Detecting breath and skin emitted tracers of humans with flame-made sensor arrays

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Abstract:

Earthquakes are lethal natural disasters frequently burying people alive under collapsed buildings. Tracking entrapped humans from their unique volatile *chemical signature* with hand-held devices would accelerate urban search and rescue (USaR) efforts. Here, a compact and orthogonal sensor array has been designed to detect the breath- and skin-emitted *metabolic tracers* acetone, ammonia, isoprene, CO_2 and RH, all together serving as *sign of life*. It consists of three nanostructured metal-oxide sensors (Si-doped WO_3, Si-doped MoO_3 and Ti-doped ZnO), each specifically tailored at the nanoscale for *highly sensitive* and *selective* tracer detection along with commercial CO_2 and humidity sensors. When tested on humans enclosed in plethysmography chambers to simulate entrapment, this sensor array rapidly detects tracers of human presence with low parts-per-billion (ppb) level accuracy and precision, unprecedented by portable detectors but required for USaR. These results were validated by bench-top selective reagent ionization time-of-flight mass spectrometry (SRI-TOF-MS). As a result, an inexpensive sensor array is presented that can be integrated readily into hand-held or even drone-carried detectors for first responders to rapidly screen affected terrain.

Key words: Earthquakes, search and rescue, orthogonal sensor array, metabolic tracer, gas sensors

Earthquakes caused more than 780'000 deaths in the last decade and alarmingly, some of the most populous cities are located on fault-lines (e.g. Tokyo, Los Angeles or Delhi). Following an earthquake, many victims are entrapped under collapsed buildings and need help within the first hours. Indispensable for urban search and rescue (USaR) are dogs with their superior ability to sniff entrapped humans from their scent. However, their availability and operational time are limited and they are rather stress-sensitive. Nowadays, specialized equipment is also available to support USaR teams, but these rely only on optical and acoustic probes, not suitable for rapid sweeping of large areas and failing in frequent cases of limited visible access or unconscious victims.

Chemical recognition of the unique volatile signature of humans could improve USaR tools by adding a "third sense", similar to the canines sophisticated nose. Particularly promising to serve as robust *sign of life* is the combined detection of breath- and skin- emitted *metabolic tracers* like acetone, ammonia and isoprene originating from lipolysis, protein metabolism and cholesterol biosynthesis, respectively.

Here, we present a novel sensor array based on *distinctly selective* gas sensors for rapid tracking of entrapped humans (Fig.1) [1]. It consists of three tailor-made gas sensors i.e. Si-doped WO_3, Si-doped MoO_3 or Ti-doped ZnO featuring high sensitivities and selectivities to the metabolic tracers acetone [2], isoprene [3] and ammonia [4], respectively (Fig. 1b). These sensors consist of nanostructured, highly porous metal-oxide films (Fig. 1d) that offer high surface area to detect tracers even at the *lowest ppb* concentrations. Such films are obtained by direct deposition of flame-made nanoparticles on substrates forming finely structured sensing networks, as shown exemplarily for Ti-doped ZnO (Fig. 1e). Combined with commercial CO_2 and RH sensors, they result in an array with nearly *orthogonal* sensing characteristics enabling superior *discrimination power* and *robustness* to accurately detect the chemical signature of humans.
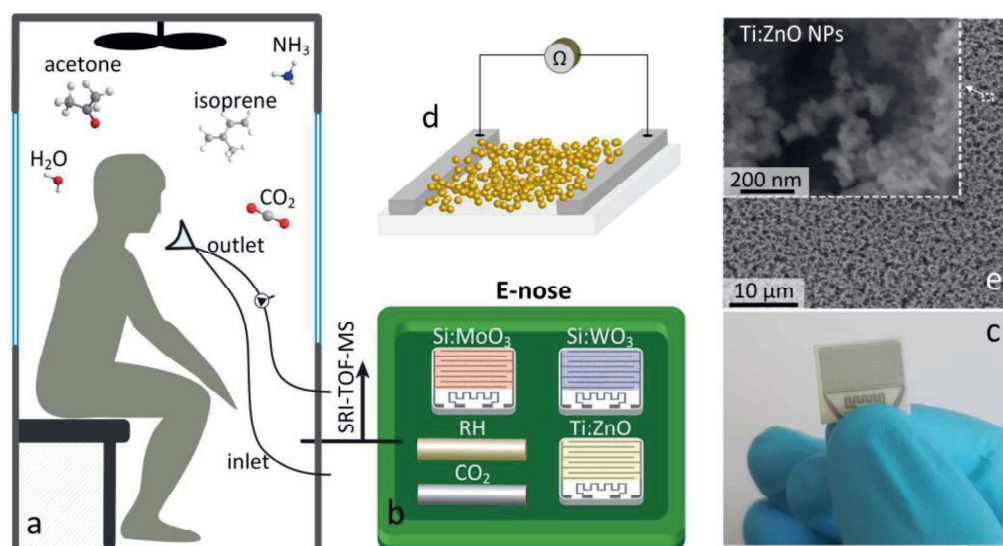
Fig. 1. a) Skin- & breath-borne volatiles of entrapped volunteers accumulate in a plethysmographic chamber. b) The sensor array consists of three chemoresistive sensors, Si-doped WO₃, Ti-doped ZnO and Si-doped MoO₃, to monitor acetone, isoprene and ammonia, respectively, together with commercial CO₂ and humidity. c) Image of a single sensor. d) Nanoparticles form a porous sensing network as shown by (e) scanning electron microscopy. [1]

We applied the sensor array to detect and monitor the volatile chemical signature of humans. Therefore, nine volunteers were enclosed individually in plethysmographic chambers (Fig. 1a) to mimic entrapment conditions. The testing course for each volunteer lasted for 120 min with skin (0 – 60 min) and skin + breath (60 – 120 min) emissions into the chamber being investigated separately. Fig. 2 shows the corresponding sensor array estimated acetone (a), isoprene (b), ammonia (c), RH (d) and CO₂ (e) concentration profiles of five volunteers when measured every 20 min. Note that the data of the other four randomly selected volunteers were used for "training" of a multivariate linear regression model
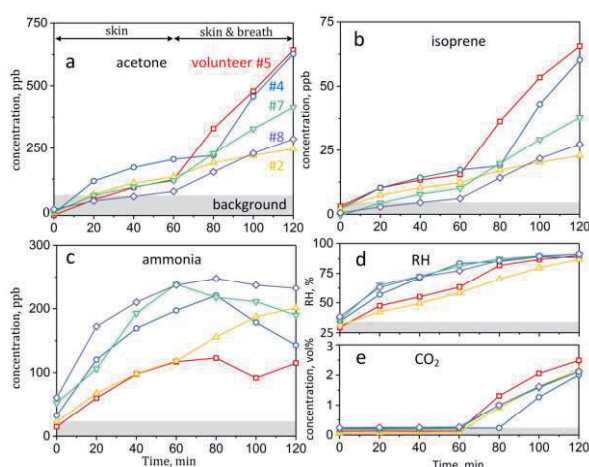

Fig. 2. Sensor array monitored acetone (a), isoprene (b), ammonia (c), RH (d) and CO₂ (e) concentrations of five volunteers as a function of entrapment time. In case of volunteer #4, skin (only) emissions lasted accidentally for 80 min. Room air (background) concentrations are indicated in grey. Adopted from [1].

Typically, acetone, isoprene and CO₂ change only little during skin emission while they increase significantly when also exhaled, as detected by the sensor array and consistent with SRI-TOF-MS analysis. As a result, these tracers indicate *human presence* during combined emissions *rather early* as their concentrations rapidly exceed background levels. On the other hand, ammonia and RH increase significantly during skin emission and differ from the background even after short entrapment. Later, both tend to level off and ammonia may even decrease in some cases, as confirmed by SRI-TOF-MS.

In conclusion, the detector recognizes human presence robustly due to multi-tracer assessment already after very short entrapment time. Furthermore, the sensor array can be incorporated easily into portable detectors to support first responders to find trapped victims after earthquakes.

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