Supporting Information

Sniffing Entrapped Humans with Sensor Arrays

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Methods

Human subjects
A total of 9 healthy volunteers (5 males, 4 females, Table S2 for physiological data) participated in this study. Volunteers fasted for, at least, 8 h before the experiment to mimic entrapped conditions. Additionally, they were asked to abstain from alcoholic beverages for 12 h and refrain from using cosmetics to avoid potential interferences with the measurements. Prior to the measurement, each subject was informed about the experimental protocol and provided written informed consent. This study was approved by the Ethics Commission of the Innsbruck Medical University (registration #1110/2017).

Body chamber and protocol
Breath- and skin-emitted volatile organic compounds (VOCs) were collected in a plethysmography chamber (BodyScope, Ganshorn Medicin Electronic GmbH, Germany) with internal dimensions of $82 \times 63 \times 161$ cm resulting in a net volume of approximately 819 L (excluding internal installations). The limited chamber space allowed the entrapment of single volunteers. The chamber was made of stainless steel and glass to avoid contamination by material outgassing and allow easy cleaning after each volunteer. Additionally, this airtight chamber featured an overpressure valve to compensate pressure changes due to sampling and breathing. A fan installed at the ceiling assured homogeneous gas mixing within the chamber.

Before taking any measurements indoor contamination was reduced by venting the room for 2 h. Furthermore, the chamber interior was thoroughly cleaned with distilled water, dried with paper towels and followed by dry air flow of 5 - 6 L min$^{-1}$ for at least 60 min. Before the volunteer entered, background gas concentrations inside the empty chamber were measured for 20 min by the SRI-TOF-MS. Background acetone, ammonia and isoprene concentrations were always below 60, 25 and 10 ppb, respectively. Next, the subjects were asked to enter the chamber dressed only in underwear and the chamber door was locked rapidly. For the
following 2 h, each volunteer maintained in a sitting position inside the chamber. In the first hour, only skin-emitted volatile compounds were targeted. To achieve this, the subjects freely inhaled and exhaled (outside-chamber) room air via a two-way non-rebreathing Y-shaped valve (Hans Rudolph Inc., USA) of a silicone head mask (V2 Mask, Hans Rudolph Inc., USA) connected with two flexible polypropylene tubes (ID = 22 mm, Flextube, Intersurgical Inc., UK) to two ports located on the side wall of the chamber. In the second hour, breath- and skin-emitted compounds were measured. For this, the volunteers disconnected the outlet tube from the mask and exhaled directly inside the chamber, while still inhaling outside air. Therefore, during the second hour of the experiment both, breath and skin-emitted volatiles were measured. Altogether, a single experiment lasted for 140 minutes.

**Selective reagent ionization time-of-flight mass spectrometer (SRI-TOF-MS)**

An Ionicon Analytik (Innsbruck, Austria) type 8000 SRI-TOF-MS, was used to monitor acetone, ammonia and isoprene continuously. Chamber air was extracted through a sampling port (34 x 30 mm, i.e. detector inlet) located at the center of the sidewall of the chamber. This port was maintained at 40 °C to avoid condensation as it was sufficiently higher than the temperature of the air inside the plethysmographic chamber during entrapment of volunteers (Figure S4b). To this, a 3 m (d = 3.188 mm) long Teflon transfer line was connected delivering a steady flow of 100 mL min\(^{-1}\) to the instrument. Protonated acetone (C\(_3\)H\(_7\)O\(^+\), m/z = 59.0492 Th) and isoprene (C\(_5\)H\(_9\)O\(^+\), m/z = 69.0704 Th) were generated through reaction of the corresponding neutral molecule with H\(_3\)O\(^+\).\(^{35}\) Given that ammonia cannot be detected accurately in this mode owing to a high instrumental background, O\(_2\)\(^+\) ions were used in a combined mode.\(^{36}\) The ion-source current, source voltage, source out voltage and valve opening were set at 5 mA, 200 V, 130 V and 100%, respectively. At 2.4 mbar and 60 °C the ionization of the VOCs took place in the drift tube with a drift voltage of 600 V (130 Td). The mass calibration was based on the three peaks of H\(_3\)O\(^+\) (21.0221), NO\(_2\)\(^+\) (45.9924) and C\(_3\)H\(_7\)O\(^+\) (59.0492), always present in the spectra. The identification of each compound relied
on the exact mass measurement of the parent ions and the quantification was based on
calibration curves obtained prior to the experiments. The curves were obtained through 3-fold
analysis of five distinct gaseous one-component standard mixtures. Calibration, was
performed by dilution of a certified ammonia cylinder (9.99 ppm in synthetic air, Air-Liquid)
whereas the standards for acetone and isoprene calibration were prepared using a method
described elsewhere.\textsuperscript{37}

\textbf{Sensors and Array}

Chemoresistive Si-doped WO\(_3\) (10 mol\%)\textsuperscript{38}, Si-doped MoO\(_3\) (3 wt\%)\textsuperscript{25} and Ti-doped ZnO
(2.5 mol\%)\textsuperscript{26} sensors were prepared by flame aerosol technology and directly deposited onto
sensor substrates\textsuperscript{28}. These were mounted on macor holders and installed in Teflon chambers,
described in detail elsewhere.\textsuperscript{39} The sensors were heated up to 350, 400 and 325 °C for
optimal sensitivity and selectivity to acetone\textsuperscript{39}, ammonia\textsuperscript{25} and isoprene\textsuperscript{26}, respectively, by a
platinum heater on the back side of each substrate supplied by a constant DC current (R&S
HMC803, Germany). A platinum resistance temperature detector (RTD) on the front
controlled the temperature. During the experiment, each sensor’s resistance was recorded
continuously by a multichannel multimeter (Kethley 2700). Small pumps (Schwarzer, SP 140
FZ) installed at the outlet of the sensor chambers assured a constant airflow over each sensor
of 0.5 L min\(^{-1}\) through a 0.5 m (\(d_i = 6\) mm) long heated Teflon transfer line. Samples from the
chamber were extracted for 3 min every 20 min to minimize the extracted sample, but still
longer than the sensor response times to target analytes\textsuperscript{25,26,39} to obtain steady-state responses
(Fig. S1, inset). The sensors were combined with a commercial hygrometer (TH 309, B+B
Thermo-Technik GmbH, Germany) and CO\(_2\) (Capnostat 5, Respironics, USA) sensor.

The chemoresistive sensor responses were calculated as:

\[
S = \frac{R_b}{R_c} - 1
\]
where $R_b$ and $R_c$ are the sensor film resistances in background (room) and chamber air, respectively. Analyte concentrations are estimated by the sensor array, as illustrated in Fig. 2 of the paper. The individual sensor responses $S_i$ are processed with a multivariate linear regression model$^{29}$, as done with a SnO$_2$-based sensor array in laboratory gas mixtures$^{22}$. Therein, the concentration of an analyte $C_x$ is described as a superposition of each sensor response $S_i$ multiplied with an individual regression coefficient $a_{i,x}$ and an intercept $b_x$:

$$C_x = \sum_{i=1}^{4} a_{i,x} \cdot S_i + b_x$$

Due to the known interference of humidity for metal oxide-based chemoresistive gas sensors$^{39}$, the RH is included also as a sensor response $S_i$ and regression coefficient $a_{i,x}$. In a “training” step, all coefficients $a_{i,x}$ and $b_x$ were calculated using SRI-TOF-MS concentrations and the sensors responses as input. The performance of the sensor array model was then assessed by applying the regression coefficient on a separate data set (not used for “training”). This was followed by stepwise-elimination to identify multicollinearity$^{40}$ between sensors, remove insignificant sensors from the prediction and determine the best composition overall. All calculations were performed with MATLAB (R2016b, MathWorks, Natick, MA).

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Figure S1. Typical sensor responses of Ti-doped ZnO (circles), Si-doped WO$_3$ (squares) and Si-doped MoO$_3$ (triangles). Note that skin only (0 - 60 min) followed by skin and breath (60 - 120 min) emissions were studied separately. Inset shows the corresponding response profiles during a 3 min exposure to sampled chamber air exemplarily after 120 min.
Figure S2. Average sensor array estimation error at a given # of persons as sample size for acetone (triangles), ammonia (squares) and isoprene (circles). Error bars (standard deviations) represent all possible combinations of volunteers.
Figure S3. Sensor array (left) and SRI-TOF-MS (right) monitored acetone (a, d), ammonia (b, e) and isoprene (c, f) concentrations of all volunteers from only skin (0 - 60 min) followed by breath and skin (60 - 120 min) during entrapment. Note that for volunteer #4, skin (only) emissions lasted accidentally for 80 min. Data of volunteers with filled symbols were used for sensor array “training” and open symbols for array estimation and validation for comparison with SRI-TOF-MS.
Figure S4. Sensor array monitored RH (a) and temperature (b) of all volunteers during entrapment.
Figure S5. a) Single Si-doped WO$_3$ sensor estimation of the acetone concentrations in comparison to bench-top SRI-TOF-MS. b) Box-and-whisker plot of the individual sensor estimation errors for acetone (green), ammonia (red) and isoprene (blue). Medians and means are shown as lines and squares, respectively. The boxes represent the first and third quartiles and whiskers indicate the full ranges. Note that concentrations were calculated based on sensor calibration curves determined at 90% RH$^{25,26,39}$. 
Figure S6. Color map for volunteers #2, 4, 5, 7 and 8 indicating human detection by their skin only (0 – 60 min) followed by breath and skin (60 – 120 min) emissions. For each analyte, a detection score ($c_c/c_b$) is calculated representing the ratio of concentration in the chamber ($c_c$) and background air ($c_b$) in the presence of the volunteer.
**Table S1.** Applied human tracking technologies in USaR.

| Principle  | Devices                                                                 | Limitations                                      |
|------------|-------------------------------------------------------------------------|--------------------------------------------------|
| Optical    | SearchCam 2000 (Search systems)⁴¹                                      | optical access required                          |
|            | ProEye System 951-S (Yone)⁴                                           |                                                  |
|            | SnakeEye⁴²                                                                |                                                  |
|            | Crylcam⁴³                                                                |                                                  |
|            | HR320 camera (Argus)⁴⁴                                                  |                                                  |
|            | ThermoCAM B2 (FLIR)⁴⁵                                                   |                                                  |
|            | Evolution5000 Series (MSA)⁴⁶                                            |                                                  |
| Acoustic   | Vibraphone ASB-8, Vibrascope BVA-6 (Scorpe)⁴⁷                           | Unconscious victims not detected.                 |
|            | TPL Model 310 D Mini (Eplam)⁴⁸                                           | Limited acoustic and seismic range.              |
|            | Audio ResQ (Leader)⁴⁹                                                   | Interference by other noise.                     |
|            | LifeDetector Mini (Delsar)⁵⁰                                            |                                                  |
| Canines    | Search and rescue dogs³                                                 | Short operational time.                         |
|            |                                                                         | Limited numbers due to expensive training.      |
|            |                                                                         | Prone to stress.                                |
Table S2. Physiological data of the volunteers and their individual correlation coefficients between sensor array and SRI-TOF-MS for breath- and skin-emitted tracers.

| Subject | Age | Gender | Smoking | Weight [kg] | Height [cm] | Correlation coefficients (Pearson’s) |
|---------|-----|--------|---------|-------------|-------------|---------------------------------|
|         |     |        |         |             |             | Acetone | Isoprene | Ammonia |
| #1      | 47  | M      | N       | 67          | 170         | 0.99    | 0.98     | 0.97    |
| #2      | 25  | M      | N       | 55          | 172         | 0.88    | 0.89     | 0.99    |
| #3      | 38  | F      | N       | 63          | 170         | 0.96    | 0.99     | 1       |
| #4      | 34  | M      | N       | 71          | 180         | 0.95    | 0.97     | 0.97    |
| #5      | 24  | F      | Y       | 62          | 164         | 0.98    | 0.99     | 0.96    |
| #6      | 59  | M      | N       | 68          | 174         | 0.97    | 0.98     | 0.82    |
| #7      | 21  | F      | N       | 65          | 177         | 0.97    | 0.97     | 0.91    |
| #8      | 19  | F      | N       | 57          | 166         | 0.98    | 0.98     | 0.96    |
| #9      | 59  | M      | N       | 75          | 179         | 0.97    | 0.98     | 0.94    |