MIGRATE-17

INTERFEROMETRIC AND COLORIMETRIC BASED SENSING FOR MINIATURISED VOCS DETECTION

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KEY WORDS

BTEX, Air Quality, Volatile Organic Compounds, Colorimetry, Interferometry

ABSTRACT

The development of ultra-portable, accurate and powerful analytical tools capable of monitoring the air pollutants in near real time is a major technical challenge. Among pollutants, Volatile Organic Compounds (VOCs) such as Benzene are of major concern for indoor air quality due to its ubiquity and carcinogenic effect. ICPEES and INR have jointly developed a miniaturized GC/PID system dedicated to BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) monitoring in near-real time conditions at ppb level. This system has a temporal resolution of 10 min, a detection limit of 0.5 ppb.
The objective of this project is to develop another type of microfluidic detector that can be complementary to an existing commercial mini-photoionization detector. For instance, colorimetric detection through a waveguide absorption cell or phase measurement interferometry could be very powerful either to confirm the presence of BTEX or to detect the presence of other VOCs. Test platforms to quantify the suitability of techniques (accuracy, access and precision) will be developed. The evaluated approaches will be incorporated into a BTEX or formaldehyde analyser and its performance assessed using controlled reference BTEX or formaldehyde concentrations in terms of detection limits, repeatability, and reproducibility. Additionally the robustness of the final design will be assessed through a field campaign.

1. BACKGROUND

Volatile organic compounds (VOCs), particulary the BTEX grouping which comprise Benzene, Toluene, Ethyl Benzene and Xylene, are an important class of pollutants encountered in indoor air [1,2]. These chemicals are ubiquitous in cleaning products, candles [3], heaters, gas boilers [4], paints and varnishes. Emissions arise where gardening products and automotive fuels are stored [5,6]. Benzene in particular is a known carcinogen [7]. In 2013, the European Union set a threshold value of 1.6 ppb for benzene in public indoor spaces [8,9] which will be decreased down to 0.64 ppb in 2018. There is therefore a current research drive to develop portable instruments that are capable of providing real-time *in-situ* measurements of air quality, ensuring exposure to harmful BTEX chemical agents is minimised through rapid continuous monitoring.

2. DETECTION TECHNIQUES

Various techniques are available for the determination of air-borne BTEX. The most commonly used techniques are based on gas chromatography (GC) coupled to various types of detectors such as flame ionization detector (FID), photo ionization detector (PID), massspectrometry (MS) [10–12] or UV and IR spectroscopy [13–16]. These methods present several advantages such as a part-per-trillion (ppt) detection limit, high selectivity and high accuracy. Many portable laboratory miniaturized GCs equipped with different kind of detectors have been recently reported [13–18]. heir gas consumption ranged between 2 mL min^{-1} for those based on MEMS technology and 21 mL min^{-1} for GC coupled with PID. Their detection limit varied between 0.02 ppb and 10 ppm depending on the detector. Commercial analyzers for online BTEX detection are also available: GC/PID 8900®[42] (Baseline mocon-USA), airTOXIC BTX PID®[43] (Chromatotec-France), VOC 72M®[44] (Environment SA – France), Synspec GC955-600®[45] (Envri Technology, UK) andPetroPROTM[46] (INFICON, Switzerland) are commercial transportable units. Whilst these are very sensitive (limit detection in sub ppb levels) and provide an answer in quasi real time (6–15 min), these instruments are still relatively heavy (ranging from 13 to 20 kg) and require a supply of gas, usually through a storage cylinder, restricting operation to of order 1 month before re-supply is required.

An alternative approach is to employ an optical technique to detection such as colorimetry or interferometry which can be combined to a separation step, similarly to GC. A disposable colorimetric sensor array methodology has been developed by a research group at the University of Illinois at Urbana-Champaign for use as an “optoelectronic nose”[19, 20]. It has been applied successfully for the identification of a wide range both of gases/vapors [21,22] and analytes in aqueous liquids [23]. The use of nanoporous pigments significantly improved the stability and shelf life of the colorimetric sensor arrays and enabled the direct printing onto impermeable polymer surfaces [24]. Different VOCs had an individual „colour signature“ that was readily detected using a flat bed scanner. A preoxidation technique using Chromic Acid was found to vaslty improve the detection and identification of volatile organic compounds (VOCs) by a colorimetric sensor array [25].

Rather than rely on a array colour signature to identify the compound, Interferometric approaches detect phase changes between a laser beam that has undertaken two different paths before being recombined. Once compensated for spatial differences, the phase change can be associated to changes in refractive index that can be further associated with temperature, pressure or concentration changes. The method is integral in that the phase change is accumulated from when the beam is split to when it is recombined, and is exceptionally sensitive [26, 27]. An advantage of the interferometric approach is that it negates the need for the VOCs to undergo a reaction to be detected, but the stability, signal processing and level of control required may present a challenge to portability.

3. PLANNED WORK

The project will initially focus on local measurement approaches. Test platforms to quantify the suitability of techniques (accuracy, access and precision) will be developed. This phase will be performed in a research academic laboratory after which a placement in a SME will enable the integration of the evaluated approaches into a BTEX or formaldehyde analyser operating in gas and aqueous phases respectively, and enable its performance to be assessed using controlled reference BTEX or formaldehyde concentrations in terms of detection limits, repeatability, and reproducibility. Additionally the robustness of the design will be assessed through a field campaign. An additional period at ASML will facilitate the integration of the new measuring approaches with optical lithography employed in the semiconductor industry.

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