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Monitoring of selected skin- and breath-borne volatile organic compounds emitted from the human body using gas chromatography ion mobility spectrometry (GC-IMS)

Paweł Mochalski[*,a], Helmut Wiesenhofer[a], Maria Allers[b], Stefan Zimmermann[b], Andreas T. Güntner[c], Nicolay J. Pineau[c], Wolfgang Lederer[d], Agapios Agapiou[e], Christopher A. Mayhew[a,f], Veronika Ruzsanyi[a]

[a]Breath Research Institute of the University of Innsbruck, Rathausplatz 4, A-6850 Dornbirn, Austria

[b]Leibniz Universität Hannover, Institute of Electrical Engineering and Measurement Technology. Hannover, Germany

[c]Particle Technology Laboratory, ETH Zurich, CH-8092 Zurich, Switzerland

[d]Department of Anesthesia and Intensive Care Medicine, Innsbruck Medical University

Anichstraße 35, A-6020 Innsbruck, Austria

[e]Department of Chemistry, University of Cyprus, P.O.Box 20537, 1678 Nicosia, Cyprus

[f]Molecular Physics Group, School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

[*] *Corresponding author e-mail*: pawel.mochalski@uibk.ac.at

Abstract

Human smuggling and associated cross-border crimes have evolved as a major challenge for the European Union in recent years. Of particular concern is the increasing trend of smuggling migrants hidden inside shipping containers or trucks. Therefore, there is a growing demand for portable security devices for the non-intrusive and rapid monitoring of containers to detect people hiding inside. In this context, chemical analysis of volatiles organic compounds (VOCs) emitted from the human body is proposed as a locating tool. In the present study, an in-house made ion mobility spectrometer coupled with gas chromatography (GC-IMS) was used to monitor the volatile moieties released from the human body under conditions that mimic entrapment. A total of 17 omnipresent volatile compounds were identified and quantified from 35 ion mobility peaks corresponding to human presence. These are 7 aldehydes (acrolein, 2-methylpropanal, 3-methylbutanal, 2-ethacrolein, n-hexanal, n-heptanal, benzaldehyde), 3 ketones (acetone, 2-pentanone, 4-methyl-2-pentanone), 5 esters (ethyl formate, ethyl propionate, vinyl butyrate, butyl acetate, ethyl isovalerate), one alcohol (2-methyl-1-propanol) and one organic acid (acetic acid). The limits of detection (0.05 -7.2 ppb) and relative standard deviations (0.6-11%) should be sufficient for detecting these markers of human presence in field conditions. This study shows that GC-IMS can be used as a portable field detector of hidden or entrapped people.

Keywords:

1. Introduction

The trafficking and smuggling of people to Europe have reached epidemic proportions in recent years. According to estimates from the European Border and Coast Guard Agency (Frontex) more than 1.8 million people entered Europe in 2015, taking into account also those who crossed European borders undetected[1]. Criminal networks have rapidly reacted to this development and substantially increased their involvement into migrant smuggling. Smugglers offer a wide range of services such as transportation, accommodation and fraudulent documents, often at excessively high prices, whilst putting at risk the health and lives of people being trafficked or smuggled. For example, in attempting to reach Europe via the Mediterranean route, between 2000 and 2015 more than 30,000 refugees are believed to have drowned or died from hypothermia and starvation[1]. Transport by road boosted a highly dangerous trend of smuggling migrants hidden inside containers or trucks. For example, on the 27th August, 2015, on a motorway between Neusiedl and Parndorf, Burgenland, Austria, 71 migrants were found suffocated in a refrigerated truck. In this context, the early detection and interception of smuggled people is of particular importance, not just to protect European borders, but also to save them from life-threatening and/or degrading situations. Consequently, there is a growing demand for highly portable, rapid security devices for non-intrusive monitoring of containers and trucks to detect the presence of hidden people. To be applicable, the time and costs of inspection play a fundamental role. Therefore, such an analytical tool should ideally be able to detect stowaways without the requirement of opening container doors and breaking custom's seals. A number of approaches have been applied to detect humans. The most common one is the use of search-and-rescue (SAR) dogs. However, this is time-consuming because containers have to be opened and cargo taken out, because often migrants are burrowed deep in the cargo. Alternative tracking tools include CO_2 sensors, thermal cameras, acoustic probes (aiming at voices or detecting heartbeats), or occasionally X-rays[2]. Interestingly, to date any chemical analysis that is capable of providing a human-specific chemical signature has received little attention, and is currently limited to the aforementioned carbon dioxide sensing. This is surprising as volatile organic compounds (VOCs) are often the products of vital metabolic pathways occurring in the human organism and they could therefore serve as signs-of-life. Indeed, a number of recent studies have provided evidence that some human-borne VOCs could be employed as markers of human presence and thereby support the detection of stowaways hidden inside shipping containers or trucks[3-5].

Ion mobility spectrometry (IMS) is a well-established sensitive technique in the analyst arsenal for volatile compounds chemical identification, and hence has a great potential in this context [6]. Currently, the main application area for IMS is in security (military and homeland) for the detection of chemical warfare agents and explosives. However, this technology has also proved to be useful in several other applications such as drugs detection/monitoring, air quality control, or monitoring of industrial processes[7-12]. This stems from its versatility, excellent sensitivity and real-time response.

IMS instruments are portable, robust, and relatively inexpensive compared to mass spectrometric instruments, have low energy consumption, and are capable of near-real time detection of human-borne VOCs at ultra-low ppb (parts-per-billion) levels without sample pre-processing. The main drawback of the IMS instruments - limited selectivity - can be compensated via their coupling with gas chromatography, or liquid chromatography, although this comes at the price of increased analysis time [13, 14].

Here we present a study of entrapped humans using an IMS coupled to gas chromatography (GC-IMS). We illustrate its application to determine and monitor skin- and breath-borne VOCs released from the human body under conditions that mimic entrapment and provide details on its potential as a field deployable system to detect people in short time.

2. Experimental

2.1. Materials and calibration mixtures

Multi-compound calibration mixtures were prepared from pure liquid substances. The reference substances, with purities ranging from 98 to 99.9%, were purchased from Sigma-Aldrich (Austria), Fluka (Switzerland), and SAFC (USA). The preparation of gaseous calibration mixtures has been described in detail elsewhere[15], and therefore only a brief outline of the procedure is provided here. Gaseous mixtures of species of interest were produced by means of a GasLab calibration mixtures generator (Breitfuss Messtechnik, Germany). The generator supports the preparation of gas mixtures at pre-defined humidity levels from pure liquid substances containing 10 ppb to 100 ppm of each solute. However, for this study, pure substances were additionally diluted at ratios of 1:2000-1:3000 to achieve lower concentration levels. Gas mixtures exhibiting analytes volume fractions ranging from 0.1 to 1000 ppb were used for calibration and validation. Calibration curves were obtained on the basis of 3-fold analyses of 5, or 6 distinct and independent concentration levels.

2.2. Human subjects

A cohort of 11 healthy subjects (7 males, age range 19-59 years, 1 smoker) was recruited. All volunteers gave written informed consent to participate and completed a questionnaire describing their basic personal data and smoking status. The experiments were performed under light fasting conditions (minimum of 8 hours). Moreover, they were asked to refrain from alcohol consumption for 12 hours prior to the experiment and from using cosmetics. The sample collection was approved by the Ethics Commission of Innsbruck Medical University.

2.3. Body chamber and experimental protocol

A detailed description of the experimental setup mimicking the entrapment is given elsewhere[16]. Therefore, only a short description will be provided here. A body plethysmography chamber

BodyScope (Ganshorn Medicin Electronic GmbH, Germany), with interior dimensions of 82×63×161 cm³ (approximately 819 L) was used during experiments. The chamber was equipped with a fan installed at the ceiling assuring the homogenous mixing of the chamber air. A heated (40 ºC) Teflon transfer line connected the chamber with the sample loop (200 µL) of the GC-IMS instrument. The inlet of the transfer line was located in the centre of the side wall. The samples were introduced into the sample loop of the instrument using a pump that was turned-on shortly before sampling. At the onset of each measurement, the chamber and the laboratory room were vented for several hours to reduce the level of indoor contaminants. Each measurement consisted of three phases: (i) background phase (20 mins), (ii) skin emission phase (60 mins) and (iii) combined breath and skin emission phase (60 mins). During the first phase, two background measurements at 0 and 20 mins were performed. Immediately after the second background measurement, a volunteer entered the chamber and the chamber door was tightly locked. Each volunteer had only underwear on in order to allow a large skin area accessible. All volunteers remained inside the chamber for 2 hours in a seated position. During the first hour of the experiment only the skin-borne VOCs were targeted and the subjects freely inhaled and exhaled outside air via a silicone head mask (V2 Mask, Hans Rudolph inc., USA) and a two-way non-rebreathing Y shape-valve (Hans Rudolph inc., USA) connected with two flexible tubes (ID = 22 mm) to additional ports located on the side wall of the chamber. During the second hour, subjects exhaled directly into the chamber interior, while still inhaling outside air. This was achieved by disconnecting the outlet tube from the mask. Consequently, during this third phase, both breath- and skin-borne volatiles accumulated in the chamber. Altogether, a single experiment lasted 140 minutes. The first air sample was drawn and analyzed immediately after a subject was enclosed in the chamber and the next ones were taken at 20 minute intervals.

2.4. GC-IMS analysis

VOCs were monitored using an in-house made high resolution GC-IMS developed at Leibniz Universität, Hannover. Samples were injected into the GC column using a stainless steel sample loop (200 µL) installed on a six-way valve. Volatiles were separated using a RTX volatiles column (10 m×0.53 mm, film thickness 2 µm, Restek) working at constant temperature of 50°C. The carrier gas flow rate program was as follows: 2 ml min⁻¹ for 10 minutes and then 10 ml min⁻¹ for another 10 minutes, resulting in a total GC-runtime of 20 minutes. The IMS, with a drift tube length of 7.5 cm, provided a resolving power of R = 90 using a drift voltage of 5 kV. The instrument operated at 40 °C, 10 mbar above the ambient pressure and with the purified air as the drift gas at the flow of 150 mL min⁻¹. A radioactive β⁻ emitter ³H (300 MBq) was used as the ionization source. The dimensions of the GC-IMS instruments are 45×45×28 cm³. A detailed description of the system can be found elsewhere [17].

The identification of compounds under scrutiny relied on the comparison of retention and drift times (ion mobilities) of ion mobility peaks with the respective libraries of retention times and drift times

obtained from standard mixtures. Here, quantification of all volatiles, with the exception of acetone, was based on monomer peaks. Owing to the high acetone levels, exceeding the dynamic range of the IMS instrument, quantification of this compound relied on the dimer ion peak. The variability of the drift and retention times was 1-1.3% and 0.5-5% respectively. Acetic acid exhibited higher variability of the retention time of 13.6%. The retention times, ion mobilities and method parameters of VOCs of interest are presented in Table 1.

3. Results and discussion

3.1. Method validation

Limits of detection (LODs) were calculated using the standard deviation of 9 consecutive blank signals[18]. The LOD values ranged from 0.05 ppb (1.95 pmol L^{-1}) for acetone to 7.2 ppb (0.28 nmol L^{-1}) for acetic acid. These LODs are adequate for the detection of the majority of potential human volatile markers in the vicinity of a hidden person[5]. The limit of quantification (LOQ) was defined as 3×LOD. Relative standard deviations (RSDs) were calculated on the basis of consecutive analyses of 10 independent standard mixtures exhibiting concentrations close to the means of the observed levels in real samples. The RSDs fall within the range of 0.6-11.7%.

3.2. VOCs resulting from human presence

An exemplary chromatogram from a GC-IMS analysis of VOCs emitted by human body is shown in Fig. 1. More than 80 ion mobility peaks were found in the air of the chamber. Thirty-five of these were found to depend on the time of entrapment. Seventeen species from this set were found to be omnipresent and were reliably identified and quantified; 7 aldehydes (acrolein, 2-methylpropanal, 3-methylbutanal, 2-ethacrolein, n-hexanal, n-heptanal, benzaldehyde), 3 ketones (acetone, 2-pentanone, 4-methyl-2-pentanone), 5 esters (ethyl formate, ethyl propionate, vinyl butyrate, butyl acetate, ethyl isovalerate), one alcohol (2-methyl-1-propanol) and one organic acid (acetic acid). The mean concentrations of the VOCs of interest are in the range of 0.3-330 ppb (0.012 – 12.9 nmol L^{-1}), as shown in Table 2. The highest mean levels (hundreds of ppb at the end of the entrapment time) were noted for acetone and acetic acid. Examples of the mean concentration profiles of acetone, 2-ethacrolein, ethyl isovalerate, and vinyl butyrate are shown in Figure 2. All 17 compounds of interest were found to be released during the skin emission phase of the experiment, with only two of them, acetone and 2-ethacrolein, having a substantial breath component. Owing to the shortage of other studies it is difficult to verify the concentrations obtained within this study. Nevertheless, several concentration values can be found for some compounds under scrutiny (see Table 2). For instance, Risberg *et al.* [19] investigated VOCs emitted by a group of 18 volunteers enclosed in Ula-class submarine (250 m³), whereas, Guo *et al.*[20] analyzed human-borne contaminants in a simulated spacecraft module. In our previous paper [21]we quantified 60 skin-borne VOCs in confine spaces

surrounding encapsulated hands and forearms of 31 volunteers. These results agree reasonably well with the levels reported here.

Although the biochemical origins of human VOCs are uncertain, a number of sources could be responsible for their emission. These include (i) systemic production related to the physiological processes in the body, (ii) oxidation of human sebum [22-24], (iii) activity of microorganisms (e.g. skin and gut flora)[25, 26], (iv) environmental exposure (dirt, dust, cosmetics, detergents, smoking, etc.), and (v) diet and its metabolites.

Three ketones were found to result from human presence. Acetone exhibited the highest levels amongst all compounds under study and was also found to be released by both skin and breath, with breath being the most dominant. This was manifested by a rapid increase of acetone levels during the breath and skin emission phase of the experiment. Acetone is the major VOC produced in the human organism exhibiting high abundances in breath [15, 27], blood [28], and urine [29, 30]. Several sources of acetone in human body can be listed. These are (i) endogenous decarboxylation of Acetyl–CoA [27, 31], (ii) oxidative degradation of squalene on human skin [32], (iii) 2-propanol metabolism [33], and (iv) diet. However, the latter two are of minor importance. In the context of human detection, acetone's high emission rates and systemic production render it a very important marker for human presence. Compared to acetone, the other ketones, 2-pentanone and 4-methyl-2-pentanone had much lower levels in the chamber air (reaching a maximum of 6.3 ppb at the end of the experiment). Their origin is unclear and may be a result of diet, environmental exposure, or secondary alcohols metabolism [34-36]. If so, 2-pentanone could stem from 2-pentanol, whereas, 4-methyl-2-pentanone from 4-methyl-2-pentanol [36].

Seven aldehydes increased in concentration as a result of human presence in the chamber. Interestingly, the concentrations of aldehydes tended to increase during the skin phase of the experiment (60 mins) and then stabilized during the last phase of the measurements. It is plausible to attribute this concentration dependence to the decrease of the aldehydes production during entrapment. The presence of aldehydes in human odor mirrors the O_3- and UV-related oxidative stress on human skin inducing peroxidation of unsaturated fatty acids forming the human sebum. While exposed to reactive oxygen species, these fatty acids degrade releasing a number of VOCs including aldehydes [22-24]. More specifically, aldehydes are produced from skin fatty acids via β-scission of alkoxy radicals formed by the homolytic cleavage of hydroperoxides. For instance, n-hexanal was demonstrated to be formed from linoleic, palmitoleic and vaccenic acids [22, 24]. The isolation of an individual from the predominant factors inducing this condition (O_3, UV) may hinder, or even suppress the skin production of the oxidative stress-related species. Acrolein emitted by the involved subjects is most probably an exogenous compound stemming from dietary or environmental sources[37]. It could also reflect the exposure to the tobacco smoke; however, only one volunteer was a smoker. The high background levels of acrolein seem to support the environmental origin of this specie. Further studies are necessary to confirm the usefulness of this compound for human location.

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Regarding esters, the levels of 5 species were found to be dependent on a human's presence in the chamber. Interestingly, within this class of compounds, different concentration profiles were observed. Ethyl propionate and vinyl butyrate exhibited profiles similar to those observed for aldehydes with rapid concentration increase during the skin emission phase and plateau during the last 60 mins of the volunteer presence in the chamber. Concentrations of ethyl isovalerate were characterized by increasing concentrations during the entrapment period. For ethyl formate and butyl acetate an increase in concentrations was observed during the skin phase measurements, followed by a decrease during the skin and breath phase. Owing to the limited knowledge on the endogenous origin of esters, it is difficult to explain the observed concentration profiles. Nevertheless, several possible sources can be suggested. Esters are typical ingredients of cosmetics or fragrances. Although volunteers were asked to refrain from using cosmetics on the day of the experiments, the observations could reflect prior exposure to these substances. Alternative sources for esters include (i) diet and its metabolites (natural occurrence e.g. in fruits, synthetic flavorings), (ii) environmental exposure (solvents), and (iii) peroxidation of unsaturated fatty acids [24]. Indeed, the observed concentration profiles of esters suggest a limited pool of these species in human body and their exogenous origin rather than a systemic production.

Acetic acid is a common VOC resulting from normal human biochemistry (e.g. ethanol metabolism, Krebs cycle, or pyruvate metabolism) and hence released from the body via breath [38, 39]. It can also be produced by cutaneous bacteria during the biotransformation of longer chain fatty acids and glycerol present in human sebum [26, 40]. Acetic acid was one of the most abundant compounds observed in the chamber air. It was emitted during both experimental phases. However, the breath contribution was not significant.

Although this study provides encouraging results, in order to propose a set of VOCs that can be used as a unique human chemical "fingerprint" further studies are required including robustness and reliability assessment under field conditions (e.g. contaminated environment of shipping containers, presence of animals etc.) This requires the creation of specific libraries containing chemical patterns representative for shipping containers or trucks containing different cargos (including animals). Moreover, losses related to e.g. absorption on materials present in the containers such as clothing or dust, or the influence of factors such as temperature and humidity (inducing condensation and formation of water films) have to be carefully evaluated. All of these confounders may considerably distort the levels of the volatile species and hinder their value as distinct markers for human presence. Therefore, extensive testing under more realistic conditions is crucial.

4. Conclusions

In the context of an escalation of people smuggling and trafficking, there is a need for analytical tools for the rapid and non-intrusive inspection of containers to detect hidden people. We have demonstrated that a GC-IMS instrument has considerable potential for use in this field. Analytically it offers distinct advantages. Firstly, it exhibits excellent detection limits without the necessity for

sample pre-concentration or pre-processing. The LODs obtained within this study are of the order of several hundreds of ppt, which are more than satisfactory for the detection of the majority of potential markers of human presence in the vicinity of the hidden person[5]. Secondly, direct sample injection improves the quality and reliability of the results, as any sample pre-concentration can result in potential losses and contamination. Thirdly, the analysis does not require external carrier/drift gases, or additional consumables (assisting in its field applicability). Several limitations of the current GC-IMS should be mentioned. Firstly, it is relatively large in size. This places some limitations on its use in field conditions. The prototype; however, has a modular design, which has a potential to be miniaturised. Another limitation is that some interesting classes of volatiles (e.g. alkanes) cannot be measured using the IMS technique. Furthermore, the current analysis time is too long to track concentration gradients, which could help to locate the victims. This; however, can be optimised in future application focussed on selected target markers. A major issue with IMS is its low temporal resolution. This leads to issues with compound identification.

However, the major obstacle for the application of GC-IMS is not instrumental, but the identification of robust and reliable markers for entrapped people. Once they have been determined, instrumental development can then take place to provide a customized, low-cost, and highly portable GC-IMS device for targeted analysis. In this context, it will be necessary to build a library of retention and drift times (mobilities), which could support the identification and monitoring of VOCs release by human body. This study has begun this process.

Conflicts of interest

There are no conflicts to declare.

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Table 1. Retention times R_t, reduced mobilities k_0, LODs, RSDs and dynamic ranges of compounds under study. Compounds are ordered with respect to increasing retention time.

Compound	CAS	Retention time, R_t [min]	Reduced mobility, k_0 [$cm^2\ V^{-1}\ s^{-1}$]	LOD		RSD [%]	Dynamic range	
				[ppb]	[pmol L^{-1}]		[ppb]	[pmol L^{-1}]
Acrolein	107-02-8	1.04	1.927	0.25	9.75	5.9	0.75-100	29-3900
Acetone	67-64-1	1.18	1.768	0.05	1.95	1.3	0.15-1000	6.0-39000
2-Methylpropanal	78-84-2	1.43	1.805	0.18	7.02	4.4	0.54-100	21-3900
Ethyl formate	109-94-4	1.51	1.688	0.16	6.24	3.5	0.48-20	17.6-780
2-Methyl-1-propanol	78-83-1	2.45	1.694	0.19	7.41	1.4	0.57-50	22-1950
3-methylbutanal	590-86-3	2.47	1.686	0.05	1.95	1.7	0.15-100	5.9-3900
2-Ethacrolein	922-63-4	2.92	1.793	0.23	8.97	4.6	0.69-50	27-1950
Ethyl propionate	105-37-3	3.22	1.245	0.41	16.0	0.6	1.23-20	48-780
Acetic acid	64-19-7	3.24	1.913	7.20	281	11.7	22-400	860-15600
2-pentanone	107-87-9	3.35	1.826	0.07	2.73	7.5	0.21-20	8.2-780
4-Methyl-2-pentanone	108-10-1	4.20	1.696	0.06	2.34	1.6	0.18-20	7.0-780
Vinyl butyrate	123-20-6	5.00	1.835	0.33	12.9	3.7	0.99-20	39-780
n-Hexanal	66-25-1	6.65	1.590	0.26	10.2	1.5	0.78-50	30-1950
Butyl acetate	123-86-4	7.00	1.915	0.20	7.80	0.6	0.6-20	23.4-780
Ethyl isovalerate	3301-94-8	10.18	1.931	0.04	1.56	3.7	0.12-20	4.7-780
n-Heptanal	111-71-7	10.58	1.492	0.30	11.7	3.5	0.9-50	35-1950
Benzaldehyde	100-52-7	12.03	1.722	0.26	10.2	3.8	0.78-50	31-1950

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Table 2. Mean (n=11) standard deviations of concentrations [ppb] of VOCs of interest.

Compound	Measurement time [min]								Literature data
	0	20	40	60	80	100	120	140	
	Background		Skin Emission			Breath and Skin Emission			
Acrolein	135±2	135±2	145±4	147±3	148±2	148±2	149±2	149±3	(a) 3.44 ppb (forearm)[21]
Acetone	20.1±6	20.3±7	25.5±8.0	33.3±14	41.8±25	137±65	228±108	330±215	(a) 126 ppb[19] (b) 206 ppb (forearm)[21]
2-Methylpropanal	18.7±1.4	18.5±0.7	21.6±1.1	22.9±1.4	23.3±1.6	23.8±1.9	23.2±2.3	23.2±2.2	(a) 2.23 ppb (forearm)[21]
Ethyl formate	37.3±3	39±4	50.23.6	51.0±3.0	50±1.7	49±3.2	48±3.4	47±2.9	
2-Methyl-1-propanol	1.85±0.65	1.9±0.53	2.46±0.51	2.74±0.65	3.06±0.71	2.95±0.66	3.02±0.68	3.06±0.66	
3-methylbutanal	5.43±2.1	5.78±1.3	6.67±1.3	7.44±1.57	8.10±1.74	7.87±1.67	8.13±1.96	8.1±1.57	(a) 2.45 ppb (forearm) [21]
2-Ethacrolein	0.35±0.4	0.39±0.29	1.75±1.9	3.02±3.1	3.40±4.65	4.52±2.94	6.53±5.1	7.76±6.26	
Ethyl propionate	2.10±1.2	2.51±1.31	3.93±0.64	4.81±1.05	5.7±1.9	6.16±3.25	6.36±4.23	6.29±4.0	
Acetic acid	66±15	70±8	98±34	121±51	133±62	141±68	147.5±70	155±60	(a) 105 ppb [19]
2-pentanone	LOD	LOD	0.24±0.25	0.47±0.45	0.76±0.54	1.04±0.78	0.96±0.75	0.99±0.77	(a) 1.17 ppb (forearm)[21]
4-Methyl-2-pentanone	4.1±0.6	4.07±1.25	4.81±0.52	6.15±0.92	6.23±1.16	6.1±0.61	6.21±0.89	6.27±1.38	
Vinyl butyrate	0.81±0.49	0.89±0.51	2.95±1.34	4.52±1.89	4.79±1.48	5.30±0.97	5.39±0.51	5.58±0.62	
n-Hexanal	12±1.58	12.5±1.17	13.05±1.33	13.55±1.76	14.35±1.7	14.24±1.36	14.23±1.26	14.14±1.52	(a) 7.6 ppb (forearm)[21]
Butyl acetate	0.3±0.43	0.43±0.73	1.05±1.95	1.28±1.18	1.32±1.18	0.89±0.8	0.87±0.6	0.45±0.9	
Ethyl isovalerate	0.08±0.16	0.12±0.2	2.04±2.0	3.87±1.7	4.60±2.3	5.50±1.9	6.18±1.6	6.77±1.4	
n-Heptanal	1.07±0.02	1.06±0.02	1.10±0.04	1.15±0.07	1.19±0.07	1.20±0.06	1.22±0.06	1.27±1.12	(a) 4.81 ppb (forearm)[21]
Benzaldehyde	1.08±0.06	1.10±0.05	1.13±0.06	1.16±0.08	1.18±0.09	1.17±0.07	1.18±0.07	1.19±0.07	(a) 29.1 ppb (forearm) [21]

Figures captions

Figure 1. Fragment of exemplary 2D GC-IMS chromatogram from the analysis of human-borne VOCs

Figure 2. Mean concentration profiles of acetone, 2-ethacrolein, ethyl isovalerate, and vinyl butyrate. Pink – skin phase, magenta – skin and breath phase.

Highlights

- Monitoring of volatiles emitted by humans by GC-IMS
- The use of volatiles as potential markers of hidden humans
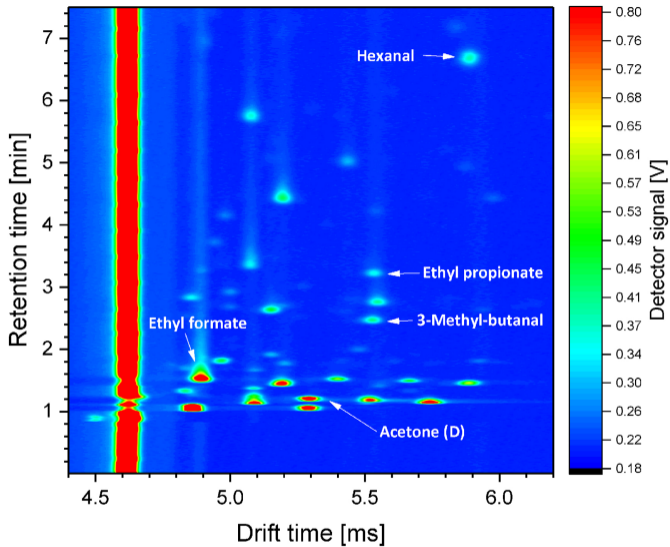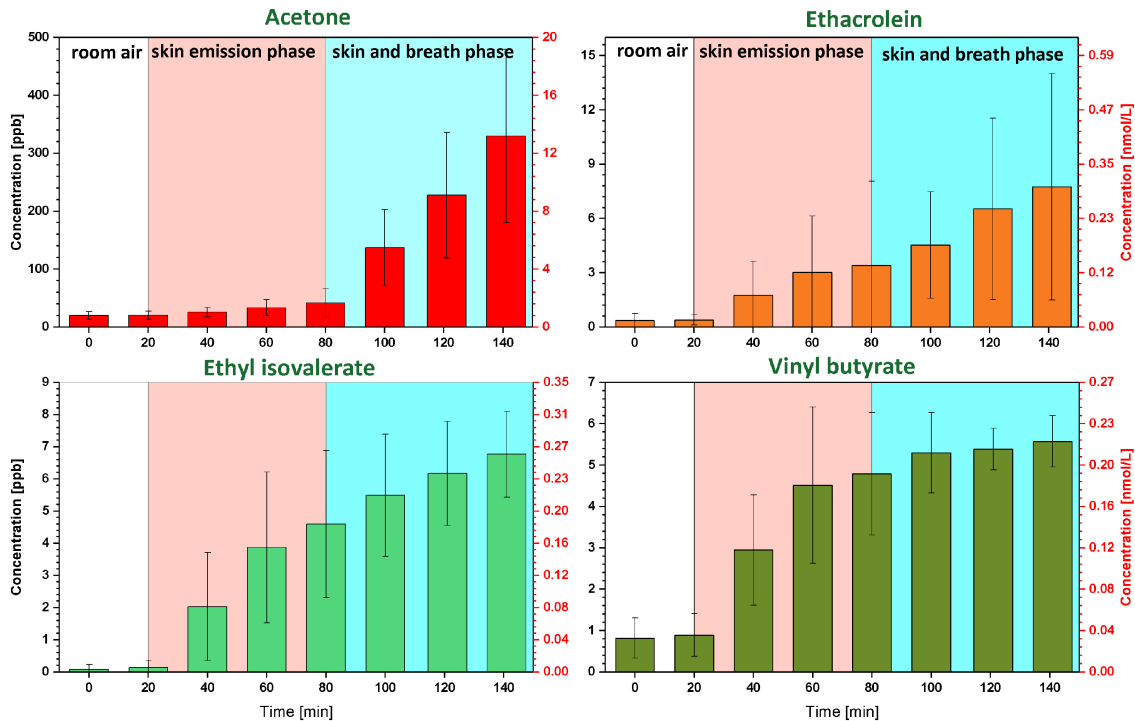- Instrumental detection of smuggled people

Figure 1

Figure 2