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Graphene packed needle trap device as a novel field sampler for determination of perchloroethylene in the air of dry cleaning establishments

Mahmoud Heidari [a,*], Abdolrahman Bahrami [b], Ali Reza Ghiasvand [c], Maryam Rafiei Emam [a], Farshid Ghorbani Shahna [b], Ali Reza Soltanian [d]

[a] Department of Occupational Health, School of Health, Guilan University of Medical Sciences, Rasht, Iran
[b] Department of Occupational Health, School of Health, Hamadan University of Medical Sciences, Hamadan, Iran
[c] Department of Chemistry, Faculty of Science, Lorestan University, Khoramabad, Iran
[d] Department of Biostatistics and Epidemiology, School of Health, Hamadan University of Medical Sciences, Hamadan, Iran

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ABSTRACT

In this paper we describe the application of a needle trap microextraction device packed with graphene nanoplatelets for the sampling and analysis of perchloroethylene in dry cleaning. The study was carried out in two phases. First the parameters for the sampling and analysis of perchloroethylene by NTD were evaluated and optimized in the laboratory. Then the sampler was used to determine the levels of perchloroethylene in a dry-cleaning shop. In the laboratory phase of the study the performance of the NTD packed with the proposed sorbent was examined in a variety of sampling conditions to evaluate the technique. The technique was also compared with NTDs packed with PDMS as well as SPME with Carboxen/PDMS-coated fibers. Both the NTDs and SPME performed better at lower sampling temperatures and relative humidity levels. The post-sampling storage times for a 95% recovery of the analyte were 5, 5 and 3 days for NTD-graphene, NTD-PDMS and SPME–CAR/PDMS respectively. The optimum desorption time was 3 min for NTDs packed with either graphene or PDMS and 1 min for SPME–CAR/PDMS. The limits of detection for the GC/MS detection system were 0.023 and 0.25 ng mL^{-1} for NTDs packed with graphene and PDMS and 0.014 ng mL^{-1} for SPME coated with CAR/PDMS. In the second stage of the study the evaluated technique was applied to the sampling and analysis of perchloroethylene in dry cleaning. In this environment the performance of the NTD-graphene as a field sampler for PCE was similar to that of the SPME-CA/PDMS, and better than the NIOSH 1003 method which had greater measurement variations. The results show that a NTD packed with carbonic graphene nanoplatelets and used as an active exhaustive sampling technique is effective for determination of VOC and HVOC occupational/environmental pollutants in air.

1. Introduction

Perchloroethylene (PCE or PERC) also called tetrachloroethylene, is a volatile, nonflammable, and colorless liquid with a sweet odor. It has been commercially available since the early 1900s and is now one of the most widely used chlorinated solvents worldwide. It is the solvent of choice in dry cleaning facilities. In 1994 its usage in this industry reached 90% within the European Union [1]. PCE is currently also used as a degreaser of metal parts, as an extraction solvent in chemical processing, as a heat-exchange fluid, and as a typewriter correction fluid. Those working in the degreasing of metals are most heavily exposed to PCE contamination, primarily by inhalation [2].

PCE has been detected in the air, water and soil, as well as in food and in animal tissues. The United States Environmental Protection Agency (USEPA) ranks PCE as a hazardous air pollutant because of its toxicity and resultant impact on health [3]. The International Agency for Research on Cancer (IARC) classified PCE as a probable human carcinogen (Group 2A) [4,5]. In occupational studies, chronic exposure to PCE has been shown to adversely affect the kidneys, liver, central nervous system, and reproductive system. PCE can remain stored in fat tissue.

The OSHA method for determination of PCE in the workplace involves the use of adsorbent tubes for sample collection and GC–FID for sample analysis [6]. In the case of outdoor atmospheric samples, PCE as well as other VOCs are determined by the USEPA TO-14 method [7], which involves sampling in canisters and

* Corresponding author. Tel.: +98 9113203058; fax: +98 1313228843.
E-mail address: Heidari@gums.ac.ir (M. Heidari).

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GC–MS analysis. The development of rapid screening methods is becoming increasingly important in analytical chemistry. Conventional methods used in analytical laboratories are usually not compatible with the need for routine and extensive monitoring [8,9].

In recent years there has been a growing demand for rapid, single-step and solvent-free microextraction sampling and analysis methods for volatile organic compounds. Solid-phase microextraction (SPME) and needle trap microextraction (NTME) with a needle trap device (NTD) sampler are examples of solventless sample preparation and introduction methods being developed today. SPME, first reported by Pawliszyn et al. in the early 1990s, is a simple, time-efficient, and solvent-free sample preparation technique [10]. It has been successfully applied to the extraction of various compounds at trace levels such as organic pollutants in environmental, food, biological, pharmaceutical, and clinical samples.

Despite its advantages SPME has some drawbacks. One of these is that, when applied to air samples, the extraction capacity is limited and normally based on equilibrium. In contrast the NTD technique combines the concept of miniaturized exhaustive active sampling and passive diffusive sampling with new microextraction concepts first introduced by Pawliszyn et al. [11]. For extraction, the sample is drawn inside the needle through the sorbent bed. Direct desorption is then facilitated by inserting the needle inside the GC injection port [12]. The NTD can be used for both active and passive sampling and its extraction capacity can easily be augmented by increasing the quantity of sorbent inside the needle. Another drawback of SPME is the fragility of the fibers. The NTD is more robust because the extraction phase is protected inside a stainless steel shield [13].

Until now the NTD technique has been used with commercial sorbents such as polydimethylsiloxane (PDMS), divinylbenzene (DVB) and Carboxen 1000 [14,15], Carbopack X and Tenax [16–18] and Porapak Q[19]. Combining NTD with new nano- material sorbents was first introduced by Heidari et al. [20,21]. Among the new nano-material sorbents, graphene, a single-atom-thick, two dimensional carbon material, is considered as the basic building block of all graphitic forms (including carbon nanotubes, graphite and fullerene (C_{60})) [22].

In sampling techniques with an adsorption mechanism, the specific surface area of the sorbent plays an important role in the sampling process. The high surface area to weight (2630 $m^2\,g^{-1}$) ratio of graphene is, therefore, an outstanding advantage. Other advantages of graphene include its remarkable thermal and chemical stability, ultra-high mechanical strength and low production cost [23–24]. These advantages make graphene a good candidate to use as a sorbent in modern microextraction techniques such as SPME [25] and NTD.

The aim of this study is to introduce a novel and powerful field sampler for the occupational and/or environmental assessment of trace elements in air. In this paper we describe the application of needle trap microextraction devices packed with graphene nanoplatelets for sampling and analysis of perchloroethylene in the laboratory and the field. This study was carried out in two phases. In the first the laboratory parameters for sampling and analysis of perchloroethylene by NTD sampler were evaluated and optimized. Then the sampler was used for determination of perchloroethylene in dry cleaning.

2. Experimental

2.1. Reagents and standards

Multi-layer graphene nanoplatelets (Fig. 1) with fewer than 30 layers, a purity higher than 95.5 wt%, a thickness of 4–20 nm, and a particle diameter 5–10 μm were obtained from the Chinese Academy of Sciences (Chengdu Organic Chemicals, Chengdu, China). Perchloroethylene in analytical grade was purchased from Sigma-Aldrich (Munich, Germany).

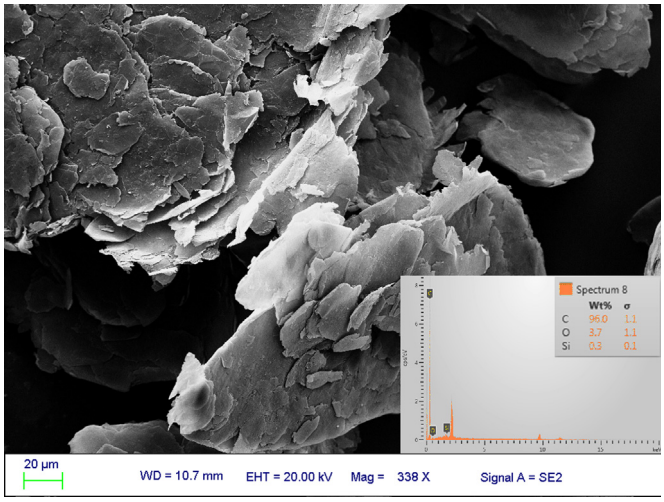

Fig. 1. Scanning electron micrograph and EDS analysis of the graphene nanoplatelets which used as sorbent in NTD.

2.2. Instrumentation

Chromatography was performed using a Varian 3800 GC with a capillary column (VOCOL with 60 m × 0.25 mm × 0.25 μm) equipped with a Saturn 2200 MS system and a split-splitless injector. The column was initially set at 40 °C. This temperature was maintained for 4 min and then increased at a rate of 6 °C per min to 160 °C, for a total run time of 24 min. Injection of the NTDs was performed in splitless mode at a GC injector temperature of 300 °C. The flow rate of the Helium (99.999%) carrier gas was 1 mL min^{-1}. A home-made narrow-neck glass liner with a 1.5 mm I.D. and a 0.5 mm neck diameter was used in the GC injector for conducting the carrier gas into the NTDs via the hole in the side of the needle. The glass liner also ensured the efficient delivery of the analyte of interest to the GC column and served to prevent peak broadening. A home-made chamber was used to accurately adjust the analyte concentration, temperature and humidity of the sample matrix. A 21-gauge needle (10.5 cm length × 510 μm I.D. × 820 μm O.D.) was purchased from Kosan LTD. (Tokyo, Japan). A syringe pump (JMS SP-510, Hiroshima, Japan) was used to inject a predetermined measure of pure PCE into the standard sampling chamber thus providing the desired concentration of analyte. The manual SPME holder with 100 μm polydimethylsiloxane (PDMS) was purchased from Supelco (Bellefonte, PA, USA). For use of PDMS in NTD, a predetermined amount of sorbent packed inside the needle. PDMS purchased from Sigma-Aldrich (Munich, Germany). When sampling with NTDs, a low volume sampling pump (SKC 222 series, PA, USA) with a flow rate range of 1–200 mL min^{-1} was used to draw accurate quantities of air into the needles and through the sorbent bed.

2.3. Preparation of the needle trap device

Each NTD was prepared by filling a 21-gauge stainless steel needle with sorbent material. To allow the sorbent to be packed inside the needle the internal metal plunger was shortened by 26 mm. The end of the shortened internal plunger determined the position of the first glass wool layer inside the needle. Three more plungers where cut so as to be 3, 18 and 21 mm shorter than the