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Outdoor air 1,3-butadiene monitoring: Comparison of performance of Radiello® passive samplers and active multi-sorbent bed tubes

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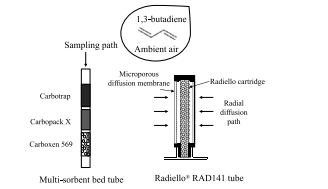
GRAPHICAL ABSTRACT



Multi-sorbent bed-Radiello comparative:
-Similar analytical performances:
-low limits of detection
-low levels of blank values
-good precision and desorption efficiency
-low breakthrough for multi-sorbent bed tubes
-Radiello® samplers were not able to uptake high episodic 1,3-butadiene concentrations

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ABSTRACT

A comparison was made between the relative performance of active and passive sampling methods for the analysis of 1,3-butadiene in outdoor air. Active and passive sampling was conducted using multi-sorbent bed tubes (Carbotrap, Carbopack X, Carboxen 569) and RAD141 Radiello® diffusive samplers (filled with Carbopack X), respectively. Daily duplicate samples of multi-sorbent bed tubes were taken over a period of 14 days (9 + 5 days) at El Morell (Tarragona, Spain), near the petrochemical area. As 1,3-butadiene is a reactive pollutant and can be rapidly oxidized, half of the samplers were equipped with ozone scrubbers. Samples consisted in two tubes connected in series (front and back) to allow the determination of breakthrough. Quadruplicate samples of Radiello® tubes were taken over a period of 14 days (9 days and 5 days), too. During those days, ozone concentration was measured using RAD172 Radiello® samplers. In addition to this, daily duplicate samples of multi-sorbent bed tubes were taken in the city of Barcelona over a period of 8 days. Simultaneously, 4 samples of Radiello® tubes were exposed to outdoor air. Sampling was done throughout June and July 2017. Analysis was performed by thermal desorption coupled with gas chromatography/mass spectrometry. Analytical performance of the two sampling methods was evaluated by describing several quality assurance parameters, with results showing that performances are quite similar. They display low detection limits, good precision, linearity and desorption efficiency, low levels of blank values, and low breakthrough for multi-sorbent bed tubes. However, Radiello® samplers were not able to uptake episodic 1,3-butadiene high concentrations, leading to underestimation of real values. Hence, we can conclude that Radiello® samplers can be used for baseline 1,3-butadiene levels whereas multi-sorbent bed tubes would be advisable when relevant episodes are expected.

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1. Introduction

1,3-butadiene is an ubiquitous pollutant in the atmosphere which is emitted from several sources such as combustion of organic matter, residential heating, traffic or fuel distribution (Arayasiri et al., 2010; Aurell et al., 2017; Curren et al., 2006; Delgado-Saborit et al., 2011; Nagpure et al., 2016; Özkaynak et al., 2008; Sapkota and Buckley, 2003). Petrochemical industry processes, especially those occurring at manufacturing plants using or producing this compound (Axelsson et al., 2010; Bari and Kindzierski, 2017; European Communities, 2002; Liang et al., 2017; Mo et al., 2015; Myers et al., 2015) may result in significant fugitive and episodic emissions (Czader and Rappenglück, 2015; Gallego et al., 2018; Grant et al., 2007) that can be difficult to evaluate due to their intermittent nature (Chen et al., 2015). 1,3-butadiene is carcinogenic to humans (Group 1) according to IARC (IARC, 2012, Simpson et al., 2013), can cause DNA damage (Ruchirawat et al., 2010), affects the hematopoietic system (Arayasiri et al., 2010), has been related to central nervous system primitive neuroectodermal tumours in children (PNET) (von Ehrenstein et al., 2016), and has been found to significantly contribute to estimated inhalation cancer risk worldwide (de Blas et al., 2012; Dhaini et al., 2017; Huy et al., 2018; Zhou et al., 2011). Additionally, 1,3-butadiene can contribute to high ozone concentration events as it is an important ozone precursor in the presence of NO_x and solar radiation (Liang et al., 2017; Simpson et al., 2013). That is why air quality long-term evaluation must take this compound into account (Gallego et al., 2018), especially because of its toxic properties (Mo et al., 2015).

In recent years, passive and active sampling methods have been used to determine 1,3-butadiene levels in outdoor air (Gallego et al., 2018; Oliver et al., 2017; Sakurai et al., 2013; Strandberg et al., 2014; U.S. EPA, 2015a, 2015b; Vallecillos et al., 2018). Passive samplers are easy to operate, are generally low cost and do not need electricity supply. They provide average pollutant concentrations based on uptake rates (Gallego et al., 2009a, 2011). In this line, EPA 325A/B methods (U.S. EPA, 2015a; 2015b) have been established to monitor fenceline fugitive and area source VOC emissions using passive samplers coupled with TD-GC/MS analysis to define regional emission inventories (Eisele et al., 2016; Oliver et al., 2017). Additionally, the Regulations Respecting Reduction in the Release of Volatile Organic Compounds (Petroleum Sector) came into force in Canada on 1 January 2018. These Regulations also propose fenceline monitoring of benzene, 1,3-butadiene and all retainable VOC using passive samplers in petroleum and petrochemical facilities (Government of Canada, 2017). However, the effectiveness of passive samplers in displaying environmental pollutant concentrations is limited because their way of operating can underestimate episodic high peak concentratios. By contrast, even though active samplers need power supply, they enable short-term sampling, from a few minutes to several hours (Gallego et al., 2009a), to assess concentration peak profiles (Dettmer and Engewald, 2003; Strandberg et al., 2014). This must be taken into account when establishing monitoring strategies such as those proposed in Canada and USA. Thus, it can be concluded that the two sampling approaches are valid depending on the information required. However, in order to evaluate the performance of Radiello® passive samplers, mainly related to their capacity to display episodic 1,3-butadiene high concentrations accurately, a widely used active sampling methodology based on multi-sorbent bed tubes (Carbotrap, Carbopack X and Carboxen 569) and Radiello® passive samplers (Carbopack X) specific for analysis of 1,3-butadiene were compared.

Concentrations of 1,3-butadiene in outdoor air were measured in two Catalan locations, namely El Morell, near a 1,3-butadiene manufacturing plant with an annual production of 202,000 t located at 41°11′26.8″ N and 1°13′13.9″ E in the Tarragona petrochemical complex, and the city of Barcelona. 1,3-butadiene is a highly volatile and reactive compound (Martin et al., 2005), and so special attention must be paid to the sampling and analytical methodologies used for its evaluation. This compound can be transformed into a variety of products in the atmosphere through oxidation by ozone (Kramp and Paulson, 2000; Martin et al., 2005; Sakurai et al., 2013) and its collection in several samplers can be altered by ozone interferences (Sakurai et al., 2013). Therefore, ozone scrubbers were attached to several active samplers to evaluate the possible effects of outdoor ozone concentrations on 1,3-butadiene sampling.

Analysis of 1,3-butadiene was performed by automatic thermal desorption coupled with capillary gas chromatography/mass spectrometry (TD-GC/MS). TD-GC/MS has been widely used in VOC and 1,3-butadiene analysis (Gallego et al., 2009a, 2012, 2016, 2017, 2018). This selective methodology allows good chromatographic separation, and identification and quantification of target analytes through their characteristic mass spectrum and quantification ion, respectively (Ribes et al., 2007). The performance of the two sampling methodologies was evaluated by describing several quality assurance parameters, i.e. detection limit, linearity range, precision, desorption efficiency, blank values, and breakthrough values for active samplers. Additionally, outdoor ozone concentrations were determined using Radiello® ozone passive samplers and analyzed by spectrophotometry.

2. Materials and methods

2.1. Chemicals and materials

1,3-butadiene solution (20% wt in toluene), 3-methyl-2-benzothiazolinone hydrazine hydrochloride (MBTH), 4-pyridylaldehyde, potassium iodide ozone scrubbers of 1.5 g, and RAD141 and RAD172 Radiello® passive sampling tubes were obtained from Sigma-Aldrich Chemie (Steinheim, Germany). Toluene for gas chromatography (SupraSolv®) with a purity ≥ 99.8% was obtained from Merck (Darmstadt, Germany). Concentrated sulphuric acid (96%) was obtained from Panreac (Montcada i Reixac, Spain). Perkin Elmer glass tubes (Pyrex, 6 mm external diameter, 90 mm long), unsilanized wool, and Carbotrap (20/40 mesh), Carbopack X (40/60 mesh) and Carboxen 569 (20/45 mesh) adsorbents were purchased from Supelco (Bellefonte, PA, USA).

2.2. 1,3-Butadiene sampling tubes

Multi-sorbent bed tubes used for 1,3-butadiene sampling were custom packed and composed of Carbotrap (activated graphitized black carbon, weak sorption strength, 70 mg), Carbopack X (activated graphitized black carbon, medium sorption strength, 100 mg) and Carboxen 569 (spherical carbon molecular sieve, high sorption strength, 90 mg) (Fig. 1). They were evaluated in an earlier study and found to be highly versatile regarding polarity and volatility of a wide range of target VOCs (Ribes et al., 2007), and were used for analysis of 1,3-butadiene in outdoor air (Gallego et al., 2018). 1,3-butadiene in outdoor air was actively sampled with multi-sorbent bed tubes for 24 h by connecting the self-packed glass multi-sorbent cartridge tubes to air collector pump samplers specially designed in the LCMA-UPC laboratory (Roca et al., 2003). The flow sampling rate was set at 70 ml min^{-1}. The sorbents are hydrophobic enough to avoid interferences derived from the humidity in the air sampled (Ribes et al., 2007). As an additional measure, tubes are purged at ambient temperature for 2 min with a helium flow rate of 50 ml min^{-1} prior to TD-GC/MS.

RAD141 Radiello® tubes specially designed to evaluate 1,3-butadiene passively were filled with Carbopack X by the manufacturer (Fig. 1).

Both sampling tubes were conditioned before use at 400 °C, sealed with Swagelock end caps fitted with PTFE ferrules and stored at 4 °C for 1 week at most before use. Once sampled, tubes were injected into a TD-GC/MS system with a maximum storage time before injection of 1 week (clean refrigerator at 4 °C).