



Reliable passive-sampling method for determining outdoor 1,3-butadiene concentrations in air



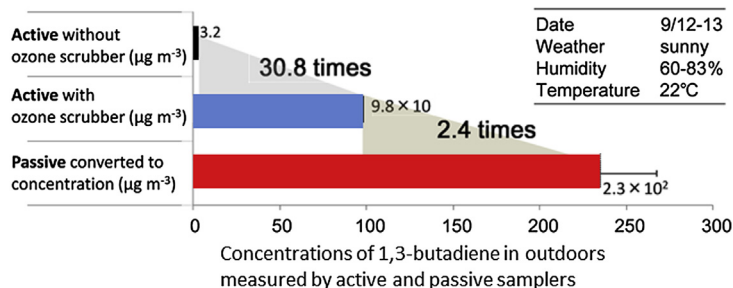
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HIGHLIGHTS

- 1,3-butadiene was analyzed by passive sampling-thermal desorption GC/MS.
- Ambient ozone does not react with 1,3-butadiene adsorbed by the passive sampler.
- Ozone could penetrate the passive-sampling tube.

GRAPHICAL ABSTRACT



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ABSTRACT

We have developed a simple and reliable passive-sampling method for determining outdoor 1,3-butadiene concentrations in air. In this method, 1,3-butadiene is adsorbed on Carboxen 1000 uniformly packed in a porous polytetrafluoroethylene tube and then analyzed by thermal desorption–gas chromatography/mass spectrometry. The amounts of 1,3-butadiene adsorbed on Carboxen 1000 were 2.8 times as high as those adsorbed on activated carbon. Much greater amounts of 1,3-butadiene were collected with the passive sampler than with an active sampler even though ozone, which reacts rapidly with 1,3-butadiene, could penetrate the passive-sampling tube. These results demonstrate that our method sensitively and reliably determines outdoor 1,3-butadiene concentrations in air, that ambient ozone slowly reacts with 1,3-butadiene adsorbed by the passive sampler, and that the KI ozone scrubber in an active-sampling system does not completely remove ozone from the system.

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1. Introduction

Monitoring volatile organic compounds (VOCs) in both the outdoor and the indoor environment has attracted much attention (Tong et al., 2012; Zhu et al., 2005; Ohura et al., 2006). The VOC 1,3-butadiene is a highly reactive hazardous air pollutant with a

short lifetime and is quickly transformed in the atmosphere to a variety of products, some of which are also toxic (Hsieh and Tsai, 2003; Baldasano et al., 1998; Barletta et al., 2002; Martina et al., 2012).

1,3-Butadiene has a low acute toxicity following a single-inhalation exposure, although the eyes, nose, mouth, and respiratory tract are irritated at high concentrations (Arthur and Carroll, 2007; Narisa et al., 2011; Sorsa et al., 1996). Animal studies, however, indicate that epoxide metabolites may be genotoxic. Penn and Snyder (2007) reported epidemiological evidence for the association between occupational exposure to 1,3-butadiene and cardiovascular disease as well as experimental evidence for 1,3-butadiene-associated atherosclerosis and cardiac injury.

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Therefore, 1,3-butadiene should be regarded as a potential human carcinogen.

Routine analysis of 1,3-butadiene is difficult because of its instability. Several methods have been developed for analysis of 1,3-butadiene in air. In NIOSH method 1024 (1994), 1,3-butadiene is collected on activated charcoal in a tube connected to an air pump, extracted with dichloromethane, and analyzed by GC-FID. Because 1,3-butadiene is a gaseous compound, the preparation and injection of a 1,3-butadiene standard must be performed carefully or erroneous results will be obtained. Sample storage seems to dramatically affect the analytical results. OSHA method 56 (1985) is similar to NIOSH method 1024. Air is drawn through the sampling tube containing charcoal adsorbent coated with 4-*tert*-butylcatechol, and samples are then extracted with carbon disulfide and analyzed by GC-FID. Methods based on solvent extraction are inherently less sensitive than methods that do not use solvent extraction because the sample is diluted by a factor of about 1000 during extraction.

Samples can also be analyzed by the thermal desorption method (Martin et al., 2005). Since this method does not use solvent extraction, the sample is not diluted by solvent. This method, however, has a typical dilution factor of 50–100, arising from the combination of secondary and primary splits, which are adjustable depending on the expected amount of analytes (SUPELCO, 2007).

Active sampling techniques have an advantage that the air volume drawn by the pump was known. But ozone scrubber is necessary for some compounds and KI ozone scrubber is easily deliquescent under high humidity. On the other hand, the passive sampler has some advantages. It is light weight, small in size, low cost and easy to handle and it can also work without electricity (Brown, 2000; Bohlin et al., 2007; Kot-Wasik et al., 2007). Several passive samplers can also be employed for determination of 1,3-butadiene. Martin et al. (2005) used a badge-type passive sampler using Carbopack X adsorbent to collect 1,3-butadiene. Supelco technical staffs (2007) were used a radially symmetric sampler with Carbograph 5 adsorbent. Strandberg et al. (2006) used a thermal desorption – GC-FID method to evaluate the performance of these samplers and adsorbents for collecting 1,3-butadiene.

We have developed both active- and passive-sampling techniques for analyzing indoor and outdoor VOC concentrations (Amagai, 2011; Olansandan et al., 1999). The passive sampler used in this study consisted of a porous poly(tetrafluoroethylene) (PTFE) tube filled with 194 ± 4 mg of activated charcoal. VOC passed through the porous PTFE which was the boundary layer of the passive sampler, and was collected by the adsorbent inside of the PTFE tube.

Because 1,3-butadiene is rapidly oxidized by ozone, ozone can interfere with the collection of 1,3-butadiene. In general, we have used a KI ozone scrubber to protect VOCs that can be degraded by ozone. Thus, we compared 1,3-butadiene concentrations determined by the passive-sampling method with those determined by an active-sampling method with an ozone scrubber. In these comparisons, sampling was performed in an indoor chamber or outdoors.

2. Materials and methods

2.1. Chemicals and reagents

A standard solution of 1,3-butadiene dissolved in toluene (40 wt %), potassium iodide for oxidant analysis, magnesium perchlorate, and indigo carmine were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Carboxen 1000, a spherical carbon molecular sieve, was obtained from Sigma–Aldrich, Inc. (St. Louis, MO, USA).

2.2. Sampling methods

We used two types of passive sampler. The first type consisted of a porous PTFE tube (Sibata Scientific Technology, Tokyo, Japan) packed with either granular activated charcoal or Carboxen 1000 (Olansandan et al., 1999; Trefz et al., 2011; Gallego et al., 2011). The surface area of Carboxen 1000 is $2000 \text{ m}^2 \text{ g}^{-1}$, which is greater than the surface areas of other collection media. The second type of passive sampler was a porous polyethylene tube (VOC-TD sampler, Supelco Inc., Tokyo, Japan) packed with Carboxen 1000.

An active sampler consisting of 250 mg of Carboxen 1000 packed inside a glass tube (4 mm i.d. \times 90 mm) was used to determine the concentration of 1,3-butadiene in air. The sampling flow rate was 0.25 or 0.15 L min^{-1} .

Sampling was conducted from October to December 2011 in Gotenba City, Shizuoka, Japan. Gotenba City (latitude $35^\circ 19' \text{N}$, longitude $138^\circ 56' \text{E}$) is a typical commercial city in Japan, with a temperate climate (average temperature 25.3°C) and 88,896 inhabitants (June 2012). We measured 1,3-butadiene concentrations at the side of a heavily traveled (>200 vehicles per hour) trunk road in Gotenba City.

2.3. Sample preparation and analysis

Desorption from the sampling tube and preconcentration of 1,3-butadiene were carried out with an automated thermal desorber (Turbomatrix 650ATD, Perkin–Elmer, Norwalk, CT, USA). After sampling, the Carboxen 1000 in the sampling tube was transferred into a stainless steel desorption cartridge (89 mm \times 4.5 mm i.d.). 1,3-Butadiene was desorbed under a 20 mL min^{-1} helium flow at 280°C for 15 min and then cryofocused on a Carboxen trap at 5°C . This trap was heated to 350°C at $\sim 40^\circ \text{C s}^{-1}$ and then held at 350°C for 4 min. The desorbed 1,3-butadiene was transferred to the GC column through a methylpolysiloxane line heated at 350°C . Inlet and outlet split flows were 3 mL min^{-1} (Almén et al., 1993).

The GC/MS instrument consisted of a GC6890 gas chromatograph coupled with a 5975C mass spectrometry detector (Agilent Technologies International Japan, Ltd., Hachioji, Japan). A (5%-phenyl)methylpolysiloxane column (DB-5, 60 m length \times 0.32 mm i.d., 0.25- μm film thickness, Agilent) was used. The column oven temperature was programmed from 35 to 80°C (at $5^\circ \text{C min}^{-1}$) over 9 min, and held for 2 min at 80°C , then raised to 250°C (at $20^\circ \text{C min}^{-1}$) over 8.5 min, and held for 10.5 min at the temperature of 250°C . Helium at a flow rate 1.0 mL min^{-1} was the carrier gas. Mass spectra were recorded in the electron impact mode at 70 eV, scanning the m/z 29–250 range. The interface and source temperatures were 150 and 250°C , respectively. The MSD Productivity ChemStation (Agilent) was used for data acquisition and data processing.

2.4. Quality assurance/quality control

We verified that the concentration of 1,3-butadiene in sample blanks was below the limit of detection (detection limit defined as 3 times the standard deviation of the lowest concentration of the standard solution). A field blank sample was taken on each sampling day, and the concentrations of 1,3-butadiene in the blank samples were below $0.01 \mu\text{g m}^{-3}$. Sample recovery ratios were from 94% to 99%, and relative errors were small, validating our procedure.

2.5. Calculation of concentration of 1,3-butadiene in air sampled with passive samplers

The amounts of 1,3-butadiene collected with the passive samplers were converted to air concentrations using a conversion

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