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Use of exhaled air as an improved biomonitoring method to assess perchloroethylene short-term exposure

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ABSTRACT

This paper shows the use of exhaled air as a biomonitoring method to assess perchloroethylene (PERC) environmental and occupational exposure. A sensitive, fast, and solvent free analytical method was developed to determine PERC in ambient and exhaled air of individuals occupationally exposed. The developed method used cold fiber solid phase microextraction (CF-SPME) as the sampling technique, and a standard permeation method to simulation of air matrix. The analysis were conducted by gas chromatography coupled to mass spectrometry (GC/MS). The methods were validated and were found to be precise, linear and sensitive for environmental and biological monitoring. The developed methods were applied to twenty-seven sampling points spread across Belo Horizonte city, Brazil, twenty four dry cleaners, an electroplating industry, a research laboratory, and an automotive paint preparation shop. The results of ambient air analyses ranging from 14.0 to 3205.0 μg m^{-3} with median concentration of 599.0 μg m^{-3}. Furthermore, sampling of exhaled air of individuals occupationally exposed presented results ranging from 6.0 to 2635.0 μg m^{-3} with median concentration of 325.0 μg m^{-3}. The strong correlation observed between ambient and exhaled air ($r = 0.930$) demonstrates that exhaled air is a suitable biomarker for evaluating occupational exposure to PERC.

1. Introduction

Tetrachloroethylene or Perchloroethylene (PERC) is a solvent widely used as a cleaning agent, predominantly in the dry cleaning industry (Petrucci et al., 2015). It can also be used for sulfur recovery, degreasing metal, rubber dissolution, paint removal, pre-cleaning operations for electroplating, spot removal, paint stripping, catalyst regeneration, silicone lubricants and multiple uses in the textile industry (Gold et al., 2008). The main route of human exposure is contaminated air inhalation leanding significant numbers of workers continuously exposed to this solvent every year (Tucker et al., 2011). Repeated exposure to PERC is a dangerous because it results in body accumulation, especially in fatty tissues as well as in liver, kidneys, lungs, and brain (WHO, 2010). Owing to its high solubility in fatty tissues PERC has a half-life in vivo of 65 h that is considerably longer than most other solvents (Aggazzotti, 1994). The rate-limited metabolism and pulmonary excretion are main routes to PERC elimination from the body. The primary pathway to excretion of PERC absorbed in an organism is unchanged exhalation. This allows the use of alveolar air to assess exposure to this compound (Dallas et al., 1994). The United States Environmental Protection Agency (EPA) inhalation Reference Concentration (RfC) for PERC is 40.0 μg m^{-3} based on its neurotoxicity (EPA, 2016). The main chronic effects due to PERC inhalation are neurological effects such as sensory disorders, headaches, cognitive dysfunction, motor, and neurobehavioral effects on color vision (Lucas et al., 2011). Moreover, PERC is classified by the International Agency for Research on Cancer (IARC) as a likely human carcinogen (group 2A) (International Agency for Research on Cancer IARC, 2014). Considering the health effects of occupational exposition to PERC, specific legislation has been proposed. The United States Occupational Safety and Health Administration (OSHA) established an 8 h time-weighted average permissible exposure limit of 678.6 mg m^{-3}. The American Conference of Governmental Industrial Hygienists (ACGIH) has indicated a threshold limit value (TLV) of 169.6 mg m^{-3}, a short term exposure limit (STEL) of 678.6 mg m^{-3} and a biological exposure indices (BEI) of 34.0 mg m^{-3} of PERC in exhaled air (ACGIH, 2015). According to the U.S. National Institute for Occupational Safety and Health (NIOSH) the recommended exposure limit should be as low as possible, based on PERC carcinogenicity potential (NIOSH., 2003). Therefore, the interest in PERC trace analysis in ambient and exhaled air has grown considerably. However, the low PERC concentration require the addition of a pre-concentration step in the analysis method. Several classical techniques can be used for sampling PERC in ambient air such as stainless steel canisters (Shao et al., 2011), bags (Dincer et al., 2006), and solid

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phase extraction (SPE) in active or passive mode (Roda et al., 2013). On the other hand, alternative techniques of extraction have proposed to analyze PERC in air such as membrane introduction mass spectrometry (MIMS), solid phase microextraction (SPME) and needle trap microextraction (NTME) with a needle trap device (NTD). MIMS performs continuous permeation of an analyte through a membrane followed by sorbent trapping that allows good capabilities for automated and on-line analysis (Ras et al., 2009). NTME is a solvent free technique that combines sampling and sample preparation in one step. NTME with NTD seeks to associate the design of active exhaustive miniaturized diffusive sampling and passive sampling with new concepts microextraction (Heidari et al., 2015). On the other hand, SPME enables VOCs extraction from air to the fiber surface through molecular diffusion (Koziel et al., 2000). Besides, the use of cold fiber solid phase microextraction (CF-SPME) is an improvement because the sorption process is endothermic and fiber cooling shifts equilibrium towards increasing performance of the extraction (Menezes and Cardeal, 2011).

The analysis of unmetabolized PERC and its metabolites as trichloroacetic acid (TCA) and trichloroethanol have been proposed as biomarkers for the assessment of occupational exposure (Pirsaraei et al., 2009; Poli et al., 2005). In humans, about 2.0% of the PERC volume absorbed is metabolized, the remainder being eliminated unchanged in exhaled air (Prado et al., 2003). Analysis of exhaled air shows almost instantaneous equilibrium between PERC in pulmonary blood and lung air, therefore, this information describes a good indicator of PERC levels in the bloodstream (Dyne et al., 1997). The determination of PERC in exhaled air of workers presents numerous advantages over other methods; the most important is that it is not an invasive method, willingly agreed to subjects and can be used in large population surveys (Dallas et al., 1994). Furthermore, the analysis is simplified because the air matrix is less complex than blood or urine (Ruder, 2006). Several sampling methods have been reported for the determination of PERC in exhaled air. The most common is to use gas sampling tubes, such as using one-way glass tubes equipped with two valves (Dallas et al., 1994); or direct solvent extraction in gas sampling tubes (Ziener and Braunsdorf, 2014); or adsorbent tubes (WHO, 2010) or coconut shell charcoal tubes using sampling pumps (Pirsaraei et al., 2009). There are also examples of analyses using Tedlar gas sampling bags that collect breath through multibed sorption trap (Sanchez and Sacks, 2006). Field method for near real-time analysis of PERC in end-exhaled breath also be successfully used by portable GC with a photoionization detector (Sweet et al., 2004). The present work reports the development of a sensitive method for PERC analysis in ambient and exhaled air using CF-SPME and GC/MS. A standard PERC generation by permeation method was used to simulate the ambient and exhaled air.

The proposed method was successfully applied to an occupational study of 27 workplaces Belo Horizonte, Brazil. The results enabled to the use of exhaled air as a useful biomarker of PERC exposure.

2. Experimental

2.1. Instruments and materials

The following fibers from Supelco (Bellefonte, USA) were used: 100 μm polydimethylsiloxane (PDMS), 65 μm divinylbenzene–polydimethylsiloxane (PDMS-DVB), 50/30 μm divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS), 75 μm carboxen-polydimethylsiloxane (CAR-PDMS) and 70 μm carbowax-divinylbenzene (CWX-DVB).

Standard PERC generation by permeation method.

A homemade system (Amorim et al., 2008) was used for standard PERC generation containing a permeation tube from Vici Metronics (Poulsbo, USA) certified by NIST Standards, with a permeation rate of 20.0 ng min^{-1}. The dilutions required for the construction of PERC analytical curve were calculated from the following expression (Menezes et al., 2013):

$$C = 10^3 \times Q/F$$

where C (μg m^{-3}) is the PERC concentration at 101.3 kPa and 298 K, Q (ng min^{-1}) is the permeation rate, and F is the corrected flow (mL min^{-1}) at 101.3 kPa and 298 K. The flow was altered to attain each concentration level of the analytical curves, after 15 min equilibrium time, the flow was measured in replicate (n = 7) followed by CF-SPME extraction with GC/MS determination. *CF-SPME method.*

A cooling system (Menezes et al., 2013) containing 500 mL of liquid nitrogen was used for the cold fiber solid phase microextraction (CF-SPME) device. The PERC sampling in air used CF-SPME device with an exposure time of 15 min. This time is the short term exposure limit (STEL) established by National Institute for Occupational Safety and Health (NIOSH) (NIOSH, 2007). On the other side, for the exhaled air it was used 30 s collection time that is equivalent to sampling the air alveolar portion.

2.2. GC/MS system

A Thermo Electron Trace gas chromatographic system coupled to a POLARIS Q ion trap spectrometer from Thermo Scientific (West Palm Beach, USA) was used. A capillary column (30 m × 0.25 mm × 0.25 μm) containing 5% diphenyl, 95% dimethylpolysiloxane HP-5 MS from Agilent Technology Inc. (Santa Clara, USA) was used. The oven temperature program began at 35 °C for 1 min; heated at a rate of 10 °C min^{-1} to 135 °C, held for 1 min, then heated at 70 °C min^{-1} rat to 220 °C. The helium flow rate was 1.2 mL min^{-1}. The injector was maintained at 300 °C in splitless mode for 1 min, followed by a split ratio of 1:50. The mass spectrometer was operated in electron impact mode at 70 eV. The temperature of the ion source was 250 °C, and the GC/MS interface was 300 °C. The analysis was performed in selected ion monitoring (SIM) mode using the *m/z* fragments 94, 131, 164 and 166.

2.3. Sample collection

Sampling of PERC in ambient air and exhaled air was performed from May to July 2015, with an mean indoor temperature of 24 ± 3 °C. The 27 selected sampling points in Belo Horizonte, Brazil (19° 55 '57 'S, 46° 56'32 "W) were in 24 dry cleaners, 1 electroplating industry, 1 research laboratory, and 1 automotive paint preparation shop. The occupational environments were selected according to type of activity, location, and availability of administrative facilities to cooperate with the investigation. The selected workers had a work shift of 8 h. There were 22 women and 3 men aged between 21 and 65 years. All samples were collected at the end of the work shift. The individuals were trained to perform a slow exhalation to completely empty the lungs so as to obtain the same amount of sample from all the participants. First they inhaled through their noses holding their breath for about 5 s. Subsequently, they exhaled for 30 s direct to CF-SPME inserted in a Teflon tube fit to a disposable card board mouthpiece (Fig. 1). Simultaneously, for PERC sampling in ambient air, the CF-SPME system was exposed in the breathing zone of worker during 15 min. After collection, the fiber was withdrawn and wrapped in aluminum foil at (0 ± 1) °C until the time of analysis. The maximum period between collection and analysis did not exceed 2 h to minimize analyte volatilization. All samples were collected in triplicate. The research protocol for exhaled air sampling was approved by the Ethics Committee of the Universidade Federal de Minas Gerais (UFMG).

2.4. Statistical analysis

Considering the heteroscedasticity of instrumental responses, linear models for calibration curves were constructed by the least squares method weighted by experimental variance, p values below 0.05 were considered significant. The Shapiro–Wilk test was used to verify the