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Real-time monitoring of respiratory absorption factors of volatile organic compounds in ambient air by proton transfer reaction time-of-flight mass spectrometry

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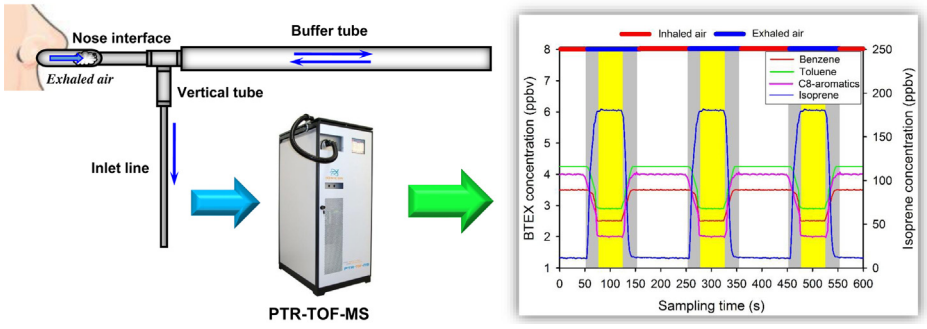
HIGHLIGHTS

- Real-time monitoring of VOC respiratory absorption factors (AFs) by PTR-TOF-MS.
- A homemade breath sampling device with a buffer tube to optimize signal peaks.
- Isoprene in breath air was an excellent breath phase tracer.
- BTEX respiratory AFs less than 100% or 90% assumed previously for risk assessment.
- Female subjects showed significantly higher respiratory AFs of BETX than male ones.

GRAPHICAL ABSTRACT



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ABSTRACT

Respiratory absorption factors (AFs) are essential parameters in the evaluation of human health risks from toxic volatile organic compounds (VOCs) in ambient air. A method for the real time monitoring of VOCs in inhaled and exhaled air by proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) has been developed to permit the calculation of respiratory AFs of VOCs. Isoprene was found to be a better breath tracer than O_2, CO_2, humidity, or acetone for distinguishing between the expiratory and inspiratory phases, and a homemade online breath sampling device with a buffer tube was used to optimize signal peak shapes. Preliminary tests with seven subjects exposed to aromatic hydrocarbons in an indoor environment revealed mean respiratory AFs of 55.0%, 55.9%, and 66.9% for benzene, toluene, and C8-aromatics (ethylbenzene and xylenes), respectively. These AFs were lower than the values of 90% or 100% used in previous studies when assessing the health risks of inhalation exposure to hazardous VOCs. The mean respiratory AFs of benzene, toluene and

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C8-aromatics were 66.5%, 70.2% and 82.3% for the three female subjects; they were noticeably much higher than that of 46.4%, 45.2% and 55.3%, respectively, for the four male subjects.

1. Introduction

Volatile organic compounds (VOCs) are a class of trace gases that are ubiquitous in the atmosphere. They are not only important precursors of both surface ozone and secondary organic aerosols (SOA) affecting air quality and climate change [1–5], but are also hazardous air pollutants (HAPs) with adverse health effects in indoor and outdoor environments [6–10]. Inhalation is a major pathway of human exposure to toxic VOCs due to their volatility [11], and respiratory exposure to toxic VOCs is associated with health risks including sensory irritation [12,13], asthma [14,15], chronic obstructive pulmonary disease (COPD) [16], cardiovascular diseases, leukemia, and other cancers [13,17–20]. To exert an effect on internal organs, a toxicant must be absorbed; respiratory absorption factors (AFs), i.e., the percentages of inhaled toxics that are absorbed and retained inside the body, are therefore essential to estimate the chronic daily intake (CDI) and lifetime cancer risk (LCR) of the corresponding toxic VOCs [6,21–25].

Modern breath analysis began decades ago when Pauling et al. [26] first detected around 250 different VOCs in exhaled air by gas chromatography (GC) method. Nowadays, human breath analysis has become an emerging bio-monitoring tool frequently used in clinical disease diagnosis for endogenous VOCs and exposure risk assessment for exogenous VOCs [27]. Compared to blood or urine analysis, breath analysis has many advantages, such as non-invasive, easily repeated, totally painless and agreeable to subjects. Traditionally, human exposure to toxic VOCs has been evaluated by measuring ambient air concentrations, and the external exposure level is merely treated as the internal dose [28]. Although inhalation studies have demonstrated that VOCs can be rapidly and efficiently absorbed into the human body via the inhalation route [29–31], respiratory AFs of VOCs are rarely 100% as some inhaled VOCs are exhaled from the lung without entering systemic circulation [32]. A number of recent human breath studies (Table 1), which were mainly conducted in environmental chambers or occupational workplaces with high exposure concentrations of VOCs, revealed respiratory AFs of toxic VOCs seldom over 70%. These AFs for toxic VOCs, however, were measured under extremely high exposure concentrations, mostly tens of parts per million by volume (ppmv), or even more than one hundred ppmv. Since the absorbed dose of toxic VOCs is related to the exposure concentration and duration, blood to air partition coefficients, and the pulmonary ventilation rate [55,56], it is questionable whether these AFs can be applied to low-level exposure in ambient or indoor environments. Additionally, previous results have mainly been obtained from time-consuming offline GC measurements after breath sampling using bags, adsorbents, and canisters [37,40,43]. Errors might be caused by moisture in exhaled air and during the collection and storage of breath samples [57–59]. Partly due to the difficulty in obtaining their respiratory AFs, toxic VOCs were still assumed to be totally absorbed in many studies on inhalation exposure health risk [60–68]. Alternatively, a number of studies have instead assumed AFs of 90% for toxic VOCs [6,21–24,69–71], and very recently a few studies proposed 50% or 60% as the AFs of toxic VOCs [72,73]. Therefore, authentic respiratory AFs are important parameters to be determined for accurate assessment of human health risks by inhalation exposure of toxic VOCs.

With the advent of direct VOCs analysis techniques, analytical methods based on real-time breath analysis have displayed promising perspectives. For example, proton transfer reaction mass spectrometry (PTR-MS) is a high-sensitivity technique allowing the real-time online analysis of VOCs in air, with detection limits down to single-digit parts per trillion by volume (pptv). The technique avoids sample preconcentration steps and some other disadvantages of offline GC measurements. It is widely used today in a variety of fields, including the direct online analysis of VOCs in breath samples in medical diagnostics and disease screening [74–79]. In this study, through a homemade online breath sampling device, VOC levels in air inhaled and exhaled by healthy test subjects were measured in real-time by proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS), and thus immediately obtained respiratory AFs from the differences in VOC concentrations between the inhaled and exhaled air. This method can be applied to in-situ monitoring of real-time internal dose for human inhalation exposure to a variety of toxic VOCs, even at sub part per billion by volume (ppbv) levels in ambient air.

2. Materials and methods

Because aromatic hydrocarbons, including benzene, toluene, ethylbenzene, and xylenes (collectively BTEX), are a major class of toxic VOCs [80–82], with a wide occurrence and distribution in both indoor and outdoor environments, and in both urban and rural areas, particularly in developing countries [83–90], BTEX were chosen as model toxic VOCs during our measurements of respiratory AFs. Another reason for choosing BTEX as our target VOC group is that humidity effects in breath samples can be ignored when measuring BTEX by PTR-TOF-MS, as previous studies have shown little humidity dependence on their sensitivity [91–93].

2.1. PTR-TOF-MS

BTEX in the breath samples were measured with a commercially available PTR-TOF-MS 2000 (Ionicon Analytik GmbH, Innsbruck, Austria). Detailed descriptions of the measurement principle and the structure of PTR-TOF-MS can be found in previous publications [94–97]. Briefly, the PTR-TOF-MS 2000 is an improved version of a PTR-MS instrument, using a time-of-flight mass spectrometer. The principal parameters for the operation of PTR-TOF-MS included a mass resolution ($m/\Delta m$): 1000–1500 (full width at half maximum); typical full mass spectrum range m/z: 10–440; drift tube operating voltage: 610 V; pressure: 2.20 mbar; and temperature: 60 °C, with an E/N ratio of about 139 Townsend (Td) (where E is the electric field strength and N is the number density of a neutral gas; 1 Td = 10^{-17} V cm^2). The primary ion H_3O^+ count rate, calculated from the count rate at m/z of 21.022 ($H_3{}^{18}O^+$) multiplied by 500, was approximately 1.4×10^7 counts per second (cps). The PTR-TOF-MS 2000 acquired data continuously at a frequency of 0.5 Hz in real time mode, using TofDaq data acquisition software (version 1.2.94, Tofwerk AG, Thun, Switzerland).

2.2. Quality assurance and quality control

Target compounds were identified based on their exact mass to charge ratio (m/z) and quantified by external calibration meth-