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Advances in chemical sensing technologies for VOCs in breath for security/threat assessment, illicit drug detection, and human trafficking activity

S. Giannoukos,^a A. Agapiou,^{b,*} S. Taylor^{a,c,*}

^aUniversity of Liverpool, Department of Electrical Engineering and Electronics, Liverpool, L69 3GJ, UK

^bUniversity of Cyprus, Department of Chemistry, P.O. Box 20357, 1678 Nicosia, Cyprus

^cQ Technologies Ltd, 100 Childwall Road, Liverpool, L15 6UX, UK

*Corresponding authors: e-mail: agapiou.agapios@ucy.ac.cy; S.Taylor@liv.ac.uk

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ABSTRACT

On-site chemical sensing of compounds associated with security and terrorist attacks is of worldwide interest. Other related bio-monitoring topics include identification of individuals posing a threat from illicit drugs, explosive manufacturing, as well as searching for victims of human trafficking and collapsed buildings. The current status of field analytical technologies is directed towards the detection and identification of vapours and volatile organic compounds (VOCs). Some VOCs are associated with exhaled breath; where research is moving from individual breath testing (volatilome) to cell breath (microbiome) and most recently to crowd breath metabolites (exposome). In this paper, an overview of field deployable chemical screening technologies (both stand-alone and those with portable characteristics) is given with application to early detection and monitoring of human exposome in security operations. On-site systems employed in exhaled breath analysis i.e. mass spectrometry (MS), optical spectroscopy and chemical sensors are reviewed. Categories of VOCs of interest include: a) VOCs in human breath associated with exposure to threat

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3 compounds, and b) VOCs characteristic of, and associated with, human body odour (e.g.
4 breath, sweat). The latter are relevant to human trafficking scenarios. New technological
5 approaches in miniaturised detection and screening systems are also presented (e.g. non-
6 scanning digital light processing linear ion trap MS (DLP-LIT-MS), nanoparticles, mid-
7 infrared photo-acoustic spectroscopy and hyphenated technologies). Finally, the outlook for
8 rapid and precise, real-time field detection of threat traces in exhaled breath is revealed and
9 discussed.
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20 21 **Introduction**

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24 The world community is witnessing a complex, multilevel and rapidly evolving international
25 security crisis. This involves terrorist activities using chemical means (chemical weapons,
26 biological threats, etc.), bombing attacks, illicit drug transportation and illegal human
27 trafficking. On-site and real-time sensing (detection and monitoring) of chemical analytes
28 indicating human presence in confined spaces or identifying suspect human motives (e.g.
29 people under stress) during security and forensic operations is an emerging area of high
30 scientific, political and public interest. On-site drug-testing is also a significant challenge.
31 Human exposome consists of characteristic chemical markers of the human body odour
32 (breath and skin), which can be applied for non-invasive extraction of molecular information
33 for medical diagnostics, psychological, criminal, law enforcement and other applications [1].
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35 The complexity and richness of human volatilome (components from exhaled breath, skin
36 emanations, urine, saliva, human breast milk, blood and feces) has been reviewed [2, 3].
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53 This article outlines: a) the chemistry of human body odour with the principal focus being
54 human detection and tracking in security applications, b) the breath detectable illegal
55 activities associated with exposures to threat compounds (e.g. drug-testing) and provides c)
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3 an overview of the current technological status of field deployable systems focusing on
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5 human exposome and breath screening capabilities.
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8 9 **Human odour screening in national security scenarios**

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11 National security authorities (i.e. the Department of Homeland security, the U.S. Immigration
12 and Customs Enforcement, the U.K. Border Force and the E.U. border control security
13 services such as the FRONTEX, border police, coast guards and civil defence) target the
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15 timely and precise detection and identification of hidden people travelling illegally or
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17 passengers who have the intention to perform malicious actions or carrying hazardous and/or
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19 illegal substances. People under the light or heavy influence of narcotics are also under the
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21 eye of the law enforcement personnel. Human body chemistry and specifically human body
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23 odour may reveal such activities.
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31 The principle responsibilities of the border control agencies are a) to perform custom
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33 controls for people and goods entering a country with physical and technological means, b) to
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35 rapidly identify possible threats and c) to ensure national safety and wellbeing. In this
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37 content, they develop risk analysis plans for designated stand-alone or joint actions for
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39 migrants or refugees' detection, train staff members and border guard teams to work
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41 effectively, invest in the development and use of innovative technologies, develop best
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43 practices for migrants return operations and share information via online platforms and
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45 workshops.
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51 The composition of human body odour is the combination of VOCs originating from both
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53 the exhaled breath and secreted sweat from the human skin. Human breathing is a dynamic
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55 process, which entails a continuous exchange of both inorganic gasses and VOCs with the
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57 ambient environment (e.g. household or workplace environment). The composition of human
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59 exhaled VOCs depends on endogenous sources (e.g. biological processes, oxidative stress or
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3 inflammation) and exogenous factors such as environmental exposures. The main compounds
4 found in the exhaled breath (872 VOCs) of healthy humans have been recently revised [3].
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8 Human sweat is produced by the three types of skin glands (eccrine, sebaceous and
9 apocrine). These are unevenly distributed and/or sometimes overlapping in various regions of
10 the human body with different microbiota composition. The primary form of human sweat is
11 an odourless liquid, with different formation depending on the type of the secreting gland.
12
13 Eccrine glands secrete mainly water with traces of proteins, ammonia, urea and lactic acid.
14
15 Sebaceous glands produce sebum consisting of lipids and apocrine glands produce lipids and
16 proteins. These are transformed into an odorous matrix due to bacterial metabolic processes
17 on the surface of the human body [1-4]. Volatile emissions identified in human skin can be
18 classified according to their body source and include compounds such as alkenes, alcohols
19 and phenols, aldehydes, esters, short and long chain carboxylic acids, aromatic compounds,
20 ketones and steroids [1]. Most of the volatile chemical moieties found in human body odour
21 in normal conditions (excluding VOCs for medical diagnostics) are easily revealed through
22 numerous studies with the existing technologies available in the market. However, the overall
23 chemical profile of human presence in enclosed areas with complicated chemical background
24 chemistries has not been extensively studied [1-7] and thus further investigation is needed.
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26 Such studies should relate to all possible environmental exposures and complex situational
27 factors and how they interact with and influence the human chemical profile.
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49 On-site chemical detection of human body VOCs in security checkpoints such as airports,
50 land ports, sea ports, cargo services, etc. is challenging compared to the traditional laboratory
51 analysis due to the trace levels of such compounds and the continuously dynamic complex
52 background environment. Another important issue, is the ethical protocol needed for such
53 studies, limiting the time and activities of researchers. Characteristic research on the chemical
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3 signs of human life in confined spaces was conducted within simulation environments during
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5 the trapped human experiment (THE) [8, 9] with bench top and portable molecular sensing
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7 instrumentation (thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS),
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9 GC-differential mobility spectrometry (GC-DMS) and multi-capillary column-ion mobility
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11 spectrometry (MCC-IMS)) at the University of Loughborough and during the human
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13 detection experiments [6, 7] in a container simulator using portable membrane inlet mass
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15 spectrometry (MIMS) at the University of Liverpool. The front-end applications of the above
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17 projects were different (search and rescue for the first and homeland security for the second).
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19 Both experiments targeted the generation of the chemical profile of live humans in defined
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21 spaces over a period of 6 hours, the study of human body odour under various conditions and
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23 alongside background events. Experimental observations showed that CO₂, NH₃, and VOCs
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25 such acetone, isoprene and volatile fatty acids (e.g. butyric acid, propanoic acid, lactic acid)
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27 could be possible indication markers of human presence in confined spaces. Experimental
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29 data showed that the relative intensities and the ratios of such compounds to each other is of
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31 importance. In a similar confined space, twelve skin VOCs were detected using an on-line
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33 selective reagent ionization time-of-flight mass spectrometry with NO⁺ system (SRI-TOF-
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35 MS (NO⁺) [10]. Table 1 presents human body VOCs detected in various confined space
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37 scenarios. This evidence shows the uniqueness of human body odour, and allows
38
39 differentiation between the chemical profiles of different genders, in the determination of
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41 people with deceptive behaviours via their body odour. This latter features highlight a
42
43 possible application for the integration of molecular sensors (either handheld or stand-off)
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45 with human exposome screening capabilities in border security checkpoints and customs
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Table 1: Volatiles detected in confined spaces under different entrapment scenarios

Volatiles	Instrument	Confined space	Reference
acetone, isoprene, ammonia	MCC-IMS, GC-DMS	In-house made entrapment simulator: (a) environmental chamber (gas-tight glass-lined tank with an internal volume of approximately 500 dm ³ (2010 mm × 510 mm × 505 mm), (b) void simulator (2 m long, 72 cm wide and 51 cm high) and (c) collapsed building simulator (glass column 1.5 m long, 15 cm ID fitted with layers of construction materials)	[8]
2-ethyl-1-hexanol, acetone, acetophenone, ammonia, benzaldehyde, benzene, 1-methylethyl, decanal, hexanal, limonene, octanal, nonanal	MCC-IMS and TD-GC-MS		[9]
propanal, hexanal, heptanal, octanal, nonanal, 2-methyl 2-propenal, acetone, 2-butanone, 3-buten-2-one, 6-methyl-5-hepten-2-one, 2-methyl 2-pentene, dl-limonene	SRI-TOF-MS-NO ⁺		[10]
acetone, acrolein, 2-methylpropanal, ethyl formate, 2-methyl-1-propanol, 3-methylbutanal, 2-ethacrolein, ethyl propionate, acetic acid, 2-pentanone, 4-methyl-2-pentanone, vinyl butyrate, n-hexanal, butyl acetate, ethyl isovalerate, n-heptanal, benzaldehyde	MCC-IMS	A body plethysmography chamber, BodyScope (Ganshorn Medicin Electronic GmbH, Germany), with interior dimensions of 82 × 63 × 161 cm	[12]
methanol, acetaldehyde, hexane, lactic acid, nonanal, isoprene, acetone, limonene, phenol, pentane, heptane, 1-pentene, hexanal, isopropanol, 2-nonenal, ethanol, propanoic acid	Membrane Inlet Mass Spectrometry (MIMS)	Container simulator using eight different experimental setups (3.37 m × 5.00 m × 2.50 m)	[6]

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Illegal human trafficking has been observed in shipping containers, maritime cargos, trucks, coffins or boxes. People being trafficked often lack of personal hygiene due to few or many days without showering, and urination or defecation residues onto clothes. In addition, the victims often have limited opportunity for food consumption, and experience increased levels of fear, stress and hardship. The above factors affect the chemical composition of the human body odour, either by introducing VOCs from biological secretions or by altering the intensities and/or proportions of endogenous VOCs (as specific metabolic pathways are triggered). For example, the concentration of breath acetone is highly increased after fasting [13]. However, research on a common core of chemical substances characteristic of human body odour could be utilised for the field detection and localisation of the emitting source [6, 14].

Breath detectable illegal activities

Increased use of psychotropic narcotics (e.g. marijuana, cocaine) can cause abnormal and dangerous behaviours in public places. A characteristic recent example is the cocaine intake of three men in the plane toilets during an Easyjet flight (June 2017) [15]. Conventional drug testing techniques utilize blood, saliva or urine testing in the laboratory. However, many drugs of abuse can be metabolised quickly from the human body, making their detection difficult or even sometimes impossible. Hand-held breathalysers allow the instantaneous detection of drugs of abuse in the exhaled human breath of a suspect *in-situ* [16]. Recently, Cannabix Technologies Inc. and the Yost Group (University of Florida) worked together and developed a lightweight handheld device (similar to the alcohol breathalysers) based on field asymmetric ion mobility spectrometry (FAIMS) for the detection of (-)-trans- Δ^9 -tetrahydrocannabinol (THC) in human breath [16, 17]. Hound labs Inc. have also developed a

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3 miniature portable breath THC detection device with a patent-pending approach with low
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5 detection limits (below 500 pg) [18].
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8 Laboratory-based breath testing using bench top instrumentation such as liquid
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10 chromatography tandem mass spectrometry (LC-MS-MS) equipped with positive
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12 electrospray ionisation and selected reaction monitoring and gas chromatography (GC)
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14 coupled with MS have shown the capability of multiple detection of drugs of abuse in
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16 exhaled breath [19-21]. The outcomes are encouraging, allowing testing of such compounds
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18 in exhaled breath using portable miniaturised MS systems with both in vacuo and ambient
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20 environment ionisation techniques and further commercial exploitation. Compared to the
21
22 demanding requirements of laboratory analysis (e.g. specialised personnel, sample
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24 preparation, time and cost consuming), in-field breath testing could be a fast and valid
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26 analytical methodology for law enforcement that will provide accurate, confident and
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28 efficient scientific evidence of acquittal or guilt at the point-of-analysis.
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34 35 **Field deployable chemical sensing technologies and instrumentation**

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38 Traditionally, canines are considered to be the gold-standard for threat and hidden human
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40 detection. However, due to the requirements for extensive training and their maintenance
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42 costs, limited working lifetime and other shortcomings, there is a need for development and
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44 deployment of portable artificial sniffers, with advanced chemical sensing characteristics
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46 including high sensitivity and specificity and ease of use. Machine olfaction mimics natural
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48 olfactory processes to enable the deep sensory comprehension of the nature and consistency
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50 of the threat and threat related compounds. The information obtained is required during
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52 decision making at the point-of-analysis (e.g. scene of arrest) [22].
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57 Existing analytical approaches [1] for the qualitative detection and quantitative
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59 determination of VOCs in human body odour in the laboratory, employ mainly GC-MS [5],
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3 GC coupled to ion mobility spectrometry (IMS), multi-capillary columns (MCC)-IMS [23],
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5 GC connected to flame ionisation detection (FID), thermal desorption (TD)-GC-MS, proton
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7 transfer reaction mass spectrometry (PTR-MS) [24], selected ion flow tube mass
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9 spectrometry (SIFT-MS) [25-28], laser spectroscopy [29] and electronic noses [30]. GC-MS
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11 techniques have powerful detection and quantification capabilities due to the 3D acquired
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13 data (retention time, intensity, m/z ratio), assisted by very well developed and integrated
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15 spectral libraries of millions of chemical compounds. Other mass spectrometric techniques,
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17 such as PTR-MS, SIFT-MS and IMS, although offering near-real time monitoring of analytes
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19 of interest, they lack spectral libraries. Flame-aerosol synthesis enabled the development
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21 of nanostructured metal-oxide sensors Si:WO₃, Ti:ZnO and Si:MoO₃ for
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23 the selective identification of breath acetone [31], isoprene [32] and ammonia [33] in the low
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25 ppbv levels, respectively. Demands for real time measurements of VOCs of interest and
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27 threats in a systematic way, have led to the development and system integration of either
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29 handheld or remotely controlled devices equipped with smart molecular sensorial or sampling
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31 approaches.

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34 In the last 5 years, the European Union has funded several large security projects (e.g.
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36 SNIFFLES, SNOOPY, DOGGIES) [34-36] to investigate the operational challenges of
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38 human body VOCs detection in urban areas and border checkpoints in order to offer reliable
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40 and user-friendly portable technological solutions based on gas sensing. Characteristically,
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42 during the SNIFFLES project [34], a portable MS sensor based on a novel non-scanning
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44 linear ion trap (LIT) technology was designed and developed for hidden human and threat
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46 compound screening and detection [38, 39]. The prototype unit was fabricated using digital
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48 light processing (DLP), which is a low-cost rapid manufacturing technique for realisation of
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50 complex 3D structures. Compared to other rapid prototyping techniques, such as selective
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52 laser ablation (SLA), DLP offers exceptional nanoscale surface smoothness which is essential
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3 for accurate and reliable mass analysis required in the development of commercial systems.
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5 The non-scanning mode allows the selective and rapid detection and/or monitoring of mass
6 fragments of interest with optimal RF and DC voltages on the LIT electrodes for each ion
7 mass, speeding up chemical analysis in the field. Experiments with threat simulants showed
8 encouraging results. The SNOOPY [35] and DOGGIES [36] project were running in parallel
9 with the same aim. The SNOOPY prototype sniffer was based on chemi-resistor and
10 microbalance gas sensors, coated with layers of either porphyrins or corroles, targeting the
11 detection of hidden humans in vehicles and cargos. The above sensors were developed using
12 novel materials based on nanoparticles, nanowires and metallo-porphyrines/-corroles and the
13 prototype e-nose was evaluated in trials with human participants. The DOGGIES project
14 developed a novel orthogonal gas sensing approach consisting of mid-infrared photo-acoustic
15 spectroscopy (MIR-PAS) and GC-IMS for olfactory traces detection. For gas sampling, a fast
16 pre-concentrator (few seconds) was deployed and the data obtained created a database of
17 characteristic chemical signatures of VOCs found in human scent (mainly volatile short-chain
18 fatty acids such as the (E)-3-Methylhex-2-enoic acid and in the headspace area above illicit
19 drugs and explosives. Remarkably, human detection (after 15 minutes of human presence) in
20 a confined area of 50m³ was demonstrated [37]. These results are promising, considering that
21 illegal immigrant concealment cases take place in much smaller spaces and for longer times,
22 allowing significant built-up of concentrations of characteristic markers of human presence.
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49 Machine olfaction intends to complement sniffer dogs' work for detection of hidden
50 persons and illicit compounds on-site. Artificial sniffers do not target the replacement of
51 canines, but aim at a thorough comprehension and reproduction of the sniffing process with
52 appropriate analogies and metaphors. For example, a 16-fold improvement was demonstrated
53 on a commercial trace vapor detector when biomimetic sniffing was applied [40]. Compared
54 to detection dogs, electronic noses offer both qualitative and quantitative information of a
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3 potential threat component, however in contrast to canines, they lack fast response times and
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5 the ability to locate the emitting source. In contrast to machine olfaction, detection dogs may
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7 give unreliable behaviour due to distractions, loss of attention and/or boredom. This requires
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9 sufficient pausing of their operation for a 'rest break' or for retraining purposes. The
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11 olfactory capabilities of sniffer dogs' are debated in the literature [1, 41] as an alternative to
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13 sensorial approaches.
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17 More recently, Q-Technologies Ltd. (United Kingdom) [42] has developed the
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19 VapourSense-500, a robust, portable dual filter quadrupole MS system with two sample
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21 introduction techniques (a membrane inlet and a short-length heated capillary column) and
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23 mass range up to 500 amu, allowing direct detection and online monitoring of VOCs from
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25 humans in security operations. A signal processing algorithm developed in the University of
26
27 Liverpool, UK may also be implemented with the above system to extract ultra low-
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29 intensities peaks of interest from the noise level. This is important for field applications,
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31 where usually analytes of interest have concentration levels in very low levels.
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40 **Future perspectives**

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42 Investigation plans for hidden human detection in the field using artificial sniffing integrate a
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44 multilevel operational approach (from a science and technology perspective to everyday
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46 policy making). Molecular sensing systems are required to provide answers regarding human
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48 presence in confined spaces in real-time, both for localisation and identification purposes and
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50 also to supplement canines use. Prediction alarm tools (with 24-7 service capabilities) for
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52 humans with possible malicious intent based on human exposome or breath testing need to be
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54 developed and implemented at all possible security checkpoints (e.g. in lorries, shipping
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3 containers, airports, subways/train stations, stadiums or shopping malls, etc.) to assist in the
4
5 safe transportation of passengers and goods [43, 44].
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9 Portable MS and IMS analysis can provide spatio-temporal information regarding the
10 tracking history of a suspect through monitoring of bio- or odour-print residues. Hand-held or
11 stand-off distance analytical tools with real time accurate gas sniffing and trace detection
12 capabilities can accommodate the creation of human exposome storage databases and the use
13 of breath and skin VOCs as biometric identifiers alongside fingerprint, face recognition and
14 retinal scans. The development of complete personalised human exposome databases could
15 ensure the continuous tracking of illegal activities. Current analytical means and
16 technological expertise has the potential to explain the chemical complexity of threatening
17 challenges-scenarios.
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31 In this regard, the continued evolution of field chemical analysis (FCA) to mitigate the
32 escalating chemical threats is an urgent necessity. FCA is a vital and integrated part of
33 emergency preparedness and planning, early warning and control to mitigate and manage
34 threats and attacks. Integration of miniaturised analytical apparatuses with unmanned ground
35 vehicle (UGV) and unmanned aerial vehicle (UAV) technologies have clear potential for
36 rapid (i) detection, (ii) localisation and (iii) monitoring of threatening actions while
37 guaranteeing maximum flexibility. Integration of FCA with olfactory or data communication
38 networks for the transmission of encrypted information on human exposome or exhaled
39 breath in distant areas could enhance national security diagnostics through better
40 identification of individuals. A characteristic application could be the usage of human breath
41 as an advanced level molecular security key.
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57 Combining odour data with visual and/or other data for transmission over the internet and
58 re-creation elsewhere, allows odour teleportation to locations elsewhere. The key aspects here
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3 are the abilities to identify and to re-create a given odour. The former may be accomplished
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5 using a mass spectrometer and the latter by use of an odour generation device [45, 46]. These
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7 latest developments illustrate the future of exhaled breath analysis: handheld point-of-use or
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9 wearable devices [47] for applications outside the laboratory, such as personal or crowd
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11 medical, identification and security applications.
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