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Development of one-step hollow fiber supported liquid phase sampling technique for occupational workplace air analysis using high performance liquid chromatography with ultra-violet detector

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ABSTRACT

In this study, a simple and novel one-step hollow-fiber supported liquid-phase sampling (HF-LPS) technique was developed for enriched sampling of gaseous toxic species prior to chemical analysis for workplace air monitoring. A lab-made apparatus designed with a gaseous sample generator and a microdialysis sampling cavity (for HF-LPS) was utilized and evaluated to simulate gaseous contaminant air for occupational workplace analysis. Gaseous phenol was selected as the model toxic species. A polyethersulfone hollow fiber dialysis module filled with ethylene glycol in the shell-side was applied as the absorption solvent to collect phenol from a gas flow through the tube-side, based on the concentration distribution of phenol between the absorption solvent and the gas flow. After sampling, 20 μL of the extractant was analyzed by high performance liquid chromatography with ultraviolet detection (HPLC–UV). Factors that influence the generation of gaseous standards and the HF-LPS were studied thoroughly. Results indicated that at 25 °C the phenol (2000 μg/mL) standard solution injected at 15-μL/min can be vaporized into sampling cavity under nitrogen flow at 780 mL/min, to generate gaseous phenol with concentration approximate to twice the permissible exposure limit. Sampling at 37.3 mL/min for 30 min can meet the requirement of the workplace air monitoring. The phenol in air ranged between 0.7 and 10 cm^3/m^3 (shows excellent linearity) with recovery between 98.1 and 104.1%. The proposed method was identified as a one-step sampling for workplace monitoring with advantages of convenience, rapidity, sensitivity, and usage of less-toxic solvent.

1. Introduction

Sampling and analysis of chemicals from occupational workplace air is used by occupational health and safety professionals to assess contaminants and associated worker exposures. The validity of an assessment is based on the procedures applied for sampling, analysis, and result interpretation [1]. Conventionally, target organic contaminants are collected by withdrawing workplace air through sampling train using sorbent sampling tubes or impingers with sampling pump, and then extract the target species with different extraction solvents prior to chemical analysis [2–4]. Although these methods afford correct and representative results, there were some drawbacks such as being tedious, expensive, and inconvenient in sampling or in sample preparation, as well as usage of toxic solvents for the extraction of analytes from sorbent or trapped solution [5]. Therefore, a simple, convenient, inexpensive, and eco-friendly sampling method applicable to most organic compounds is worthy to investigate.

Gas–liquid membrane contactors have been proposed in many industrial processes and wastewater treatment since Qi and Cussler [6] first proposed the idea of the hollow-fiber membrane (HFM) contactor for absorption of carbon dioxide in aqueous sodium hydroxide solution. The application of the microporous HFM contactor for gas absorption has gained appreciable attention recently and is still a relatively new concept [7]. Moreover, in the last two decades, HFM based extraction has also been widely applied to collect analytes from complicated matrix aqueous sample solutions before the chromatographic analysis [7,8], which offers several advantages over conventional extraction methods. These advantages include simplicity, convenience, selectivity, possession of high surface area for extraction, inexpensiveness, and eco-friendliness [9–11]. Therefore, it has potential to be the method to collect gaseous organic contaminants from sampling gas stream for occupational workplace monitoring.

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Phenol is an important commodity chemical used in many industrial activities for the production of pesticides, insecticides, herbicides, synthetic resins and in medical products [12]. Smoking cigarette, breathing contaminated air, workplace exposure or skin contact are possible routes of human exposure of phenol [13]. It was recognized that over exposure to phenol exerts a marked corrosive action on any tissue of contact and also affects the respiratory and cardiovascular systems [14]. Moreover, time-weighted-average (TWA) exposure limit value for phenol is 5 ppm by volume or 19 mg/m^3 has been adopted with a tentative 15-min short-term exposure limit (STEL) of 10 ppm by volume or 38 mg/m^3 [15]. Therefore, monitoring the concentration of phenol in workplace is necessary to protect the health of workers.

Thus, the analysis of phenols in workplace air has been the subject of several studies, some reported in published literature [16–19]. Initially, phenol from air was analyzed by NIOSH method by using an impringer containing alkaline solution to collect vapors, prior to GC-FID analysis [16,17]. Then, Kuwata et al. [18] developed a sensitive method for detecting phenol in air by using a 0.1 M NaOH bubbler solution to collect the phenol vapors and followed by derivatization with p-nitrobenzenediazonium tetrafluoroborate for sensitive analysis by HPLC–UV. Later on, a solid sorbent XAD-7 tube was applied to preconcentrate phenol from air and then desorbed with methanol followed by HPLC–UV or GC-FID analysis [19,20]. However, these methods possess its own drawbacks such as needs of large amount of extraction solvents, derivatization setups, and tedious setups [21]. Therefore, phenol from occupational workplace was selected as the model contaminant in the proposed sampling method.

In the present work, to the best of our knowledge, we report for the first time in examining the applicability of the hollow fiber supported liquid phase sampling (HF-LPS) modified from gas/liquid membrane contactors [22,23] for the efficient one-step sampling of phenol in workplace air toward effective HPLC–UV determination. The effect of various experimental conditions on the extraction as well as the conditions for producing standard gaseous sample are investigated and discussed in detail.

2. Experimental

2.1. Chemicals and materials

Milli-Q UV Plus System (Millipore, Billerica, MA) was used to produce ultra-pure water for all aqueous solutions. ACS reagent grade of phenol, sodium hydrogen phosphate, sodium dihydrogen phosphate, HPLC grade of acetonitrile, and GC grade of ethylene glycol were purchased from Riedel-de Han (Seelze, Germany). Polyethersulfone (PES) Midikros hollow fiber modules (pore size 0.5 μm, i.d. 0.5 mm, surface area 55 cm^2) was purchased from Spectrum Laboratory (Rancho Dominguez, United States), and used for sampling. Nitrogen (N_2, 99.99%) was obtained from a local supplier, To-Yo Gas Company (Taichung, Taiwan).

2.2. Instrumental

The JASCO HPLC system (Tokyo, Japan) system equipped with a LC pump (PU-2080), a Rheodyne 7010 injector valve (Cotati, CA, USA) and a 7125 switching valve both with 20 μL sample loop, and an ultraviolet/visible (UV/VIS) detector (UV-2075) set at 210 nm was used to analyze the collected phenol sample. Separations were achieved using a C18 column (5 μm, 250 mm × 4.6 mm inner diameter) (JASCO) with the elution performed by the mobile phase containing acetonitrile and 0.02 M phosphate buffer solution (pH 6.6) in 55:45 (v/v) at the flow rate of 1.0 mL/min. The SISC software system (Taipei, Taiwan) was used to control operation of HPLC, obtain the chromatogram and perform data calculations.

A syringe pump (Univentor 801, Zejtun, MALTA) was used to deliver the phenol standard solution into the N_2 flow to produce standard gaseous sample. A SKC 222 series gas sampling pump (Seoul, Korea) was applied for the HF-LPS, and was calibrated by the Ultraflo 709 IR flow-meter (SKC). A Varian Satum 2000 gas chromatography/mass spectrometry (GC/MS) (Varian, CA, USA) was used to re-confirm the phenol peak in HPLC chromatogram after collection and enrichment.

2.3. Apparatus for generation of standard gaseous sample for sampling

An apparatus for generation of standard gaseous phenol sample was designed based on the dynamic dilution method, as shown in Fig. 1. A syringe pump was used to deliver phenol standard solution stably into the N_2 flow from storage tank. After mixing well in the mixing cavity, the standard gaseous flow of phenol in N_2 started flowing into the sampling cavity with a stable concentration of phenol to simulate a gaseous contaminant occupational workplace for the HF-LPS sampling.

2.4. HF-LPS sampling

A SKC 222 series gas sampling pump was applied for the HF-LPS after flow rate calibration. A hollow fiber dialysis module with five PES microdialysis tubes was filled with ethylene glycol (0.538 mL) in the shell-side as absorption solvent, and applied to collect phenol from gas flow in the tube-side based on the concentration

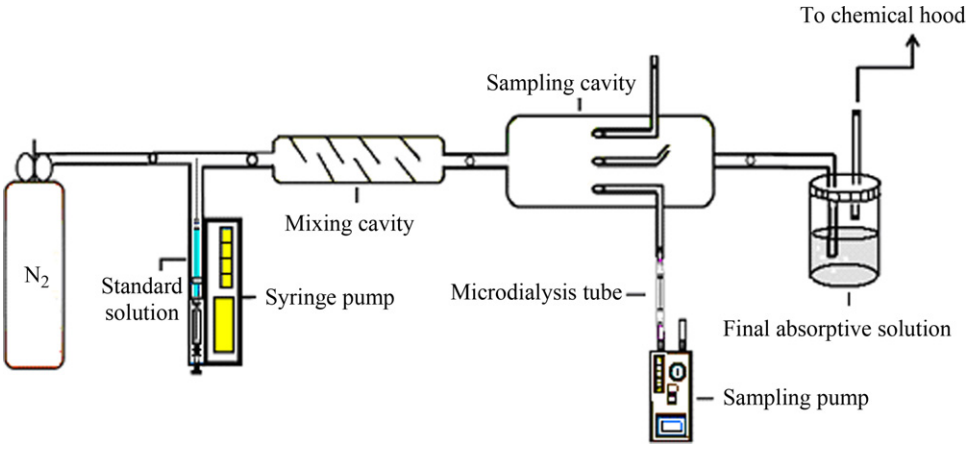

Fig. 1. Apparatus for the generation of standard gaseous sample.