



## Novel fabricated silver particles/polypyrrole printed circuit board passive samplers for volatile organic compounds monitoring

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### ABSTRACT

A simple fabricated silver particles/polypyrrole printed circuit board (PCB) was successfully developed as a passive sampler for the monitoring of the volatile organic compounds, xylene and styrene. The surface morphology of the PCB passive sampler was investigated by SEM, and a cauliflower-like structure with large surface area was obtained. After sampling, the adsorbed analytes were easily desorbed by laboratory-built thermal desorption device coupled with an on-line micro-preconcentrator and analyzed by GC-FID. Under optimum conditions, a wide linear dynamic range (0.002–10,849 ng for xylene and 0.002–10,643 ng for styrene with  $R^2 > 0.99$ ) was obtained with a low limit of detection (0.65 and 0.64 pg for xylene and styrene, respectively) and a low limit of quantitation (2.00 pg for both compounds). The developed PCB passive samplers provided a good sampler-to-sampler reproducibility with a %RSD of less than 8%, a 2 weeks storage stability, a four times reusability with a %RSD of less than 10% and an especially low cost of only 0.25 USD per sampling. The obtained results were comparable to those using a commercial passive sampler. The developed passive samplers were used to monitor xylene and styrene at two copy-print shops in Hat Yai, Songkhla, Thailand. It was found that only xylene was found in the copy-print room ranging from N.D. to  $(3.0 \pm 0.1)$  ppbV. In addition, a personal exposure was also monitored and only xylene (1.4–3.4 ppbV) was also detected.

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### 1. Introduction

Passive samplers are ideal tools for large scale and long-term monitoring of volatile organic compounds (VOCs) in indoor environment because of their simplicity, ease of operation and low cost. Many international standard methods for air pollution monitoring are also based on the application of passive samplers [1,2]. Therefore, many passive samplers are being constantly developed and made commercially available. However, their prices are still considered to be expensive for the use as regular monitoring devices especially in developing countries. The analysis process after sampling also requires the use of either a toxic organic solvent or a high cost thermal desorption unit to desorb the target VOCs from the passive samplers. Therefore, a new, simple, low cost, yet highly efficient passive sampler is still needed.

Various materials have been used as the substrate for passive samplers such as stainless steel, polypropylene plastic, polytetrafluoroethylene and metals but some of these are expensive and some are not stable at high temperatures employed during thermal desorption. One of the most

interesting alternatives could be a printed circuit board (PCB), a thin plastic sheet coated with a copper layer on one side. It is a cheap material with an excellent electrical conductivity and a high thermal stability. These properties ease the improvement of the surface area and adsorption efficiency using metal particles and/or a porous sorptive sorbent via chemical and electrochemical deposition. In addition, thermal desorption prior to gas chromatographic analysis is possible and this could provide a better limit of detection compared to the solvent desorption [3]. After the desorption, for an analysis using gas chromatography, if a large volume of the sample was injected using a syringe or a gas sampling valve, it would cause a band broadening which resulted in the decreasing of the chromatographic resolution. So, a small amount of sample is generally used and this can result in a limitation of the system when detecting samples with large volumes [4–7]. To overcome this limitation, the desorbed analytes from the passive sampler could be refocused into a micro-preconcentrator to double the concentration and subsequently improve the peak shape of the analytes. An on-line micro-preconcentrator is a small silico-steel tubing packed with a small amount of adsorbent, that can be placed after the thermal desorption device and before the capillary column of a gas chromatograph [7].

In this document we describe a new, simple, low cost and highly efficient passive sampler for monitoring VOCs using a fabrication of

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silver particles on the copper layer of a printed circuit board (PCB) to enhance the surface area. This was followed by the electropolymerization of a polypyrrole on the silver particles to form a sorptive layer for adsorbing the VOCs. The aim was to obtain a device that would allow the detection of VOCs at a very low concentration level. Xylene and styrene released from the copying and printing processes in a copy-print shop was used as the model VOCs. After sampling, xylene and styrene were thermally desorbed from the developed passive sampler by a laboratory-built thermal desorption device coupled with an on-line micro-preconcentrator to refocus analytes before being rapidly injected into a gas chromatograph equipped with a flame ionization detector. In order to obtain the highest performance of the developed system, various parameters were optimized and the analytical performances were evaluated. Then, the sampling performance of the developed passive samplers was compared with those of a commercially available sampler.

## 2. Material and methods

### 2.1. Apparatus and reagents

All chemicals used in this study were of analytical grade. Silver nitrate was from Fisher Scientific (Loughborough, UK). Sodium tartrate was from BDH Chemical Ltd. (California, USA), propylene glycol was from Farmitalia Carlo Erba SPA (Rodano, Italy), and hydrochloric acid (37%) and xylene were from LAB-SCAN (Bangkok, Thailand). Hydrogen peroxide was from Merck KGaA (Darmstadt, Germany). Pyrrole with 98% w/v purity was from Sigma Aldrich (Missouri, USA) and styrene monomer (C<sub>8</sub>H<sub>8</sub>) with ≥99% w/v purity was from Fluka (Buchs, Switzerland).

The analysis was performed using a gas chromatograph coupled with a flame ionization detector (GC-FID) (Shimadzu 14A, Kyoto, Japan) with an RTX 624 capillary column (30 m × 0.25 mm × 1.4 μm) (Restek, Philadelphia, USA). A potentiostat (Model 410, EDAQ, Australia) coupled with an electrochemical cell containing a silver particle modified PCB working electrode, a Ag/AgCl reference electrode and a Pt rod auxiliary electrode were used for electropolymerization of the polypyrrole. The surface morphology of the PCB passive sampler was investigated using an FEI Quanta 400 scanning electron microscope (SEM-Quanta) (Brno, Czech Republic).

### 2.2. Fabrication of the printed circuit board (PCB) passive samplers

A printed circuit board (PCB), cut into small rectangular pieces of 1 × 3 cm<sup>2</sup>, was used as a substrate for the fabrication of the PCB passive sampler. The copper layer was polished with alumina slurry (5 μm and 1 μm) and rinsed with distilled water. To increase its surface area, the cleaned PCB was immersed into a H<sub>2</sub>O<sub>2</sub>/HCl aqueous solution (HCl: H<sub>2</sub>O<sub>2</sub>: H<sub>2</sub>O = 1: 2: 4) to etch, hence roughen, the copper surface. During the immersion, nitrogen gas was purged into the solution in order to obtain a uniform etching of the copper layer. The flow rate of nitrogen and the immersion time were tested at 10, 20, 30 and 40 mL min<sup>-1</sup> and 10, 20, 30 and 40 s, respectively. Then the etched PCB was immersed in 2.0 M HCl to remove any copper oxide that might have been produced from the oxidation by oxygen in air during the preparation process and rinsed with distilled water. In this step, the immersion time was assessed at 10, 20, 30 and 40 s. Silver particles were then fabricated onto the PCB surface by immersing the etched PCB in 20.0 mM AgNO<sub>3</sub> prepared in propylene glycol, then rinsed with distilled water and dried with nitrogen gas. The immersion time was varied from 12, 24, 48, 72 and 84 h at room temperature. A sorptive layer of polypyrrole (distilled prior to use) was then electropolymerized onto the PCB surface by cyclic voltammetry (from 0.0 to 1.2 V) using the modified PCB as a working electrode in 15 mL of 0.50 M pyrrole prepared in 0.20 M sodium tartrate [8]. The number of scans was varied from 20, 50, 100, 120 cycles with 5 pieces of the Ag modified PCB at each scan.

### 2.3. Thermal desorption and on-line micro-preconcentration

Fig. 1 shows a schematic diagram of the system. The passive sampler (a in Fig. 1A) was placed in a glass chamber (a screw cap vial with an inner diameter of 1.24 cm and a height of 5.20 cm) and thermally desorbed by the laboratory-built device (Fig. 1A). The analytes were then preconcentrated in the micro-preconcentrator (b in Fig. 1B), thermally desorbed and injected into the gas chromatograph via the injection valve (Fig. 1C). The laboratory-built thermal desorption device was simply made by inserting a soldering iron into a block of brass (3.0 cm diameter and 5.0 cm high). This was used to heat the glass chamber, together with the passive sampler [4]. An on-line micro-preconcentrator (b in Fig. 1B) (15 cm long, 0.525 mm I.D., 0.725 mm O.D. silico steel tube packed with Carboxen 100 mesh) was placed at the outlet of the glass chamber to refocus the analytes before entering the separation column of the GC-FID through the 10-port injection valve.

The operation consists of three steps. In the first step, the heating step, the PCB passive sampler (a in Fig. 1A), with the adsorbed target analytes within the glass chamber are heated for an appropriate time without N<sub>2</sub> purging (line 2: dotted-line), whereas the N<sub>2</sub> carrier gas (line 1: solid-line) is flowing directly to the GC-FID to obtain the base-line. In the second step, N<sub>2</sub> (line 2) is purged to deliver the desorbed xylene and styrene in the glass chamber into the micro-preconcentrator to refocus the analytes while the N<sub>2</sub> gas line (line 1) is still flowing directly to the GC-FID. In the last step, a current pulse from the power supply is sent to the outer wall of the micro-preconcentrator. By this method the analytes are desorbed from the on-line micro-preconcentrator. The 10-port valve was then switched to the injection position resulting in the change of the flow direction of N<sub>2</sub> (line 1). Instead of flowing directly to the GC-FID, it flowed from the 6th to the 5th port, through the connection line to the 2nd and then the 1st port before going out to the glass chamber. The flow then went through the micro-preconcentrator, carrying the analytes that had been already desorbed to the GC-FID via the 8th port that was at this time connected to the 7th port. During this step there was no N<sub>2</sub> purging from line 2.

To obtain the highest desorption efficiency, the heating temperature and time of the two desorption steps were optimized. The temperature of the thermal desorption device was varied by adjusting the temperature knob of the soldering iron, while that of the on-line micro-preconcentrator was changed by adjusting the applied potential of the power supply. The initial condition for both heating systems was 10 min with a heating temperature of 180 °C for the thermal desorption device and 1 s with a 3.0 V heating potential for the micro-preconcentrator.

To ensure that the desorbed xylene and styrene from the PCB passive sampler were completely trapped in the micro-preconcentrator, the adsorption time was studied. The PCB passive sampler was exposed to the standard gases of xylene and styrene in the 5 mL of the standard gas chamber (3.0 ppmV; 100 times higher than the instrumental detection limit for the xylene and styrene), then transferred to the glass chamber where the target analytes were thermally desorbed using the optimum conditions. The adsorption time of the analytes in the on-line micro-preconcentrator (under the continuous flow of N<sub>2</sub>, 1.2 mL min<sup>-1</sup>, (line 2: dotted-line)) was varied from 1, 5, 9, 10, 12 and 15 min. The other parameters were fixed at their optimum values.

In this study, the standard gases, xylene and styrene, were prepared by injecting a known volume of standard solution of both compounds in a 500 mL standard bulk container. The standard bulk was filled with N<sub>2</sub> gas and allowed to stand for 2 h at room temperature before using it as the homogenous standard gas. Their concentrations were calculated by the static gas standard method as shown in Eq. (1) [9].

$$\text{ppm A} = \frac{\text{volume A} \times \text{density A} \times 24.25 \times 10^6}{\text{Mw A} \times \text{container volume}} \quad (1)$$

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