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Breath acetone monitoring by portable Si:WO_3 gas sensors

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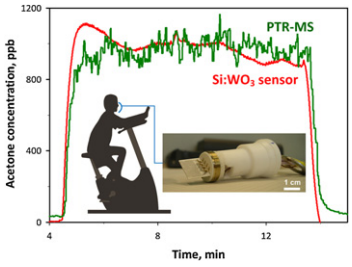
HIGHLIGHTS

- Portable sensors were developed and tested for monitoring acetone in the human breath.
- Acetone concentrations down to 20 ppb were measured with short response times (<30 s).
- The present sensors were highly selective to acetone over ethanol and water.
- Sensors were applied to human breath: good agreement with highly sensitive PTR-MS.
- Tests with people at rest and during physical activity showed the sensor robustness.

GRAPHICAL ABSTRACT



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ABSTRACT

Breath analysis has the potential for early stage detection and monitoring of illnesses to drastically reduce the corresponding medical diagnostic costs and improve the quality of life of patients suffering from chronic illnesses. In particular, the detection of acetone in the human breath is promising for non-invasive diagnosis and painless monitoring of diabetes (no finger pricking). Here, a portable acetone sensor consisting of flame-deposited and in situ annealed, Si-doped epsilon-WO_3 nanostructured films was developed. The chamber volume was miniaturized while reaction-limited and transport-limited gas flow rates were identified and sensing temperatures were optimized resulting in a low detection limit of acetone (~20 ppb) with short response (10–15 s) and recovery times (35–70 s). Furthermore, the sensor signal (response) was robust against variations of the exhaled breath flow rate facilitating application of these sensors at realistic relative humidities (80–90%) as in the human breath. The acetone content in the breath of test persons was monitored continuously and compared to that of state-of-the-art proton transfer reaction mass spectrometry (PTR-MS). Such portable devices can accurately track breath acetone concentration to become an alternative to more elaborate breath analysis techniques.

1. Introduction

Noninvasive detection of diseases by breath analysis is a fast, economically viable and simple alternative to blood analysis and endoscopy [1]. The breath, however, contains several hundred volatile organic compounds (VOC) with concentrations ranging from ppt to ppm [2]. The cellular and biochemical origin of many of these VOCs has not been determined and some of them might be of exogenous origin [3]. So the field of exhaled breath analysis is still in its infancy. Exceptions are isoprene and acetone, which appear in relatively high concentrations of ~100 and ~500 ppb, respectively [4]. Acetone has the potential of supplementing information on the

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status of patients suffering from diabetes [5]. The acetone concentration in the breath varies from 300 to 900 ppb in healthy people [4] to more than 1800 ppb for diabetics [6]. Nevertheless, acetone concentrations in the breath are not simply related to glucose levels in the blood and additional research is necessary to make it a viable marker compound for clinical routine. For example, exchange of acetone between blood and breath is taking place not only in the alveoli but also in the upper airways [7].

Even though the broad application of breath analysis is still challenging, the development of small, hand-held devices for reliable and continuous, real-time measurement of important breath markers such as acetone is desirable. Several methods have demonstrated a remarkable potential for such measurements [8]. For example, gas chromatography with flame ionization detection (FID) [9], proton transfer reaction-mass spectrometry (PTR-MS) [10] selected ion flow tube-mass spectrometry (SIFT-MS) [11], and differential mobility spectroscopy (DMS) [12] have shown high selectivity, sufficient sensitivity and low limit of detection for several VOCs. In general, however, most of these methods are quite costly and have rather limited portability except for DMS that has also high potential for miniaturization [13]. In this regard, chemo-resistive gas sensors based on semiconductor nanoparticles are attractive for breath analysis [14] offering low fabrication costs, high sensitivity, sufficiently low limit of detection and further miniaturization potential [15].

Recently, Cr- or Si-doped WO_3 nanoparticles have shown high sensitivity and selectivity to acetone [16], even up to 90% relative humidity [17]. This has allowed detection of low concentrations of acetone (down to 20 ppb) with high signal to noise ratio and high selectivity to ethanol and water vapor [17]. These promising results, however, were obtained in large heated chambers and simulated breath conditions. The application of such nanoparticles as acetone detectors in portable devices is not trivial [18] as reaching sufficiently high temperatures (300–450 °C) at reasonable power consumption requires a locally heated substrate that may result in inhomogeneous temperatures and concentration profiles within the sensing film [19]. Thus, the development of a portable device for breath acetone detection is still challenging [8] but quite attractive.

Here, a portable, chemo-resistive sensor has been developed and applied to real breath acetone detection. The sensor was based on a back-heated substrate with a sensing film consisting of optimally performing 10 mol% Si-doped WO_3 nanoparticles [17]. The sensitivity and selectivity of this device to acetone was investigated at various concentrations, temperatures, relative humidities and gas flow rates. Using this device, the breath acetone concentration of test persons at rest or during physical activity was measured and compared to that measured by highly accurate PTR-MS.

2. Materials and methods

A flame spray pyrolysis (FSP) reactor was used for synthesis and direct deposition of 10 mol% Si-doped WO_3 nanoparticle films [20] onto Al_2O_3 substrates featuring a set of interdigitated electrodes (Fig. 1a). A solution of ammonium (meta)tungstate hydrate (Aldrich, purity > 97%) and hexametyldisiloxane (HMDSO, Aldrich,

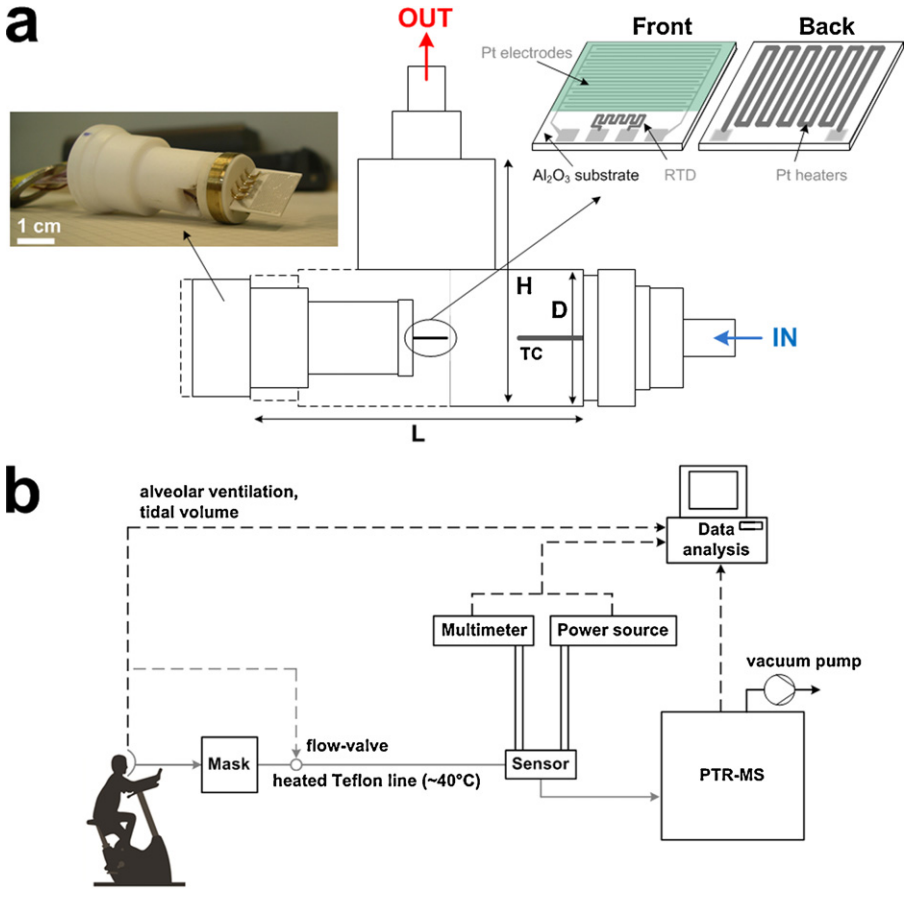

Fig. 1. Schematic of the T-shaped chamber (L = 75, H = 50 and D = 18 mm) and thermocouple (TC) placed inside. A Macor piece is holding the sensor prior to deposition of a tungsten oxide (WO_3) film onto interdigitated Pt electrodes laid on an Al_2O_3 substrate along with a resistance temperature detector (RTD) on the front side and a Pt heater on its back. (b) Schematic of the experimental set-up during breath analysis. The breath flow (grey lines) is controlled by the mask and kept constant by the PTR-MS pump. All the data (dashed lines) are collected and analyzed by the computer.