Supporting information:

Novel Monitor Paradigm for Real-Time Exposure Assessment

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Description of monitor components

Sensing Elements and Sensor Cartridge

The monitor uses a sensor cartridge based on an array of sensing elements. The basic sensing element used in the wearable/handheld unit of the monitor is a quartz tuning fork, a piezoelectric resonator that can be used for various sensing applications.[1-5] The tuning forks are modified with polymer or blend coatings. In the current application, a new polymer and blend specially developed in our laboratory is used to provide sensing selectivity to the tuning forks. The polymer is a molecular-imprinted polymer (MIP) for detection of aromatic and alkyl hydrocarbons. The blend is a mixture of a hydrophobic ionic liquid and a strong base for detection of acid vapors. When analyte molecules are present, they interact with the polymer or blend, binding on to it. For a film coating on a tuning fork, this causes a change in mass of the tuning fork. Since the coating is tuned to be selective to a specific chemical group, this results in a tuning fork sensor that is both selective and sensitive to target analytes. Experimental details of tuning fork sensor technology are described in previous publications.[3-5] Briefly, tuning forks have a resonant frequency given by the equation (1):

$$f = \frac{1}{2\pi}\sqrt{\frac{k'}{M}}$$

(1)

where f is the resonant frequency of the tuning fork, k' is the effective spring constant, and M is the effective mass. It can be seen from equation (1) that any change in effective mass will also cause a change in resonant frequency, which can easily be detected by digital electronics. We have characterized this behavior under different conditions and performed a calibration of resonant frequency change against analyte concentration.

In this work, we have used an array of modified tuning fork sensing elements for detection of non-methane hydrocarbons, acid vapors, humidity, and temperature. As mentioned in the publication, the sensors are securely placed inside a sensor cartridge made of Teflon® (Fig S-1). The cartridge has pin connectors that plug directly into the control circuit board, similar to the concept of "plug-and-play" devices. This cartridge offers many advantages: (1) fragile tuning fork sensors are protected against damage, (2) dead volume is extremely low (~3.2 mL), and (3) due to the chemical inertness of Teflon, there is no interaction of analyte molecules with the walls of the cartridge itself. To prevent disturbances in sensor readings due to external electromagnetic interference, a thin stainless steel sheet runs along the inside of the cartridge and is connected to circuit ground. Within the cartridge, each tuning fork slot is separated from the others by a stainless steel mesh that is connected to ground. This ensures that there is no electronic coupling between individual tuning forks, resulting in extremely low noise level and consequently, a low detection limit.

Sample collection and conditioning system

Apart from the sensors and driving circuitry, the device has a separate system for handling the sample and directing the flow of air. Fig. 1 illustrates this layout. There are two inlets for air, a sampling channel and a purging channel. The former has an in-line particle filter to prevent dust and other particulate matter from reaching the sensors, while the latter employs a zeroing filter that absorbs all chemical species, resulting in clean air passing through. This is used to purge the system of residual analyte and interferent molecules after a detection. The filters are connected to a valve that receives a programmed signal to select which channel supplies air to the sensing elements and switches between them for predetermined intervals. For the current study, the device is set to operate with a two-minute clean air (purging) cycle followed by a one-minute sampling cycle. This valve interval timing is programmable and can be changed as per requirements. The zeroing filter is composed primarily of activated carbon and sodium

permanganate, while the particle filter is composed of polyester fibers carefully coated with poly-methyl methacrylate (PMMA) solution. The PMMA coating makes sure that no acid vapors are absorbed by the fibers. The valve is followed by a pump, which draws air in from the selected inlet and forces it through a dew line. The dew line serves two functions - it brings humidity down to a constant value and additionally removes interferents. This improves selectivity of the device beyond inherent selectivity of the polymer-modified tuning fork sensor elements. After passing through the dew line, the air enters the sensor cartridge, where detection of the sample takes place.

Detection Circuit

A custom printed circuit board (PCB) is used in the device to perform four main functions: (1) control of valve switching, (2) tuning fork drivers, (3) digitization of tuning fork responses, and (4) wireless data transmission and communication with a user interface module. The circuit to drive each tuning fork of the array has a dedicated oscillator. The periodic signal produced by each tuning fork is integrated for a predefined number of cycles and the resulting period is timed using a high frequency crystal (18MHz). In this manner, resonant frequency can be expressed as number of clock cycles. Bluetooth® technology is used for wireless transmission of the digitized sensor responses to any Bluetooth® enabled device such as a cellular phone or a computer. We have developed user interface tools for both cellular phones and computers, using Windows Mobile SDK and LabVIEW, respectively.

Signal Processing and User Interface Features

A cellular phone user interface was developed for the Motorola Q9h ™ smart phone on a Windows Mobile platform. This application displays a real-time plot showing the responses of the different sensing elements. It also processes data that it receives from the device, greatly simplifying user interaction. The device transmits current valve status, indicating the stage of operation (i.e., sampling or purging). To avoid false positives from long term drift that sometimes occur with temperature changes, the application uses slope readings from the last quarter of the two-minute purging period as the baseline to calculate the response during sampling. There is also a feature to subtract the response of a control tuning fork from the

response of the sensors. This eliminates false signals due to mechanical vibrations or potential sudden pressure changes.

The user interface has features for real-time raw data display and real-time concentration plot display as described in the main body of this publication.
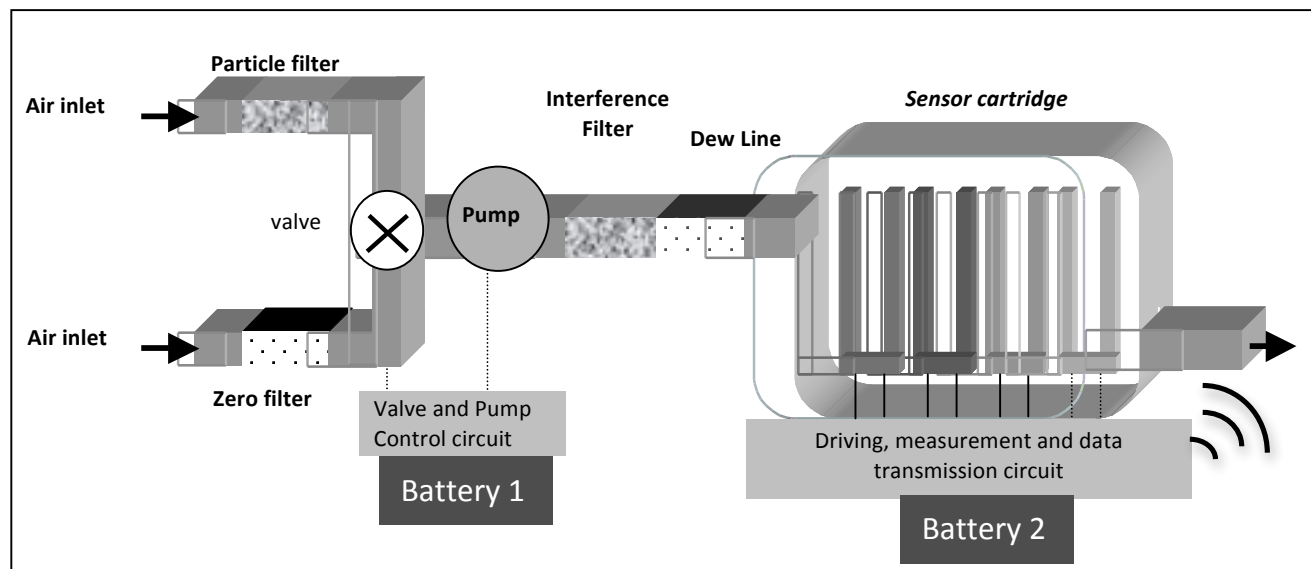

Fig. S-1. The sample delivery and conditioning system consists of the pump, valve, control circuit, and filters. The sensor cartridge contains an array of different sensing elements for hydrocarbons, acids, and humidity. The detection circuit runs on rechargeable Li-ion polymer batteries and is integrated with a Bluetooth[®] chip that transmits results to a user friendly interface.

Acid sensor performance

In order to characterize the selectivity of the acid sensor, the sensor was exposed to acids, regular environmental gases and volatile organic compounds. Form this group, only strong acidic vapors such as hydrochloric acid and hydrogen sulfide detected by the sensor (Fig. S-2).
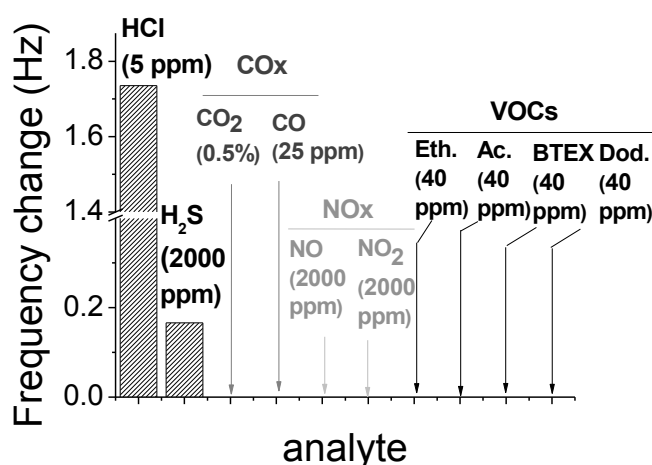
Fig. S-2. The selectivity of the acid sensing elements is tuned to avoid other groups of elements such as common inorganic gases (CO_2, CO, NO_x) and volatile organic compounds (VOCs) such as ethanol (eth.), acetone (ac.), aromatic hydrocarbons (BTEX), and alkyl hydrocarbons (dodecane: doc.), while giving a high signal for strong acidic vapors such as hydrochloric acid and hydrogen sulfide.

The validation of the acid sensors was done by calibration of the sensor response and use of recovery assays. Standard acid gas vapors were used to calibrate the acid sensors of the monitor. Once the sensors were calibrated, real samples with injected known concentration of acid gases, such as hydrochloric acid, were used to determine the recovered concentration of known injected fractions. The recovered acid concentrations were compared to the known injected concentrations and recovery factors between 95 – 104 % were obtained.

Cigarette smoke analysis by GC-MS

As it is mentioned in the manuscript, specific components of cigarette smoke were first characterized by GC-MS which identified hydrocarbon components detected by our wearable monitor. We concluded that benzene and toluene (Fig. S-3) components were the fraction of cigarette smoke being tested by our monitor, therefore, the monitor was suitable for assessment of exposure to toluene and benzene in cigarette smoke exposure studies.
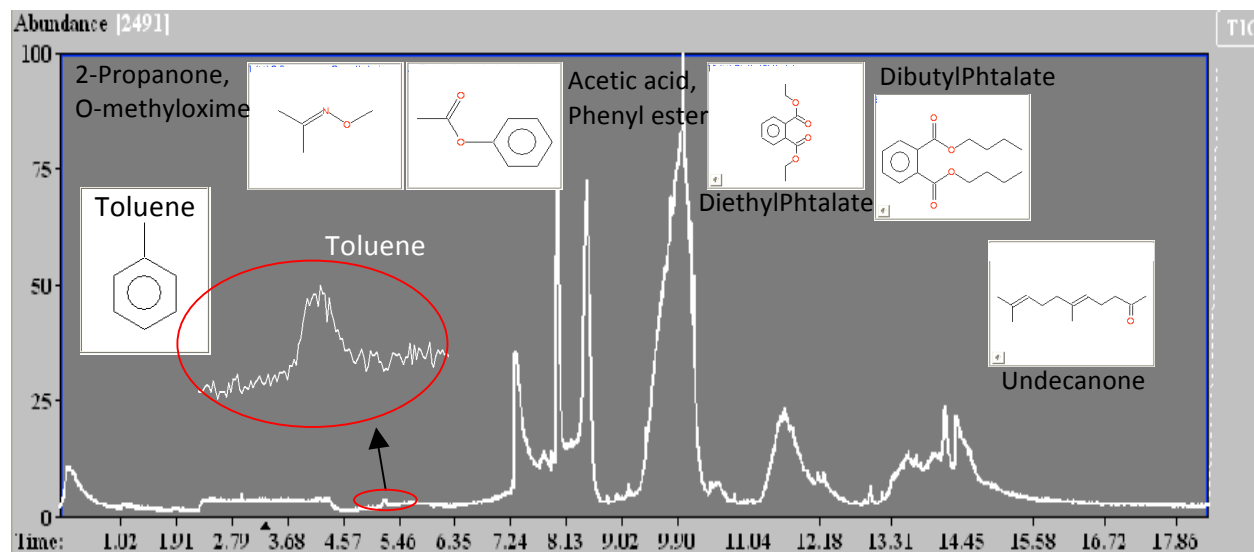
Fig. S-3. Gas chromatogram from a sample of cigarette smoke, showing different components identified in the sample and contaminants from the GC system. Only toluene and small traces of benzene were detected by the hydrocarbon sensor in this type of sample.

References

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