New Radiello diffusive sampler for monitoring 1,3-Butadiene and Isoprene in Workplace Air

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Abstract

Radiello radial diffusive sampler provides higher sampling rates than comparable axial samplers allowing for an easy and fast screening of 1,3-Butadiene and Isoprene in the ppb range in workplace atmospheres.

Introduction

The manufacturing of elastomers makes wide use of 1,3-butadiene (CAS no. 106-99-0) and isoprene (2-methyl-1,3-butadiene, CAS no. 78-79-5). Both compounds are classified as carcinogenic by the International Agency for Research on Cancer (IARC). 1,3 butadiene is currently listed in group 1, carcinogenic for humans, and isoprene is in group 2B, possibly carcinogenic for humans. These compounds may also be present in lower concentration in the environment (lower ppb levels).

The measurement of these compounds in workplace air requires high sensitivity and also the control of explosive hazards, which are frequent in chemical plants. Diffusive sampling followed by thermal desorption and GC-MS analysis represents a simple and affordable tool for this measurement, while satisfying the above requirements.

In general, the measurement of volatile organic compounds (VOC's) suspected of carcinogenic properties in workplace air requires high sensitivity, down to ppb level. The existing methods for the measurement of 1,3-butadiene involve the pumping of air through activated charcoal or molecular sieves, followed by solvent or thermal desorption and gas chromatography [1, 2]. Methods based on solvent desorption are inherently less sensitive, because of the dilution of the sample by a factor of about 1,000 during extraction. Thermal desorption, when carried out by two-stage thermodesorbers (desorption and concentration/trapping step), have a typical "dilution" factor of 50-100, arising from the combination of secondary and primary split, which are adjustable depending on the expected amount of analytes.

More recently, methods based on diffusive sampling onto molecular sieves or graphitised carbon blacks, were proposed [3, 4]. However, the sampling rates of such methods, based on axial diffusion tubes, are lower than 1 ml/min and do not allow ppb level sensitivities. The use of radial symmetry diffusive samplers like Radiello, provide commonly higher sampling rate values [5] in combination with thermal desorption, allow the measurement of 1,3-butadiene and isoprene in workplace air with a sensitivity in the ppb range.

Figure 1 Radiello Butadiene adsorbent cartridge with Carbopack X (RAD141)

Sampling

The sampling of 1,3-butadiene and isoprene with ***radiello***® diffusive samplers is performed using an adsorbing cartridge (4.8 mm diameter stainless steel net), packed with Carbopack X, the strongest adsorbent in the range of Supelco' graphitised carbons, with a specific surface area of 240 m^2/g [6]. The Carbopack X cartridges (RAD141) are marked with an etched "Carbopack X" writing along the side of the cartridge body (**Figure 1**).

The sampler is easily assembled like any other Radiello sampler, by placing the cartridge into a yellow diffusive body RAD1202 (**Figure 2**), and attaching it to the triangular support plate (RAD121). Once assembled, the sampler is typically exposed during the entire workshift (8h). It can be attached to the worker's clothing by the clip that is delivered with the support plates (**Figure 3**). The user needs to record the start time and the end time of of the exposure on the bar code label delivered with the cartridges. After sampling, the adsorbing cartridge is placed again in the glass storage/transport container and the barcode label is placed on the container. Until analysis is performed, the samples should be kept cold and stored in the freezer. Time until analysis should not exceed 24h.

Figure 2 Place radiello cartridge into yellow diffusive body (RAD1202)

Figure 3 Radiello butadiene sampler clipped to workers clothing

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Analysis

The analysis of diffusive samples includes two-stage thermal desorption (TD), followed by HRGC-MS. The sample loaded adsorbing cartridge is transferred into an empty SS thermal desorption tube (¼ inch OD, min. 4.9mm ID), which is then placed into the TD instrument. The collected sample is desorbed by heat and transfered onto a GC column.

When choosing the proper GC column, the potential interference from other C4 alkenes which may occur in real samples, like 1-butene, 2-butene (trans- and cis-) and isobutylene, must be taken into account.

Typical Thermal desorption conditions:
primary desorption temperature: 320 °C for 6 min
primary desorption flow: 90 ml/min
primary split ratio: 3:1
cold trap: Tenax TA 60/80 mesh
cold trap cryofocusing temperature: -20 °C
cold trap heating temperature: 290 °C
cold trap heating time: 1 min
secondary desorption flow: 21 ml/min
secondary split ratio: 26:1

Calibration

The calibration standards for 1,3-butadiene can be prepared by the gas syringe spiking procedure, using a gastight microsyringe (10 µl or more) and measured volumes of either pure or 1:50 diluted gas that is loaded onto the Carbopack X cartridges fitted into an empty SS thermal desorption tube that is connected to a GC injector (40 ml/min nitrogen purge stream). Cartridges used for preparing calibration catridges should have a tight fit in the TD tube (slight resistance when pushing in tube) to ensure a reliable adsorption of standard volume. Otherwise, use another cartridge. The isoprene calibration standards are prepared by injecting measured volumes of a methanol solution of the analyte.

The analysis is best performed within 24 hours after the exposure. If the analysis is performed later, the storage requirement of the EN 838 standard [7] is satisfied within 14 days of storage: in such a case, the maximum analyte loss is 7 % for 1,3-butadiene and 8 % for isoprene, which is less than the maximum loss (10 %) allowed by the standard [7].

Calculation

The concentration C of 1,3-butadiene and isoprene determined by diffusive sampling are calculated by the general equation:

$$C_{(\mu g/m^3)} = \frac{(m_{(ng)} - mb_{(ng)}) \cdot 1000}{Q_{(cm^3/min)} \cdot t_{(min)}} \quad [1]$$

where
m = sampled mass of the analyte ;
mb = mass of the blank (usually negligible);
Q = diffusive uptake rate ;
t = exposure time.

The diffusive uptake rate values for both compounds (**Table 1**) were determined according to EN838, which gives guidance for using diffusive samplers in workplace air monitoring [7].

Table 1 Diffusive uptake rate for 8-h exposure at 20 °C, 50 % RH

Analyte	Concentration range (µg/m³)	Diffusive uptake rate Q (cm³/min)
1,3-butadiene	34 – 2,960	30.5 ± 0.3
isoprene	2 – 6,680	41.2 ± 4.9

The combined effect of temperature and humidity may affect the sampling rate,with a significant decrease at high temperature and high humidity (40 °C and 80 % RH): therefore it is recommended to avoid taking measurements when such extreme conditions are expected. At lower temperatures (5 °C, the effects are comparably small.

A field validation on 40 workers (18 °C temperature and 75 % relative humidity, on average) demonstrated that the measured concentrations agree with the results obtained by the OSHA method 56 (solvent desorption from TBC-treated charcoal and GC). The results obtained with radiello samplers, plotted against the results of OSHA 56 method, show a regression line with slope very close to 1 and no significant intercept (data not shown).

Measurement of uncertainty

The following table shows the values of the uncertainty in the measurements of 1,3-butadiene in the workplace, assessed by two different approaches. The uncertainties were first determined under laboratory conditions, following the methods of the ISO GUM (Guide to Expression of Uncertainty in Measurement, International Organization for Standardization, Geneva, 1993) and ISO 5725:1994 (Accuracy (trueness and precision) of measurement methods and results). In this case, the uncertainty accounts for all contributions involved in the measurement process (effect of time, T, RH on uptake rate, uncertainty of measured mass and so on), which were determined according to EN 838:1995. Afterwards, the uncertainty was determined by a field comparison with the method OSHA 56 (as the reference method), following the standard ISO 13752.

Conclusion

The thermal desorption ***radiello®*** sampler filled with Carbopack X represents a new and simple tool for assessing the workplace exposure to two carcinogenic chemicals: 1,3-butadiene and isoprene at ppb concentration levels. It is convenient in use and can be applied for any workplace where explosive hazards exist.

Future

Previous literature data [8] also suggest the applicability of the method for environmental measurements of low levels of 1,3-butadiene in urban air.

Measurement uncertainty for 8-hour diffusive sampling of 1,3-butadiene in workplace air

Relative combined expanded uncertainty (2 • uc)	200 µg/m³	442 µg/m³ (0.1 TLV)	2,210 µg/m³ (0.5 TLV)	4,420 µg/m³ (TLV-TWA ACGIH)
Laboratory tests at 20 °C, 50 % RH (EN 838, calculations by ISO GUM)	48.4 %			
Field comparison (ISO 13752)	37.0 %	25.0 %	11.1 %	7.9 %

References

1] NIOSH Manual of Analytical Methods, 4th Edition
2] U.S. Department of Labor – OSHA – Method no. 56 – OSHA, Washington, 1985,
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4] Health and Safety Executive, Methods for the Determination of Hazardous Substances, MDHS 63/2, HSE Books, Sudbury, 2003.
5] Cocheo V., Boaretto C., Sacco P. *Am. Ind. Hyg. Assoc. J.* 57 (897-904), 1996.
6] Brown, J., Shirey, B. A tool for selecting an adsorbent for thermal desorption applications, Supelco Technical Report, Bellefonte, PA, 2001, ***www.sigmaaldrich.com/Graphics/Supelco/objects/11400/11342.pdf***
7] EN 838:1995 Workplace atmospheres – Diffusive samplers for the determination of gases and vapours – requirements and test methods.
8] Strandberg B., Sunesson A., Olsson K., Levin J., Ljungqvist G., Sundgren M., Sällsten G., Barregard L. Evaluation of two types of diffusive samplers and adsorbents for measuring 1,3-butadiene and benzene in air *Atmos. Environ.* 39 (4101-4110), 2005.

Ordering Information

Description	PK.	Cat. No.	Price £
Radiello Cartridges 1,3-Butadien/Isoprene w/Carbopack X	20	**RAD141**	**507.00**
Radiello Triangular Support Plate	20	**RAD121**	**65.00**
Radiello Diffusive Body, Yellow	20	**RAD1202**	**164.00**
Radiello Vertical Adapter for Personal Sampling	20	**RAD122**	**23.00**
Starter Kit 1,3-Butadien/Isopren Sampler Includes: 1 support plate, 1 yellow diffusive body, 1 vertical Adapter, 2 adsorbing cartridges w/Carbopack X	1	**RAD141S**	**103.00**

For more information on the Radiello product line visit us at ***sigma-aldrich.com/radiello***

Radiello Butadien
Starter kit
(Cat.No. RAD141S)

ATIS – Adsorbent Tube Spiking System

to spike thermal desorption (TD) tubes with standards.
Also suitable to spike radiello cartridges in TD tubes.

To learn more about the ATIS system and accessories, please visit us at ***sigma-aldrich.com/air_monitoring*** or contact our Technical Service

Ordering Information

Description	Cat. No.	Price £
ATIS System 220V	**28521-U**	**964.00**