Adsorbing cartridge for 1,3-butadiene and isoprene thermally desorbed (Cat. No. RAD141)

CAUTION: Do not swallow. Do not smoke. Wash the hands thoroughly after use. Avoid contact with the eyes, skin and clothes. In case of contact with eyes, flush with large amounts of running water for at least 15 minutes. See MSDS for complete safety information.

Principle

Cat. No. RAD141 is a stainless steel net cylinder, with $3x8 \mu m$ mesh grid opening and 4.8 mm diameter, packed with approx. 480 mg of graphitised carbon (Carbopack X, particle size 40/60 mesh). The name of the adsorbent is permanently marked onto the s.s. net cylinder.

1,3-butadiene and isoprene are trapped by adsorption and recovered by thermal desorption; the analysis is carried out by capillary gas chromatography and MS detection. The RAD141 sampler is designed for workplace measurements up to 8 hours. Ambient air measurements for longer durations are also possible (see below).

Part list for sampling 1,3-butadiene and isoprene (thermal desorption) onto Cat. No. RAD141

- Yellow diffusive body, Cat. No. RAD1202 (required)
- Vertical adapter, Cat. No. RAD122 (for personal monitoring)
- Support plate, Cat. No. RAD121 (required)
- Shelter, Cat. No. RAD196 (recommended for outdoor sampling)

Uptake rates

The values of diffusive uptake rate were **experimentally measured** at 20°C (273 K) and 1013 hPa in a standard atmosphere chamber.

The uptake rate for **1,3-butadiene** in **workplace air** is 30.5 ± 0.3 ml·min⁻¹ (nominal value at a concentration level between 114 and 226 μ g/m³ for 8-hour exposures). For longer term sampling (e.g. 7 days) of **1,3-butadiene** please refer to Strandberg et al. (1) (2).

For **isoprene** the uptake rate is **41.2** \pm **4.9** ml·min⁻¹ (best estimate in the range 2 – 6,680 μ g/m³ for exposures from 30 to 480 min).

Effect of temperature and humidity

Both temperature and relative humidity affects the uptake rate for 1,3-butadiene. If the temperature decreases to 5 $^{\circ}$ C, the bias is + 12.9% at 20% RH or -2.4% at 80% RH, with respect to 20 $^{\circ}$ C and 50% RH. Avoid sampling at temperatures as high as 40 $^{\circ}$ C, because the uptake rate shows a significant decrease.

The effect of temperature and relative humidity on the uptake rate for isoprene is lower: at low temperature and humidity (5°C, 21% RH) the uptake rate is 10% higher, while at high temperature and humidity (41°C, 77% RH) there is a 23% decrease.

Do not expose the Radiello sampler directly to rain. Always use the shelter Cat. No. RAD196 when sampling outdoors, to avoid water entering the membrane and wetting the sorbent.

Calculations

The mean concentration C over the exposure time interval is calculated from the mass of analyte found onto the cartridge (corrected for the blank, if any) and from the exposure time, using the above values of the uptake rate, as follows

$$C_{[mg+m^{-3}]} = \frac{m_{[mg]} - m_{b[mg]}}{U_{[ml+min^{-1}]} \cdot t_{[min]}} \cdot 1,000,000$$

where:

 $m = \text{mass of analyte in } \mu g$ $m_b = \text{mass of blank in } \mu g$ $U = \text{uptake rate in ml} \cdot \text{min}^{-1}$

t =exposure time in minutes

The desorption efficiency, determined by repeated desorption of the same tube, is higher than 99.9% for both compounds. Therefore, there is no need of introducing correction factors.

Limit of quantitation

Blank response, the limit of detection (LOD) and the limit of quantitation (LOQ) depend on the instrumentation and on the analytical conditions. Under the analytical conditions specified below, the blank value is not detectable, i.e. less than 0.5 ng for both compounds. The LOQ for 8-hour workplace exposure is $0.1 \,\mu\text{g/m}^3$. For 7-day ambient air exposure the LOQ is $0.03 \,\mu\text{g/m}^3$; see also Strandberg et al. (2)

Measurement uncertainty

The following table shows the values of the uncertainty in the measurements of **1,3-butadiene** in 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 whole 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.

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

Relative combined expanded uncertainty (2·u _c)	200 μg/m ³	442 μg/m ³ (0.1 TLV)	$2.210 \mu \text{g/m}^3$ (0.5 TLV)	4.420 μg/m ³ (TLV-TWA ACGIH)
Laboratory tests at 20 °C, 50% RH	48.4 %			
(EN 838, calculations by ISO GUM)				
Field comparison (ISO 13752)	37.0 %	25.0 %	11.1 %	7.9 %





Shelf life

Kept in a cool place and away from volatile organic compounds, the cartridges maintain unchanging blank level and adsorbing capacity for at least eighteen months. Expiry date and lot number are printed onto the plastic envelope wrapping each cartridge: its integrity stands as warranty seal. Expired adsorbent cartridges can be re-conditioned. It is recommended to run a blank analysis for cleanliness. See analytical protocol below. The leak test, performed according to EN 838, at 100 ppb for 8 hours, showed no detectable uptake of the analytes by new, sealed cartridges.

Exposure

Workplace environment

Apply the sampler to worker's clothing by using the vertical adapter RAD122. Expose either for the whole workshift (8-hour) or for half shift (4-hour) or for 30 minutes. The uptake rate for 1,3-butadiene has a little dependency on the exposure duration (in this range), which is accounted for in the overall uncertainty budget (see the above paragraph "Measurement uncertainty"). The uptake rate for isoprene has no significant dependency on exposure duration.

If sampling process has to be stopped during lunch break, unscrew the diffusive body and transfer the adsorbent cartridge to the test tube it originally came in. Keep note of the time of stop/restart of sampling.

Storage

After the exposure, the samples, well capped in their glass tubes, have to be stored in the freezer, because 1,3-butadiene and isoprene are reactive compounds. Laboratory tests according to EN 838 showed for both compounds a loss of analyte of 7-8% after 14-day storage. The samples shall therefore be analysed within 14 days from the end of exposure, in order to ensure the maximum loss of analyte remain within 10%.

Procedure for sampling and analysis

Follow the procedure described in the technical sheet of diffusive body (Cat. No. RAD1202). For outdoor sampling, the use of the shelter (Cat. No. RAD196) is recommended. Record the date and time of start and end of exposure (AVOIDING THE USE OF MARKING PENS, which contain solvents!). It is strongly recommended to keep separate record of your sampling data, because one week of exposure to bad weather can make your writings completely unreadable!

Place the bar code label so that the barcode is parallel to the axis of the tube: any other position will compromise the barcode automated reading by the optical reading device.

The recommended analytical procedure includes:

- Thermal desorption by commercial thermal desorption apparatuses (i.e. Perkin Elmer, Dani, Markes...): the
 outer diameter of Cat. No. RAD141 cartridges is fitted to the inner diameter of most stainless steel
 desorption tubes that have a ID of 4.9 mm;
- GC/MS determination, split injection, external standard quantitation.



Typical analytical conditions are listed below as guidelines. Adjust the temperature program in order to separate and elute all the compounds present in your samples. Look at the possible presence of 1-butene, 2-butene (*trans* and *cis*), 2-methyl-1-propene (isobutylene), which show the ion 54 a.m.u. in their mass spectra and thus could interfere with 1,3-butadiene quantitation (see below).

Automated thermal desorber

Carrier gas: Helium at 12 psi

Primary desorption temperature: 320 °C for 6 min Total primary desorption flow-rate: 120 ml·min⁻¹

Inlet split flow-rate: 100 ml·min⁻¹ Outlet split flow-rate: 40 ml·min⁻¹ Overall split ratio: 1:150 Valve temperature: 150 °C

Cold trap packing: Tenax TA 60/80 mesh

Cold trap temperature: -20 °C

Secondary desorption temperature: 290 °C for 1 min

Transfer line temperature: 200 °C

GC/MS system

Column: any capillary column capable of separating permanent gases Column temperature program: 80 °C, 0.5 min; 25 °C•min-1 to 175 °C; stand for 4 min; 25 °C•min-1 to 250 °C; 7 min

Total run time: 20 min

MS mode: SCAN from 25 to 250 a.m.u.

EM setting: autotune value

Target ions for quantitation: 54 a.m.u. (1,3-butadiene), 67 a.m.u.

(isoprene)

Analyse the samples in your laboratory following the above guidelines or make them analyse by Fondazione Salvatore Maugeri – Centro di Ricerche Ambientali – Via Svizzera, 16 – 35127 PADOVA (ITALY). Details on the analytical service provided by Fondazione are available at the address http://www.radiello.com/english/LabService.htm.

References

- 1) Strandberg et al. Atmos. Environ. 39(2005), 4101-4110.
- 2) Strandberg et al. Atmos. Environ. 40(2006), 7686-7695.



