



# Capillary microextraction of volatiles device for enhanced BTEX vapors sampling based on a phenyl modified PDMS sol-gel adsorption phase

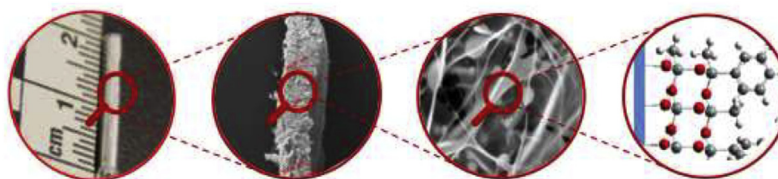
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## HIGHLIGHTS

- A new adsorption phase, phenyl-PDMS sol-gel, was developed for CMV device.
- Significant improved performance was successfully achieved in sampling BTEX vapors.
- Enhance recoveries, retaining capabilities, LODs within upto tens fold were achieved.
- Liquid extraction instead of TD was demonstrated for the first time using CMVs.
- Sub-ppb detection and screening of VOCs is possible within 5-10 min sampling.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel phenyl modified PDMS (PhPDMS) sol-gel adsorption phase was developed for use with the capillary microextraction of volatiles (CMV) device, and determined to provide significant enhancement in BTEX recoveries when sampling trace (ng) amounts of these volatiles at ambient conditions.

The previously reported reusable PDMS-CMV device has been demonstrated to rapidly and efficiently extract target compound's vapors in forensic and environmental applications. An improved recovery for VOCs was achieved with a cryofocusing system while extracting at  $-10^{\circ}\text{C}$ , but it was found to be impractical for field sampling. This report details a modification to the CMV's chemistry, by the successful introduction of phenyl groups to the PDMS sol-gel adsorption phase, allowing enhanced performance at ambient extraction conditions. Higher average recoveries, determined through a broad concentration range, were demonstrated for PhPDMS-CMV over its original PDMS-CMV, from cans simulating a closed space set-up. Within 7.8 ( $\pm 10\%$ ) and 3.5 ( $\pm 6\%$ ) folds higher for benzene and toluene, respectively and 2 ( $\pm 2\%$ ) folds for ethylbenzene and xylenes. Significant higher retaining capabilities were demonstrated also at the more challenging set-up, simulating an open space environment. Whereas, benzene had completely breakthrough the PDMS-CMV, its reliable detection was still confirmed with PhPDMS-CMV pumping at 2 L or 6 L air, concentration dependent. At least 50 folds ( $\pm 26\%$ ) more toluene was retained with PhPDMS-CMV at 6 L air than with PDMS-CMV. The enhanced overall performance lead to determination of trace LODs with the new CMV of 0.002, 0.00035 and 0.00015 ppm for benzene, toluene, ethyl benzene and xylenes, respectively. As proof of concept, for the first time solvent extraction is presented for the new CMV as an alternative to thermal desorption extraction. Extraction efficiencies of

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60% for TEX, and lower concentration dependent for benzene, were demonstrated with the ease and rapid application of 100  $\mu\text{L}$  acetone through the device.

The improvements described in this study continues to build on the potential for the use of the reusable new CMV device by expanding its possible potential applications for fast and sensitive air sampling of VOCs. The solvent extraction step may offer compatibility with LC-based systems.

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## 1. Introduction

The trace detection of benzene, toluene, ethylbenzene and the three isomers of xylene, commonly called BTEX compounds, is still of great concern in ambient air and indoor spaces [1]. These compounds, used as a model for sampling VOCs, are well-known as potential hazards to human health with benzene, in particular, being classified as a carcinogenic chemical [2–5]. According to the Occupational Safety and Health Administration (OSHA), Permissible Exposure Limits (PEL) - Time Weight Average (TWA) concentration values of 1 ppm ( $3.19 \text{ mg m}^{-3}$ ) for benzene, 200 ppm ( $754 \text{ mg m}^{-3}$ ) for toluene and 100 ppm ( $434\text{--}441 \text{ mg m}^{-3}$ ) for ethylbenzenes and xylenes isomers were determined [6,7].

Current data show that BTEX compounds are widespread in the environment, originating mostly from the burning of motor vehicle gasoline and diesel fuels in outdoor air, and from numerous household products such as cleaners, fabric and leather treatments, adhesives, and plastic and rubber components in indoor spaces [2,8]. For the analysis of BTEX compounds in environmental matrices, pre-concentrating devices have been used with an aim to improve the trace detection using GC-based instruments coupled with different FID, PID and MS detectors [7,9,10]. The sampling methods mostly vary between two approaches [11]: (a) passive samplers, diffusion controlled, such as HS-SPME fibers, coated mesh and sorbents; or (b) active samplers, air pump flow controlled, such as solvent traps (impingers), cryogenic traps, and single or multiple sorbents in different tube volumes down to needle trap device size (NTD) [5,9,12]. The active approach is preferred for quantitative measurements and allows for improved detection with shorter sampling times.

The capillary microextraction of volatiles (CMV) device is an active air sampler introduced in 2013 [13,14]. The device is based on an adsorption phase coated substrate packed inside a  $2 \text{ cm} \times 2 \text{ mm}$  double open-ended glass capillary. These dimensions were designed to fit into a commercially available thermal separation probe (TSP) and subsequently placed directly into a GC injection port for efficient thermal desorption. The applicability of the CMV-GC-MS analytical method has been demonstrated for several forensic and environmental applications that include detection of target compounds in the headspace above explosives [14], smokeless powders [1] and gunshot residue (GSR) compounds sampled by swabs from shooter's hands [15]. The method was further applied successfully as a proof of concept for characterizing the headspace above marijuana plants. The screening technique allowed to distinguish the unique markers from hemp products [16], methamphetamine vapors [17] and, more recently, CMV was used for the screening of human exhaled breath for distinguishing cigarette smokers from nonsmokers [18]. The technique has been shown to be fast (several minutes scale), sensitive and the reusability of the CMV device was proved within a life span of more than 100 times [1].

Recently, the CMV device was evaluated for the detection of a broad range of volatile organic compounds (VOCs) through a validation study following the criteria of the EPA method TO-17 for

environmentally harmful compounds [1,19]. To improve the trapping efficiency of these compounds while decreasing breakthrough effects during active sampling, a newly designed thermoelectric cooler was constructed to accommodate the CMV and apply cryofocusing of the compounds extracted from the headspace. The application of the Cryo-CMV operated at  $-10^\circ\text{C}$  was demonstrated to improve the recoveries of ng quantities of BTEX compounds between 35 and 100% compared to room temperature, allowing the detection of benzene at sampling volumes of several liters of air [1]. Although the involvement of a thermoelectric cooler for Cryo-CMV extraction is easily feasible and applicable in indoor spaces, it is less practical for outdoor field sampling. This new study introduces an alternative with enhanced BTEX vapor sampling performance while maintaining ambient temperature during the extraction.

A general improvement in the trapping efficiency of VOC's, including BTEX, was demonstrated in the literature using divinylbenzene (DVB) based sorbents or DVB-PDMS modified adsorption phase over PDMS by itself in several applications. Higher recovery for BTEX emitted from electric vaporization of anti-mosquito mats was reported by needle trap device (NTD) packed with DVB particles at different mesh [12] compared to PDMS HS-SPME fiber. DVB packed NTD resulted in lower breakthrough volumes over Carboxen sorbent in sampling BTEX from various locations in a house and a garage interior [32]. A  $65 \mu\text{m}$  PDMS-DVB HS-SPME fiber was used for the determination of dialkyl ethers and BTEX in rivers, marinas, fishing harbor surface waters [20] and from wastewater [21].

The CMV devices applied up to this current research contain all the same adsorption phase prepared in a process developed in our laboratory [22,23]. The process generated a high surface area sol-gel PDMS coating over activated glass fiber filters described elsewhere, named PSPME [23]. These coated filters were originally designed to accommodate direct introduction into ion mobility spectrometry (IMS) instruments for real time analysis. Later, PSPME coated filters were cut into strips for packing into a small glass capillary for a direct coupling with GC-MS analysis for higher sensitivity, improved selectivity and increased reliability in compound identification [14].

Different procedures for the synthesis of phenyl silica based polymers in sol-gel process have been reported. Among them are Tamaki et al. who introduced homogeneous polystyrene and silica gel polymer hybrids utilizing sol-gel reaction with different alkoxysilanes, including phenyl modified [24]. Liu and coworkers prepared novel fibers coated with co-poly hydroxy-terminated silicone oil OHTSO/DVB by sol-gel and cross-linking technology for selective and sensitive detection of phosphate and methylphosphonate from air and water [25]. Azenha et al. constructed SPME fibers coated with sol-gel using phenyltrimethoxysilane (PhTMS) and methyltrimethoxysilane (MTMS) precursors at different relative ratios, in a procedure that yields a dense microstructure coating [26], and Loy and coworkers examined the sol-gel chemistry of a variety of organotrialkoxysilanes with different organic substituents including phenyl modified in an attempt to elucidate the requirements for gelation [27]. Wang and Bierwagen

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