions steps occur by aspiration of the pipette itself [63,52]. However, it has been reported that Spin columns produce fewer errors than DPX, as DPX relies heavily upon manipulation by the analyst [64] (Fig. 3).

Monolith columns have also seen increased usage due to their ability to separate analytes from mixtures and be directly coupled to high performance liquid chromatography (HPLC) systems. One disadvantage of particle-filled extraction (e.g., as DPX and Spin columns) is the presence of irregular inter-particle voids, which results in extractions being irreproducible. Porous monoliths have been developed to overcome this shortcoming, as monoliths may be considered a ''single large particle'' that contains no inter-particle voids [52]. This results in higher reproducibility and faster mass transport, but the downfall is low mass loadings due to monoliths possessing much smaller surface areas than other sorbents.

Monoliths have been widely used since being developed in the 1990s and have already been adapted in Spin-column technology as a sorbent, termed monolith Spin-column microextraction (MSCME). This combination results in a highly reproducible extraction sorbent that is able to elute analytes from biological matrices (e.g., urine) independent of the pH of the elution buffer being used [62].

In addition to monolith columns, molecularly-imprinted polymers (MIPs) have been developed to

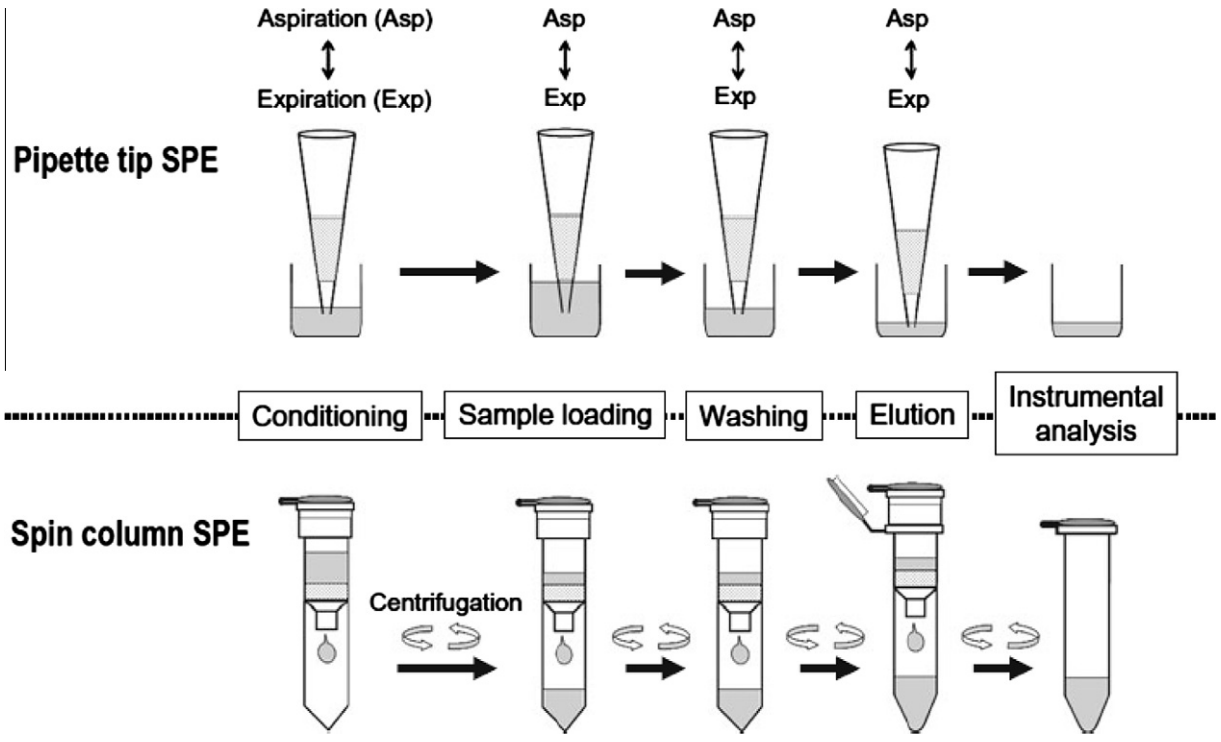

Figure 3. Comparison of procedure for DPX and Spin column extraction. (Reprinted with permission from [64],©2008, Springer).

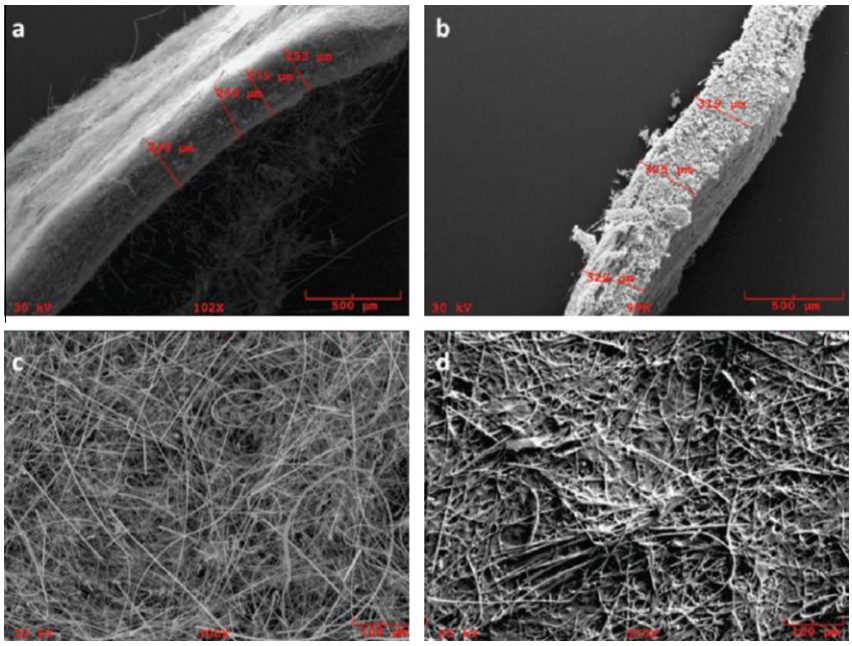

Figure 4. Scanning electron micrograph of planar SPME coating. (a, c) Images of the cross section and surface of the original glass fiber substrate, respectively; and, (b, d) images of the cross section and surface of the coated dynamic PSPME device, respectively. (Reprinted with permission from [71], ©2010, American Chemical Society).

enhance the extraction of SPE, and there has been a review of these developments [64].

The main requirement for sample extraction in forensic toxicology is the isolation of analytes from

matrices that contain high levels of proteins. To accomplish this, protein precipitation plates have been developed and are commercially available through several vendors. These plates allow for the simultaneous precipitation of unwanted proteins and the isolation of target analytes in a single step. This has greatly increased sample throughput in forensic toxicological applications and reduced errors and analyte loss associated with transferring samples in traditional multi-step protein precipitation procedures [65].

4. Micro-sampling of explosives

The sampling of explosive devices in forensic science has received much attention over the past two decades. The nature of explosives dictates that only small amounts be sampled without disturbing the bulk material. Micro-sampling is ideal for the sampling of explosives and similar materials where a small aliquot of the original sample is preferred to large amounts of the bulk. Micro-sampling of explosives has been dominated by the use of SPME [66], which has allowed for the analysis of minute quantities of volatile organic compounds (VOCs) of explosives to indicate the presence of the parent material [67]. Much research has also been devoted to sampling and preconcentrating the minute quantities of explosive vapors available in order to improve the overall LOD of a technique [68–70]. Improvements in this area have included increasing the surface area of SPME devices in order to extract greater quantities of explosive vapors through development and utilization of planar SPME (PSPME) [71,72] (Fig. 4).

Other sampling techniques have utilized cavity enhanced absorption spectroscopy (CEAS) [73]. Still others have developed disposable colorimetric devices that are sensitive enough to detect 2 parts per billion (ppb) of explosive vapors from triacetone triperoxide (TATP) in air [74], neutron based techniques have been developed that can detect ammonium nitrate [29] and other explosive simulants [75]. Sampling of low vapor pressure explosives [e.g., trinitrotoluene (TNT)] has also been reported utilizing surface acoustic wave (SAW) with a novel PDMS copolymer [76], and Cryoadsorber traps have been developed to extract extremely low amounts of volatile components of plastic-bonded explosives (PBX) [77]. Fluorescent chemosensors have been reported as being able to detect explosive vapors of TNT as low as 4 ppb [78] and selective microcantilevers have been developed that respond to vapors of hydrogen peroxide from home-made explosives [79]. Research has attempted to mimic the olfactory capabilities of animals with devices [e.g., electronic noses made of metal oxide semiconductors (MOSs)] with capabilities to detect 3.34 μg/L of explosive compounds in air [80,81]. Also molecularly imprinted sensing films can extract explosive compounds (e.g., TNT and DNT) from air with LODs as low as 5 ppb [69].

5. Analysis of ignitable liquid residues from fire-debris

Crimes involving fire, unlike other crime scenes, often destroy any direct physical evidence related to the arsonist (e.g., DNA, fingerprints), forcing investigators to rely on potential sources of ignitable liquid residues (ILRs) or accelerants that the arsonist may have used.

American Society for Testing and Materials (ASTM) classified ignitable liquids into nine primary classes: gasoline, petroleum distillates, isoparaffinic products, aromatic products, naphthenic products, n-alkanes products, de-aromatized distillates, oxygenated solvents, and others/miscellaneous [82]. Most common accelerants used by arsonists include gasoline, kerosene, paint thinners, charcoal lighter fluids, alcohols, mineral spirits, fuel oils, and vegetable oils. In order to prosecute the suspected arsonist(s), investigators use valuable information about the type of accelerants used in the case obtained from the detection or identification of ILR from the fire scene. Two recent books ''Analysis and Interpretation of Fire Scene Evidence'' [83] and ''Fire Debris Analysis'' [84] extensively cover all important aspects of fire science from a forensic perspective. Also, a number of review articles have shed light on different aspects of this important topic [85,86].

Fire-debris samples, as a source of ILR, are collected from the scene in clean, leak-free containers before being transported to a laboratory for immediate analysis. Commercial containers (e.g., metal paint cans, glass mason jars, and copolymer bags), are among the most commonly used as fire-debris evidence-collection/storage containers. A study [87] to show the best containment system out of all the commercially available for fire-debris samples identified that, in containing hydrocarbons, properly heat-sealed copolymer bags worked best of the three tested systems (metal paint cans, glass mason jars, and polymer bags). The performance of the containment systems for other ignitable liquid classes are yet to be studied.

Solvent extraction is among the oldest known and commonly used sample preparation technique to isolate ILRs from fire-debris using selective organic solvents suitable for extracting hydrocarbons (as a common ILR ingredient). A recent study comparing the relative efficiency of passive headspace concentration and solvent extraction for extracting alternative fuels (biodiesel and its blends) from fire-debris found solvent extraction being more representative of the liquid residue than passive headspace concentration in terms of chromatographic profiling [88]. However, some major limitations of the solvent extraction include the loss of highly volatile organic compounds when evaporating

the solvent, insolubility of certain ILR and extraction of unwanted components from the debris not originally in the ignitable liquid.

Passive headspace concentration of ILRs is the method of choice for many forensic chemists as it is relatively simple, being less laborious, yet based on the equilibrium extraction technique that offers the possibility of multiple extractions from the same sample without discernible loss in signal intensity. Passive headspace extraction can be performed by using activated charcoal or by SPME, and it involves natural and passive diffusion of analyte vapors onto the surface of the adsorbent. Passive headspace concentration with activated charcoal uses activated charcoal strips (ACSs) to extract residues from a closed sampling container and it is recommended to heat the matrix to 60–80°C for 8–24 h in order to achieve higher sensitivity [87]. Following extraction into ACS strips, desorption in carbon disulfide (CS_2), evaporation of CS_2 to reduce the solvent volume, and injection into the analytical instrument is suggested. From the forensic point of view, this method is better than many others, since the ACS strip can be cut into pieces and segments stored for later use if the accuracy in test results is challenged in court. Passive headspace concentration can be performed using the diffusive flammable liquid-extraction device (DFLEX), in addition to using commercially available ACS strips, using an ACS placed within a metal frame between two permeable Teflon sheets.

Radiello passive air sampler [89] is a new addition as a commercially-available passive air sampler using activated carbon as the adsorbent medium. The device is made of an adsorbing cartridge containing 530 ± 30 mg of activated carbon, a porous hydrophobic diffusive body with porosity of 25 ± 5 μm and a supporting plate holding the diffusive body. Radiello's saturation limits have been claimed to be in the range 85–100 μL, which is significantly higher than most commercial samplers. However, one major setback of this device is its poor response towards high molecular weight hydrocarbons (> n-C_{16}).

SPME has arisen as a feasible technique for passive headspace extraction over the last decade. It is superior to ACS by reducing sampling time, having higher sensitivity, eliminating usage of hazardous and toxic organic solvents (e.g., CS_2), and is able to extract analytes from aqueous matrices and headspace. Finally, SPME sample recovery is achieved by transferring the extracted analyte by inserting it into a hot GC inlet. Among the wide range of commercially-available SPME fiber chemistries, PDMS (30 μm) [90], PDMS (100 μm) [91,92] and Carboxen/PDMS (75 μm) [93] fibers are used most frequently for fire-debris analysis. A study comparing the selectivity of PDMS and Carboxen/PDMS for headspace sampling found that polydimethylsiloxane, (PDMS) and Carboxen/PDMS SPME fibers showed preferential extraction of aliphatic or aromatic compounds from the headspace, depending on fiber type and temperature. However, the Carboxen/PDMS fiber showed higher selectivity for obtaining aromatic hydrocarbons [94]. SPME of ILR from fire debris has been reported by using direct contact with the matrix [91], by exposing to the headspace [92,90] or by submerging directly into the liquid sample matrix, with optimized extraction time of 15–30 min, matrix heating in the range 20–80°C, and desorbing in the GC inlet for up to 5 min.

Very often in arson cases, the arsonist accidentally spills accelerants on himself, potentially giving investigators valuable clues about the suspect. In relation to the high demand of a simple, efficient sampling technique to collect ignitable liquid samples from the hand of a suspected arsonist, Almirall et al. [95] presented an SPME method capable of obtaining extremely low quantities of ILR present on the suspect's skin even after 3.5 h of the initial exposure. The method utilized a 100-μm PDMS fiber with gentle heating for 5 min followed by 10 min of extraction from a plastic bag around the suspect's hand.

An innovative sampling technique, known as thermal desorption cold trap (TCT) extraction [96,97], uses a TCT injector coupled on-line with GC-MS. The desorber is programmed at 120°C to drive off the ILR under a helium flow for 4 min; the analytes are then cryofocused at −100°C, followed by introducing the analytes into the GC column by increasing the inlet temperature to 250°C. This method is quick, does not require any manipulation of matrices prior to extraction and can detect as low as 100–150 mg of ILR present. One flaw, though, is the requirement that there should be absolutely no moisture in the matrix in order to minimize the risk of blockage of the cryotrap.

In dynamic headspace extraction, air or inert gas (e.g., nitrogen) is passed over the sample to force medium-high boiling ILRs to spread through the absorbents and get extracted onto it. Frequently used adsorbents include ACS, Porapack Q, Tenax GC, and Chromosorb 102. They possess very high specific surface areas and are thermally stable so that analyte(s) can be desorbed by the thermal desorption process and are commonly introduced into the GC system for separation/identification of compounds. The only exception is ACS, which requires very high temperature to release extracted analytes, so usually solvent desorption using CS_2 is used to desorb extracted analytes.

The introduction of headspace single-drop microextraction (HS-SDME) is a new advancement in sample preparation techniques for fire-debris analysis, using 2.5-μL benzyl alcohol microdrops exposed to the headspace of a 10-mL aqueous sample placed in a 15-mL vial for 20 min with continuous stirring of the aqueous phase at 1500 rpm. HS-SDME, due to the concentration difference between acceptor and donor phases, demonstrated an LOD of 1.5 μL for kerosene in the simulated fire-debris experiment [98].

6. Sample preparation in environmental forensics

As concern grows over pollution and its hazardous effect on the environment and human health, so has the field of environmental forensics. The field covers all aspects of environmental pollution and contamination within water, air, and soil. Environmental forensics involves identifying contaminant release, determining the possible sources of it, estimating the approximate timing of its release and distribution into the environment, appropriation of the liability for the damages among the sources, and prosecuting those responsible.

The US regulation, known as ''The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)'' [99], is the major defense for environmental forensics, funded by a tax on the chemical and oil industries in the USA. The Clean Water Act is another major legislation [100] authorizing each state to establish its own water quality criteria and limits on the disposal for particular contaminants.

US EPA has classified, and closely monitors, 126 compounds as the priority pollutants for their disposal, distribution and fate in the environment. EPA priority pollutants include polycyclic aromatic hydrocarbons (PAHs), asbestos, pesticides, heavy metals, polychlorinated biphenyls (PCBs). The US EPA has also classified 116 separate compounds on the Contaminant Candidate List (CCL). Compounds of this class include pesticides, disinfection byproducts, commercial chemicals, waterborne pathogens, pharmaceuticals and biological toxins. CCLs are not monitored by national primary drinking water regulations but may be regulated by the Safe Drinking Water Act (SDWA).

Morrison extensively reviewed all principal methods generally used in environmental forensics [101,102]. Several books were also published in recent years covering the entire field of environmental forensics [99,103]. Although the jurisdiction of environmental forensics encompasses all current and potential manmade pollutants, only a few have attracted the attention of environmental forensic scientists {e.g., asbestos, sewage, heavy metals, radioactive compounds, pesticides, perchlorate, polychlorinated biphenyls (PCBs), chlorinated solvents, dioxin and furans, polycyclic aromatic hydrocarbons (PAHs) and petroleum hydrocarbons [99]}. Of all the pollutants, petroleum hydrocarbons have been investigated the most. Environmental pollution by illicit drugs and pharmaceuticals has also attracted attention in recent years [104].

Sampling strategy is a crucial part in environmental forensics as the targeted contaminants are not always consistently distributed across the affected area, so it is of great importance to pay judicious attention when selecting the region of the affected area to be investigated (known as the decision unit), having confidence in the data collection, collecting the samples from the decision unit, preserving the integrity of it prior to analysis, maintaining chain of custody of the samples beginning from the collection through to analysis, and taking analytical sub-samples from the field sample. Establishing a feasible quality control measure in guaranteeing the value of the entire analytical process from any errors is another important factor, often involving trip blanks, field blanks, decontamination check blanks, splits, and replicates [99].

US EPA has developed a number of standard methods [99] in order to measure volatile and semi-volatile hydrocarbon compounds in water, soil, tissue, oil, air and other matrices.

6.1. Volatile hydrocarbon fingerprinting

Tar distillates with hydrocarbons (C_4–C_{12}) and light refined petroleum products are types of volatile hydrocarbons. Regulated compounds (e.g., benzene, toluene, ethylbenzene, and xylene isomers) belong to this group. Different toxic additives and/or bleeding agents, often added to refined petroleum (e.g., MTBE, ETBE, TBA), offer invaluable information about the origin or the source of the refined petroleum. Volatile hydrocarbon data are usually used to define the type and the origin of the pollutant, the degree of weathering and occasionally the approximate timing of its disposal into the environment [99].

6.1.1. Air. Petroleum products and tar distillates release many dangerous hydrocarbons into the atmosphere, and their efficient capture and analysis may provide valuable information for fingerprinting. EPA Method TO-15 is mostly used for potential indoor air pollutants; suspect air samples are drawn through sampling loops made of regulators controlling the rate of flow and the duration into the empty canister. Then, a known volume of air is transported through a multisorbent concentrator before analyzing the air with the suspected pollutant(s). It is then thermally desorbed into a GC/MS system to analyze the contaminants chromatographically. This method has proved to be extremely useful in generating qualitative and quantitative data for VOCs in air and sub-surface vapors.

6.1.2. Soil. EPA Method 5035A usually governs the collection of soil samples for VOC analysis. This method illustrates a closed system purge-and-trap and extraction for VOCs analysis in soil and waste samples. Soil samples are collected using an EnCore sampler, purge-and-trap soil sampler or similar sampler. In order to lessen the potential loss of VOCs during sampling, great precautions must be taken. The sample is placed in a prelabeled foil container to be shipped back to the analytical laboratory. EasyDraw™ syringes and PowerStop™ handles

are used to collect samples in small quantities if they can be processed on site. Approximately 5 g of sample is transferred into a 40-mL septum-capped volatile organic analysis (VOA) vial containing 5 mL of deionized water and a Teflon stir bar. If not analyzed immediately, the sample must be refrigerated.

VOCs are purged through Tenax GC/methyl silicone packing OV-1 (3%) on Chromosorb-W/coconut charcoal/Carbopack/Carbosieve trap to preconcentrate the VOCs on the trap. The trapped VOCs are then desorbed thermally and introduced into the GC system for separation and analysis. Chromatographic analysis of the VOCs can be carried out following EPA Method 8015/8021/8260 or any other suitable GC methods.

Direct headspace analysis can be used when the target VOC is at a relatively high concentration in soil samples. Competence in headspace analysis depends greatly on optimizing several factors (e.g., temperature, and headspace volume). Sewage samples and sediments have also been systematically analyzed by this method [105].

6.1.3. Water. Pre-cleaned Teflon bailers are used to collect water samples for VOC analyses. Draining water into a 40-mL septum-capped VOA vial containing HCl to adjust the pH of water to 2 prepares sub-samples. Samples are then stored at 4°C. Long storage of water samples containing VOCs is not encouraged as Bravo-Linares [106,107] demonstrated that even storing for 2–4 h may potentially decrease VOCs at 5–30%/h. During analysis, VOCs are stripped from the water samples by a continuous stream of an inert gas (He/N_2). The cleansed volatiles are then trapped on a sorbent cartridge or a cryotrap. The trapped analyte(s) are then transferred by thermal desorption to a GC system. Although quite lengthy and complicated, the dynamic headspace or purge-and-trap system has proved to be reliable, being used to analyze VOCs in water [108], sea water [109] and drinking water [110].

Although purge-and-trap is the most commonly used technique in VOC analysis of water, SPME has shown favorable results. Bravo-Linares et al. [107] has demonstrated that SPME performs better than purge-and-trap in the analysis of VOCs in sea water. A modified version of SPME designed to take advantage of purging the VOCs through the SPME fiber has successfully identified and quantified in a single analysis a wide range of VOCs from sea water, including sulfur-containing compounds, halogenated compounds, non-methane hydrocarbons, BTEX, aldehydes, and terpenes.

6.2. Non-aqueous phase liquid (NAPL) samples

Teflon bailers or other suitable collection systems are used to collect non-aqueous samples from the field. The collected samples are placed into 25-mL or 40-mL hard-cap VOA vials with minimal headspace. The VOA vials can be filled with water from the bailer to reduce the headspace if available NAPL samples are limited. Prior to shipping to the analytical laboratory, the NAPL samples are stored at 4°C. VOCs present in NAPL samples are also analyzed using a method similar to that used for water samples.

6.3. Semi-volatile hydrocarbon fingerprinting

Although semi-volatile hydrocarbons are not clearly distinguished from volatile hydrocarbons by the US EPA, sample preparation varies to some extent and calls for careful consideration. Semi-volatile hydrocarbons include crude oil, refinery intermediate and petroleum products (e.g., kerosene, diesel, and residual fuel oils) [99]. Coal tars, oil tars, wood tars, and their derivatives are also considered to be semi-volatile.

When environmental samples (generally soils and sediments) are highly contaminated and contain an excess of unwanted materials that may be co-extracted with the target analyte, there are usually serious matrix interferences. These samples require a cleansing step prior to extraction, some processes of which include alumina solid-phase adsorbent, gel-permeation chromatography, and silica-gel solid-phase adsorbent.

7. Gunshot residue analysis

This is done in any criminal case involving the alleged usage of firearms, the evaluation of firearm discharge residues, providing data on estimating firing distances, identifying bullet holes, and determining a suspect's involvement in the shooting [111]. Gunshot residues (GSRs), also known as cartridge discharge residues (CDRs) or firearm discharge residues (FDRs), comprise unburned or partially burned propellant powder, particles from the ammunition primer, grease, lubricants, and metals from the cartridge, and the weapon itself [112,66]. GSR contains both organic and inorganic components. Inorganic GSRs include nitrates, nitrites and metallic particles originating from primer, propellant and cartridge case. Organic GSRs may contain nitroglycerine, resorcinol, dinitrotoluene isomers, phthalates, centralites, and diphenylamine.

7.1. GSR sampling techniques

Skin, hair, body parts, clothing of the suspect, vehicles, surroundings of the incident, and any surfaces close to the firearm discharge may contain GSRs [113]. Various sample collection methods have therefore been established with the common objective of enhancing collection efficiency of GSR and lessening matrix interferences. Among all the GSR sampling techniques, tape lifts, vacuum lift, swabbing, glue lift and hair combing are most common. Although analytical techniques for analyzing inorganic and organic GSRs are quite different, their sampling methods are the same.

7.1.1. Tape lift. The most commonly used sampling technique for inorganic GSRs, applicable to collection from skin, hair and other surfaces, is tape lifting [114]. Different tape lifting adhesives include double-sided tape, adhesive tabs, adhesive liquids, glue sticks, and carbon conductive cements. A comparative study based on verifying collection efficiency of different adhesives revealed that Sellotape 404 double-sided tape performs best among all the tested adhesives in the study [66]. Another study comparing inorganic GSR collection efficiencies of tape/sticky lifts to swabs demonstrated that tape lifting is much more effective than swabs [115]. Tape lifting was said to collect organic GSRs (OGSRs) followed by extraction and introduction to GC for profiling [116]. Collection of the GSRs from a suspect's clothing by tape lifting is often challenging, as the tape collects fiber and other unwanted debris from the fabric surface in addition to the target GSR and may interfere the identification process. Carbon or gold coating of the collected samples is used to reduce the matrix effect.

7.1.2. Vacuum lift. Both organic and inorganic GSRs from fabric surfaces can be collected by vacuum lift. Collected samples are cleaned and pre concentrated by SPE before injecting into the analytical instrument. Organic GSRs are more effectively collected by Teflon filters. Methylene chloride performs better as extracting solvent when extracting propellant compounds [115].

7.1.3. Swabbing. Both organic and inorganic GSR can be collected by swabbing. Collecting samples by swabbing is usually carried out using water or organic solvents (e.g., ethanol). Ethanol is preferred for preventing microorganism growth that is likely to degrade nitroglycerine. Reardon and MacCrean [117] compared supercritical fluid extraction (SFE) and ultrasonic solvent extraction (USE) for quantitative extraction of smokeless powder. SFE did not perform well for double base powder, but performance relating to single base powder was acceptable.

7.1.4. Glue lift. To collect GSRs from the surface of a hand, glue lifting is recommended. Glue does not contain any element causing interference with GSR particle analysis in SEM, being preferable to tape lifting when it is an option.

8. Analysis of human odor

Human scent is the final result of the various combinations of the body's metabolism, gland secretions, hormonal control, and the interaction with the bacterial populations residing on the skin surface. It comprises compounds with various functional groups (e.g., alcohols, aldehydes, aliphatic/aromatic hydrocarbons, carboxylic acids, carboxylic acid methyl esters, and ketones) [118]. It is thought that every human being has a unique odor similar to having a fingerprint [119]. The individual body odor depends on many factors (e.g., genetic make-up, and environmental and internal physiological conditions) and can be classified as:

(1) primary odor, which is stable over time despite diet and environmental factors;
(2) secondary odor, which has contributions from diet and environmental factors; and,
(3) tertiary odor, which originates from an outside sources (e.g., personal hygiene or cosmetic products) [120].

Many researchers have been influenced by the individual odor hypothesis and are interested in investigating human scent as a potential biometric profile that may link a person to the scene of a crime. This is particularly useful in circumstances where no other physical evidence is present and has already been introduced in courts of law during criminal proceedings. As the primary odor of an individual can ''identify'' an individual, forensic scientists generally focus on understanding VOCs that contribute to the primary odor. A comprehensive account of human-scent collection and identification can be found in recently published review articles [121,122].

For both qualitative and quantitative analysis of human scent components, scientists are often encouraged to use a suitable sampling and/or pre concentration step so each of the individual compounds of the complex mixture (human scent) reaches the LOD for the specific analytical instrument (generally GC/MS).

As a quick, easy sample preparation technique, SPME has gained high popularity among forensic chemists active in human-scent research. Most articles published recently on profiling human scents have used SPME along with other scent collection media. Finding the right SPME fiber type is quite a challenge due to the complexity and the wide range of polarity of VOCs in human scents. Divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30-μm SPME fiber has been found to be the most efficient in human-scent profiling [119,120,123,124,125] although Zhang et al. [126] reported polydimethylsiloxane/divinylbenzene (PDMS/DVB) 65 μm to have performed the best.

When extracting directly from the body, a collection sorbent is used and is subject to headspace SPME for a predetermined time [123]. Alternatively, a flow sampling chamber may be used (Fig. 5), where human hand emanations can be carried to the SPME fiber *via* inert gas. After a predetermined extraction time, the SPME fiber can then be introduced into a GC or GC/MS [122,126]. Our (K.F.) research group utilized different sorbent media to capture VOCs emanating from human skin, equilibrated in an SPME vial for 24 h and then extracted into the SPME fiber to introduce into the

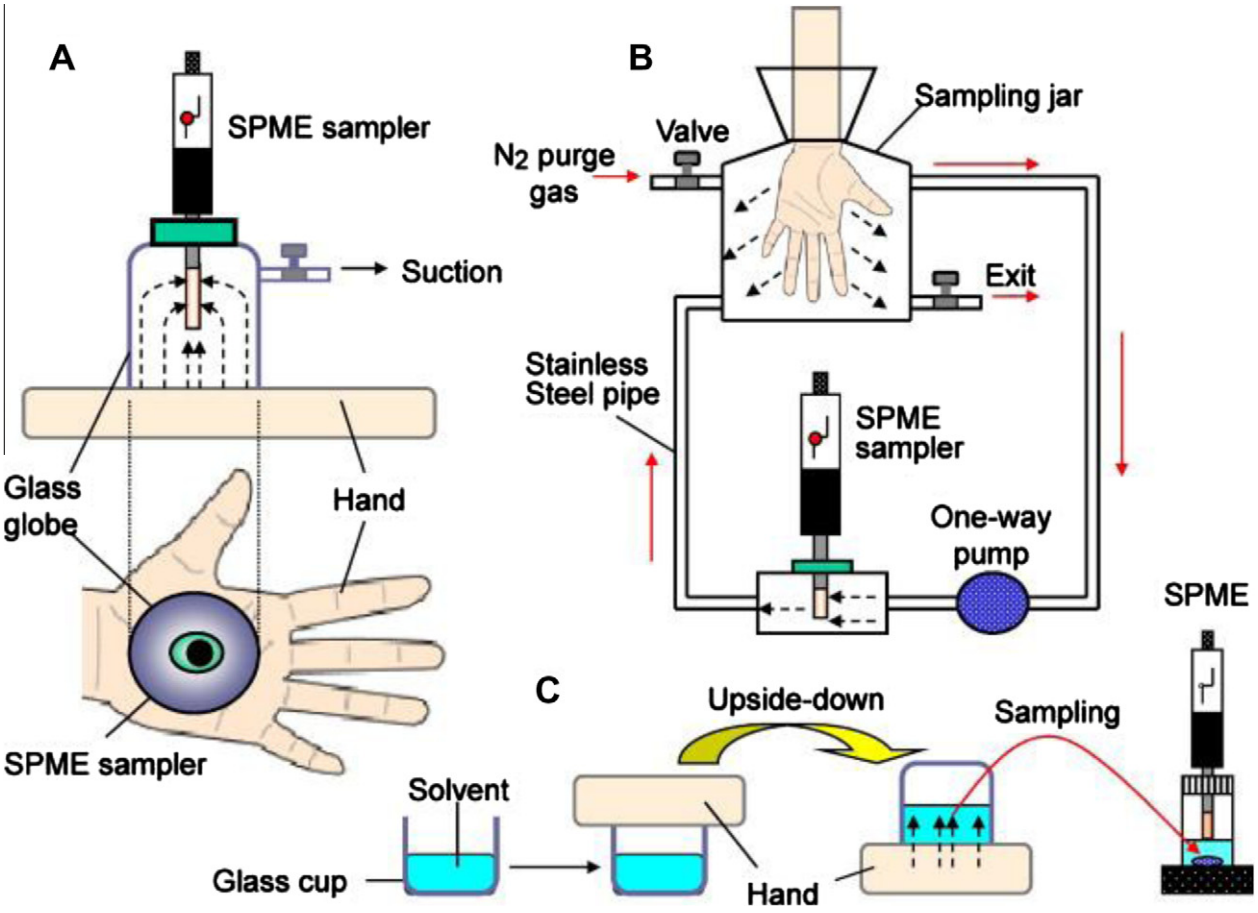

Figure 5. Systems for sampling volatile compounds emitted from the skin. (A) Direct SPME in sealed glass globes; (B) direct SPME in flow sampling chambers; and, (C) liquid sampling in glass cup. (Reproduced with permission from [122], ©2011, Elsevier Science).

injection port of the GC/MS for analysis and identification [119,120,124,127,128]. A study to define suitable sorbent media for human-scent collection in our laboratory showed that pure cotton seemed to have a strong attraction towards polar compounds because of exposed hydroxyl groups on the surface tending to release such compounds rather slowly, so that they can be extracted from the headspace by the SPME fiber. Cotton blend proved more efficient in relation to instrumental analysis [129,130]. A recent trend in human-scent collection is to collect scents on the sorbent media with a scent transfer unit (STU-100), a hand-held portable device using a vacuum to force VOCs through the sorbent media for trapping onto its surface. The greatest advantage of this is to maintain the evidential integrity of the object due to the non-contact sampling mode allowing collection of VOCs without any physical contact [131].

9. Analysis of human-decomposition products

There has been growing interest in the study of human remains among the forensic science community in recent years. Some research groups focus on understanding the chemical process of decomposition, while others focus on estimating postmortem intervals.

A varying degree of decomposition, containing protein, lipid and carbohydrate macromolecules with microbial reaction byproducts, amines, free fatty acids, and other VOCs combined with environmental factors adding to VOCs already present in the soil matrix, makes the human remains sample matrix extremely complex. As far as sample preparation is concerned, this poses a serious challenge to forensic scientists. With human remains, sample preparation mostly depends on the objective of the research:

(1) the estimation of postmortem interval;
(2) understanding the complex decomposition pathway involving the impact of different environmental and geochemical factors on the decomposition process; and,
(3) developing a victim recovery (VR) canine training aid to locate clandestine grave sites [132].

Suspected grave soils are often analyzed to detect adipocere. Suitable sample preparation techniques are needed to isolate adipocere from the complex soil

matrices and other potential interferences (e.g., non-decomposed adipose tissue). Sample preparation techniques commonly used for adipocere include thin-layer chromatography (TLC), LLE and column chromatography [133]. However, poor recovery of adipocere, excessive use of organic solvents, and potential oxidation of polyunsaturated fatty acid due to prolonged exposure of the dead body to air have made these sample preparation techniques less appealing, making quicker, less solvent consuming, and environmentally friendly sample preparation techniques continually in demand.

Forbes et al. [134,133] developed a rapid technique, in which adipocere was extracted with chloroform and derivatized with hexamethylenedisilazane (HMDS). The derivatization process transformed adipocere into fatty acid trimethylsilyl esters and allowed identification of individual esters in the ppm range by GC/MS analysis.

Lipid classes (triacylglycerides and free fatty acids) cannot be fractionated by extraction of adipocere using chloroform, so a new SPE method was created with aminopropyl disposable cartridge columns that isolate free fatty acids (FFA) from neutral lipid components in adipocere samples. Neutral lipid fraction was eluted from the column using a mixture of chloroform and 2-propanol (2:1 v/v) after extraction of adipocere samples onto the SPE cartridge. The FFA fraction was eluted with diethyl ether containing 2% acetic acid. Both fractions were then derivatized using bis(trimethylsilyl)-trifluoroacetamide (BSTFA). The TMS fatty-acid derivatives were then analyzed by GC/MS [133].

Another important aspect of human remains study is to identify and to use the VOCs released from human remains while decomposing for developing canine training aids, which are quite effective in training canines, which are later deployed for detecting hidden graves [135,136].

Hoffman et al. [137] performed SPME analysis on 14 different tissue types, previously used as victim recovery (VR) canine training aids. The samples included tissue from blood clot, blood clot from placenta, blood, muscle, testicle, skin, body fat attached to skin and teeth, adipocere, fat tissue, and bone. The headspace above the human tissues was sampled at room temperature using PDMS/DVB 65-μm SPME fiber for 40 min. GC/MS analysis of SPME extracted VOCs yielded 33 compounds that included acids, esters, alcohols, aldehydes, halogens, ketone, aromatic hydrocarbons, and sulfides.

Vass et al. [136,138] performed an analysis of decomposed odor from human remains by using Triple Sorbent Traps (TSTs) on four artificially created grave sites to perform a long-term study of VOC emanation from human remains during the decomposition process. The TSTs comprised Carbotrap, Carbotrap C, and Carbosieve S-III sorbents. The sorbents were stored in a 76-mm long stainless-steel tube with 6 mm O.D. and 4 mm I.D. The TSTs were connected to a specially-designed sampling manifold with controllable flow rates. Analytes were transferred into a cryocooled GC inlet by heating TSTs to 350°C for 5 min after the accumulation of VOCs into the TSTs. 478 specific VOCs were identified by these studies, some even liberated from the human body during the decomposition process.

Similarly, a study on VOCs released during the decomposition process was done by Statheropoulos et al. [139,140]. Three layers of sorbents comprised 300 mg carbograph 2, 200 mg carbograph 1, and 125 mg Carbosieve S-III packed in a glass tube were used. The tubes were conditioned for 2 h at 300°C for background removal.

Human remain volatiles were collected by a non-contact, dynamic airflow sampling device (Scent Transfer Unit, STU-100) in a recent study [141] by our research group (K.F.). The major advantage of this sampling method is its non-contact nature, maintaining the integrity of the sample (critical for forensic samples) and minimizing the possibility of contamination. VOCs from human remains were first collected on a pre-cleaned Dukal gauge using STU-100. The analytes captured on the Dukal gauge were then extracted on a SPME fiber (DVB/Carboxen/PDMS) and introduced into the GC/MS for separation and identification.

10. Conclusions and future outlook

Forensic samples are unique in that every case is different, so the sample preparation steps may vary significantly, depending on the matrix, analyte menu and particular case circumstances, including potential interferences and sample availability. Although conventional sample preparation techniques (e.g., LLE, SPE and purge-and-trap) still dominate in forensic laboratories, current trends clearly indicate a shift towards micro-sample preparation techniques that utilize very small quantities or even no organic solvents (SPME).

In this brief overview, we have discussed a variety of new sample preparation techniques commonly used in the analysis of forensic samples with special emphasis on emerging micro-sample preparation techniques. The inherent complexity, limited availability and evidential value of forensic samples and growing concerns over toxic and hazardous organic solvents have compelled researchers to develop miniaturized and solvent-less or solvent-minimized equilibrium based micro-sample preparation techniques. We expect that forensic chemistry applications will continue to result in the adoption of these emerging micro-sample preparation and related techniques capable of automation for high-throughput analysis in the coming years.

As we expect the new and emerging techniques of LA-ICP-MS, DART-MS, and LDI-MS to find more utility in the analysis of forensic trace evidence samples (e.g.,

glass, paint, fibers, hairs, paper, and ink), sample preparation strategies for both qualitative and quantitative analysis will need to be further developed.

Sorbent-based micro-sample preparation techniques, including SPME and its different modifications (e.g., EE-SPME, SPMEM, and TFME), may replace SPE in some forensic toxicology, environmental forensic and food forensic applications, as these novel techniques minimize usage of hazardous and toxic organic solvents.

Finally, in some particular applications, solvent-based sample preparation techniques will probably be replaced with emerging and more benign solvent-minimized techniques [e.g., SDME, hollow fiber-liquid phase microextraction (HF-LPME), directly suspended droplet microextraction (DSDME), and dispersive liquid-liquid microextraction (DLLME)].

Sampling and sample preparation in forensic applications is a very diverse field, encompassing both inorganic and organic chemical analysis, and the variety of matrices that can be encountered make it a vibrant and growing area within sample preparation development.

References

[1] J.M. Gallo, J.R. Almirall, Forensic Sci. Int. 190 (2009) 52.
[2] E.R. Schenk, J.R. Almirall, Appl. Opt. 49 (2010) C153.
[3] J.T. van Elteren, N.H. Tennent, V.S. Selih, Anal. Chim. Acta 644 (2009) 1.
[4] C.D. May, R.J. Watling, Forensic Sci. Med. Pathol. 5 (2009) 66.
[5] E.M. Cahoon, J.R. Almirall, Appl. Opt. 49 (2010) C49.
[6] E. McIntee, E. Viglino, S. Kumor, C. Rinke, L.Q. Ni, M.E. Sigman, J. Chemometrics 24 (2010) 312.
[7] E. Joseph, C. Ricci, S.G. Kazarian, R. Mazzeo, S. Prati, M. Ioele, Vib. Spectrosc. 53 (2010) 274.
[8] M. Szafarska, M. Wozniakiewicz, M. Pilch, J. Zieba-Palus, P. Koscielniak, J. Mol. Struct. 924–926 (2009) 504.
[9] D.P. Kirby, N. Khandekar, K. Sutherland, B.A. Price, Int. J. Mass Spectrom. 284 (2009) 115.
[10] E.L. von Aderkas, M.M. Barsan, D.F.R. Gilson, I.S. Butler, Spectrochim, Acta, Part A 77 (2010) 954.
[11] E. McIntee, E. Viglino, C. Rinke, S. Kumor, L. Ni, M.E. Sigman, Spectrochim. Acta, Part B 65 (2010) 542.
[12] I. Nakai, Y. Ono, Q. Li, Y. Nishiwaki, K. Tanaka, S. Nakayama, Surf. Interface Anal. 42 (2010) 402.
[13] B. Trzcinska, J. Zieba-Palus, P. Koscielniak, J. Mol. Struct. 924–926 (2009) 393.
[14] J.M. Milczarek, M. Dziadosz, J. Zieba-Palus, Chemia Analityczna 54 (2009) 173.
[15] M.F. Silva, M.T. Doménech-Carbó, L. Fuster-Lopéz, S. Martín-Rey, M.F. Mecklenburg, J. Anal. Appl. Pyrolysis 85 (2009) 487.
[16] P.M.J. Barton, Exp. Dermatol. 19 (2010) 072.
[17] Y. Gao, J. Zhang, G. Li, L. Yan, Guangpu Shiyanshi 27 (2010) 1036.
[18] M. Barroso, S. Costa, M. Dias, D.N. Vieira, J.A. Queiroz, M. Lopez-Rivadulla, J. Chromatogr., A 1217 (2010) 6274.
[19] J.Y. Kim, S.H. Shin, J.I. Lee, M.K. In, Forensic Sci. Int. 196 (2010) 43.
[20] H. Kharbouche, F. Sporkert, S. Troxier, M. Augsburger, P. Mangin, C. Staub, J. Chromatogr., B 877 (2009) 2337.
[21] K. Chojnacka, A. Zielinska, I. Michalak, H. Górecki, Environ. Toxicol. Pharmacol. 30 (2010) 188.
[22] A. Baysal, S. Akman, Spectrochim, Acta, Part B 65 (2010) 340.
[23] X. Zhang, Q. Zhou, Y. Lv, L. Wu, X. Hou, Microchem. J. 95 (2010) 80.
[24] B.L. Batista, J.L. Rodrigues, V.C. de Oliveira Souza, F. Barbosa Jr., Forensic Sci. Int. 192 (2009) 88.
[25] K.P. Kirkbride, S.R. Tridico, Forensic Sci. Int. 195 (2010) 28.
[26] A.R. Stefan, C.R. Dockery, A.A. Nieuwland, S.N. Roberson, B.M. Baguley, J.E. Hendrix, S.L. Morgan, Anal. Bioanal. Chem. 394 (2009) 2077.
[27] R. Kristensen, S. Coulson, A. Gordon, J. Anal. Appl. Pyrolysis 86 (2009) 90.
[28] L.C. Abbott, S.N. Batchelor, J.R.L. Smith, J.N. Moore, Forensic Sci. Int. 202 (2010) 54.
[29] J. Almer, E. McAnsh, B. Doupe, J. Can. Soc. Forensic Sci. 43 (2010) 16.
[30] Y. Hiroma, A. Hokura, I. Nakai, Bunseki Kagaku 59 (9) (2010) 759.
[31] J. Zieba-Palus, M. Kunicki, Forensic Sci. Int. 158 (2006) 164.
[32] J. Zieba-Palus, R. Borusiewicz, M. Kunicki, Forensic Sci. Int. 175 (2008) 1.
[33] J. Allison, Ink analysis using UV laser desorption mass spectrometry, in: R.D. Blackledge (Editor), Forensic Analysis on the Cutting Edge: New Methods for Trace Evidence Analysis, John Wiley & Sons, Chichester, West Sussex, UK, 2007.
[34] M.R. Williams, C. Moody, L.A. Arceneaux, C. Rinke, K. White, M.E. Sigman, Forensic Sci. Int. 191 (2009) 97.
[35] C. Weyermann, L. Bucher, P. Majcherczyk, W. Mazzella, C. Roux, P. Esseiva, Forensic Sci. Int. 217 (2012) 127.
[36] J. Adams, Int. J. Mass Spectrom. 301 (2011) 109.
[37] S. Donnelly, Aust. J. Forensic Sci. 44 (2012) 93.
[38] Y. Keheyan, G. Eliazyan, P. Engel, B. Rittmeier, J. Anal. Appl. Pyrolysis 86 (2009) 192.
[39] W. Dirwono, J.S. Park, M.R. Agustin-Camacho, J. Kim, H. Park, Y. Lee, K. Lee, Forensic Sci. Int. 199 (2010) 6.
[40] J. Coumbaros, K.P. Kirkbride, G. Klass, W. Skinner, Forensic Sci. Int. 193 (2009) 42.
[41] J.A. Denman, W.M. Skinner, K.P. Kirkbride, I.M. Kempson, Appl. Surf. Sci. 256 (2010) 2155.
[42] M.I. Szynkowska, K. Czerski, J. Rogowski, T. Paryjczak, A. Parczewski, Surf. Interface Anal. 42 (2010) 393.
[43] S. Pessanha, M. Manso, A. Guilherme, M. Costa, M.L. Carvalho, Surf. Interface Anal. 42 (5) (2010) 419.
[44] E.A. McGaw, D.W. Szymanski, R.W. Smith, J. Forensic Sci. 54 (2009) 1171.
[45] E.A. McGaw, D.W. Szymanski, R.W. Smith, J. Forensic Sci. 54 (2009) 1163.
[46] A. van Es, J. de Koeijer, G. van der Peijl, Sci. Justice 49 (2009) 120.
[47] T. Trejos, A. Flores, J.R. Almirall, Spectrochim. Acta, Part B 65 (2010) 884.
[48] Ma Dong, Shen Min, Luo Yi-wen, Bo Jun, Xu Che, Zhuo Xian-yi, Spectrosc. Spectral Anal. 30 (2010) 2816.
[49] S. Dhara, N.L. Misra, S.D. Maind, S.A. Kumar, N. Chattopadhyay, S.K. Aggarwal, Spectrochim. Acta, Part B 65 (2010) 167.
[50] K.D. Charleton, A.E. Smith, D.M. Goltz, Anal. Lett. 42 (2009) 2533.
[51] C.D. Klaasen, Principles of toxicology and treatment of poisoning, in: L.L. Brunto, J.S. Lazo, K.L. Parker (Editors), Goodman and Gilman's The Pharmacological Basis of Therapeutics, Eleventh Edition., McGraw Hill, Columbus, OH, USA, 2006, pp. 1739–1752 Chapter 64.
[52] X. Huang, D. Yuan, Crit. Rev. Anal. Chem. 42 (2012) 38.
[53] H. Lord, J. Pawliszyn, J. Chromatogr., A 902 (2000) 17.
[54] J. Zeng, J. Zou, X. Song, J. Chen, J. Ji, B. Wang, Y. Wang, J. Ha, X. Chen, J. Chromatogr., A 1218 (2011) 191.

[55] M. Kawaguchi, N. Sakui, N. Okanouchi, R. Ito, K. Saito, S.I. Izumi, T. Makino, H. Nakazawa, J. Chromatogr., B 820 (2005) 49.
[56] F. David, P. Sandra, J. Chromatogr., A 1152 (2007) 54.
[57] R. Yang, W. Xie, Forensic Sci. Int. 162 (2006) 135.
[58] D. Vuckovic, E. Cudjoe, F.M. Musteata, J. Pawliszyn, Nat. Protoc. 5 (2010) 140.
[59] S. Souverain, S. Rudaz, J.L. Veuthey, J. Chromatogr., B 801 (2004) 141.
[60] D. Vuckovic, E. Cudjoe, D. Hein, J. Pawliszyn, Anal. Chem. 80 (2008) 6870.
[61] M. Abdel-Rehim, J. Chromatogr., A 1217 (2010) 2569.
[62] A. Namera, A. Nakamoto, M. Nishida, T. Saito, I. Kishiyama, S. Miyazaki, M. Yahata, M. Yashiki, M. Nagao, J. Chromatogr., A 1208 (2008) 71.
[63] S.T. Ellison, W.E. Brewer, S.L. Morgan, J. Anal. Toxicol. 33 (2009) 356.
[64] T. Kumazawa, C. Hasegawa, X. Lee, K. Sato, Forensic Toxicol. 28 (2010) 61.
[65] C. Ji, J. Walton, Y. Su, M. Tella, Anal. Chim. Acta 670 (2010) 84.
[66] O. Dalby, J.W. Birkett, J. Chromatogr., A 1217 (2010) 7183.
[67] G.L. Burleson, B. Gonzalez, K. Simons, J.C.C. Yu, J. Chromatogr., A 1216 (2009) 4679.
[68] P. Guerra, H. Lai, J.R. Almirall, J. Sep. Sci. 31 (2008) 2891.
[69] N.R. Walker, M.J. Linman, M.M. Timmers, S.L. Dean, C.M. Burkett, J.A. Lloyd, J.D. Keelor, B.M. Baughman, P.L. Edmiston, Anal. Chim. Acta 593 (2007) 82.
[70] J.M. Perr, K.G. Furton, J.R. Almirall, J. Sep. Sci. 28 (2005) 177.
[71] P. Guerra-Diaz, S. Gura, J.R. Almirall, Anal. Chem. 82 (2010) 2826.
[72] M. Mattarozzi, F. Bianchi, F. Bisceglie, M. Careri, A. Mangia, G. Mori, A. Gregori, Anal. Bioanal. Chem. 399 (2011) 2741.
[73] J. Wojtas, Z. Bielecki, J. Mikolajczyk, D. Szabra, B. Rutecka, R. Medrzycki, M. Gutowska, T. Stacewicz, A. Czyzewski, Przeglad Elektrotechniczny 86 (2010) 222.
[74] H.W. Lin, K.S. Suslick, J. Am. Chem. Soc. 132 (2010) 15519.
[75] Y.G. Yang, Y.J. Li, H.D. Wang, T.Z. Li, B. Wu, Nucl. Instrum. Methods Phys. Res., Sect. A 579 (2007) 400.
[76] S. Liu, T. Ponrathnam, H.W. Sun, R. Nagarajan, J. Kumar, Z.Y. Gu, P. Kurup, J. Macromol. Sci., Pure Appl. Chem. (2010) 1172.
[77] T.M. Lovestead, T.J. Bruno, Anal. Chem. 82 (2010) 5621.
[78] Y.F. Zhang, K.M. Kubachka, J.A. Caruso, Anal. Methods 2 (2010) 1243.
[79] J.P. Lock, E. Geraghty, L.C. Kagumba, K.K. Mahmud, Thin Solid Films 517 (2009) 3584.
[80] Y.H. Gui, C.S. Xie, J.Q. Xu, G.Q. Wang, J. Hazard. Mater. 164 (2009) 1030.
[81] I. Voiculescu, R.A. McGill, M.E. Zaghloul, D. Mott, J. Stepnowski, S. Stepnowski, H. Summers, V. Nguyen, S. Ross, K. Walsh, M. Martin, IEEE Sens. J. 6 (2006) 1094.
[82] É. Stauffer, J.J. Lentini, Forensic Sci. Int. 132 (2003) 63.
[83] J.R. Almirall, K.G. Furton (Editors), Analysis and Interpretation of Fire Scene Evidence, CRC Press LLC, Boca Raton, FL, USA, 2004.
[84] E. Stauffer, J. Dolan, R. Newman, Fire Debris Analysis, Academic Press, Boston, MA, USA, 2008.
[85] R. Borusiewicz, Z. Zagadnien Nauk Sadowych 50 (2002) 44.
[86] J.J. Lentini, J. Forensic Sci. 45 (2000) 1358.
[87] M.R. Williams, M. Sigman, J. Forensic Sci. 52 (2007) 579.
[88] R.J. Kuk, M.V. Spagnola, J. Forensic Sci. 53 (2008) 1123.
[89] S. Baechler, S. Comment, O. Delemont, Talanta 82 (2010) 1247.
[90] E.S. Bodle, J.K. Hardy, Anal. Chim. Acta 589 (2007) 247.
[91] H. Yoshida, T. Kaneko, S. Suzuki, J. Forensic Sci. 53 (2008) 668.
[92] Y. Lu, P.B. Harrington, Anal. Chem. 79 (2007) 6752.
[93] P.M.L. Sandercock, Forensic Sci. Int. 176 (2008) 93.
[94] J. Lloyd, P. Edmiston, J. Forensic Sci. 48 (2003) 130.
[95] J. Almirall, J. Wang, K. Lothridge, K. Furton, J. Forensic Sci. 45 (2000) 453.
[96] R. Rella, A. Sturaro, L. Doretti, G. Parvoli, D. Ferrara, LC.GC Eur. 15 (2002) 603.
[97] R. Rella, A. Sturaro, G. Parvoli, D. Ferrara, U. Casellato, G. Vadala, Sci. Justice 45 (2005) 29.
[98] M.M. Sanagi, R.S. Basri, M. Miskam, W.A.W. Ibrahim, U.K. Ahmad, H.Y. Aboul-Enein, Anal. Lett. 43 (2010) 2257.
[99] B.L. Murphy, R.D. Morrison, Introduction to Environmental Forensics [electronic resource], Academic Press, San Diego, CA, USA, 2007.
[100] R.M. Harrison, R.E. Hester, Environmental Forensics, RSC Publishing, Cambridge, UK, 2008.
[101] R.D. Morrison, Environ. Forensics 1 (2000) 175.
[102] R. Morrison, Environ. Forensics 3 (2002) 203.
[103] P.J.P.D. Sullivan, F.J. Agardy, R.K. Traub, Practical Environmental Forensics: Process and Case Histories, John Wiley, New York, USA, 2001.
[104] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, Environ. Pollut. 157 (2009) 1778.
[105] D.R. Baker, B. Kasprzyk-Hordern, J. Chromatogr., A 1218 (2011) 8036.
[106] C.M. Bravo-Linares, S.M. Mudge, R.H. Loyola-Sepulveda, Mar. Pollut. Bull. 54 (2007) 1742.
[107] C.M. Bravo-Linares, S.M. Mudge, J. Environ. Monit. 9 (2007) 411.
[108] L. Zoccolillo, L. Amendola, C. Cafaro, S. Insogna, J. Chromatogr., A 1077 (2005) 181.
[109] S. Hashimoto, T. Tanaka, N. Yamashita, T. Maeda, J. Sep. Sci. 24 (2001) 97.
[110] C.V. Antoniou, E.E. Koukouraki, E. Diamadopoulos, J. Chromatogr., A 1132 (2006) 310.
[111] R. Saverio F., P. Margot, Forensic Sci. Int. 119 (2001) 195.
[112] M. Bernal Ernesto, V. Revilla Alma L., J. Chromatogr. A 1061 (2004) 225.
[113] A.J. Schwoeble, D.L. Exline, Current Methods in Forensic Gunshot Residue Analysis, CRC Press, Boca Raton, FL, USA, 2000.
[114] F.S. Romolo, P. Margot, Forensic Sci. Int. 119 (2001) 195.
[115] O. Dalby, D. Butler, J.W. Birkett, J. Forensic Sci. 55 (2010) 924.
[116] A. Zeichner, Anal. Bioanal. Chem. 376 (2003) 1178.
[117] M.R. Reardon, W.A. MacCrehan, J. Forensic Sci. 46 (2001) 802.
[118] P.A. Prada, A.M. Curran, K.G. Furton, J. Forensic Sci. 56 (2011) 866.
[119] A.M. Curran, P.A. Prada, K.G. Furton, J. Forensic Sci. 55 (2010) 50.
[120] A.M. Curran, The Analytical Determination of the Uniqueness and Persistence of the Volatile Components of Human Scent using Optimal Collection Methods, PhD Thesis, Florida International University, Miami, FL, USA, (2005).
[121] S.K. Pandey, K. Kim, Trends Anal. Chem. 30 (2011) 784.
[122] H. Kataoka, K. Saito, J. Pharm. Biomed. Anal. 54 (2011) 926.
[123] A. Ostrovskaya, P.A. Landa, M. Sokolinsky, A.D. Rosalia, D. Maes, J. Cosmet. Sci. 53 (2002) 147.
[124] A.M. Curran, C.F. Ramirez, A.A. Schoon, K.G. Furton, J. Chromatogr., B 846 (2007) 86.
[125] M. Gallagher, J. Wysocki, J.J. Leyden, A.I. Spielman, X. Sun, G. Preti, Br. J. Dermatol. 159 (2008) 780.
[126] Z. Zhang, J. Cai, G. Ruan, G. Li, J. Chromatogr., B 822 (2005) 244.
[127] A. Curran, S. Rabin, P. Prada, K. Furton, J. Chem. Ecol. 31 (2005) 1607.
[128] A.M. Curran, P.A. Prada, K.G. Furton, Forensic Sci. Int. 199 (2010) 103.

[129] D.T. Hudson, Variables Affecting the Collection and Preservation of Human Scent Components through Instrumental and Biological Evaluations, PhD Thesis, Florida International University, Miami, FL, USA, (2009).
[130] D.T. Hudson, A.M. Curran, K.G. Furton, J. Forensic Sci. 54 (2009) 1270.
[131] L.E. DeGreeff, A.M. Curran, K.G. Furton, Forensic Sci. Int. 209 (2011) 133.
[132] L.M. Swann, S.L. Forbes, S.W. Lewis, Anal. Chim. Acta 682 (2010) 9.
[133] S.J. Notter, B.H. Stuart, B.B. Dent, J. Keegan, Eur. J. Lipid Sci. Technol. 110 (2008) 73.
[134] S. Forbes, J. Keegan, B. Stuart, B. Dent, Eur. J. Lipid Sci. Technol. 105 (2003) 761.
[135] A.A. Vass, S. Barshick, G. Sega, J. Caton, J.T. Skeen, J.C. Love, J.A. Synstelien, J. Forensic Sci. 47 (2002) 542.
[136] A.A. Vass, R.R. Smith, C.V. Thompson, M.N. Burnett, D.A. Wolf, J.A. Synstelien, N. Dulgerian, B.A. Eckenrode, J. Forensic Sci. 49 (2004) 760.
[137] E.M. Hoffman, A.M. Curran, N. Dulgerian, R.A. Stockham, B.A. Eckenrode, Forensic Sci. Int. 186 (2009) 6.
[138] A.A. Vass, R.R. Smith, C.V. Thompson, M.N. Burnett, N. Dulgerian, B.A. Eckenrode, J. Forensic Sci. 53 (2008) 384.
[139] M. Statheropoulos, C. Spiliopouiou, A. Agapiou, Forensic Sci. Int. 153 (2005) 147.
[140] M. Statheropoulos, A. Agapiou, C. Spiliopouiou, G.C. Pallis, E. Sianos, Sci. Total Environ. 385 (2007) 221.
[141] L.E. DeGreeff, K.G. Furton, Anal. Bioanal. Chem. 401 (2011) 1295.