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Evaluation of three types of passive samplers for measuring 1,3-butadiene and benzene at workplaces

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Abstract

1,3-Butadiene and benzene are common pollutants in both workplace and ambient air that have received attention for their adverse effects on human health. In exposure studies, simple and sensitive personal monitoring methods are preferable. Thermal desorption passive samplers seem optimal for this purpose, although in occupational studies chemical desorption samplers have been used more often. This may be because their utility for monitoring occupational atmospheres has not been thoroughly validated. Therefore, we evaluated thermal desorption passive samplers containing Carbopack X adsorbent from three manufacturers: Perkin Elmer, SKC-Ultra and Radiello. The uptake rates of benzene and 1, 3-butadiene by these samplers were determined over 4 h or 8 h in exposure chamber studies at three concentrations likely to be found in occupational air. The samplers were also tested in a field study, at a petroleum refinery. The results were analyzed using multiple linear regression, and intra class correlation coefficients (ICC) were calculated to compare uptake rates of the three passive samplers to those of an active sampler. The three samplers had similar and acceptable accuracy (ICC≥0.9) for measuring benzene concentrations in the field environments, but only the Perkin Elmer sampler gave acceptable ICC values (~0.85) for 1,3-butadiene over a full 8 h working shift in the field test. The results indicate that passive thermal desorption monitors can provide considerably lower limits of detection than chemical desorption monitors after 4-8 h sampling time, even down to environmental background concentrations, enabling comparison with measurements in ambient air.

Introduction

Interest in the determination of volatile organic compounds (VOCs) in ambient as well as occupational air has increased in recent decades. VOCs originate from various sources, predominantly motor vehicles' exhausts. In particular, 1,3-butadiene and benzene are common pollutants in both ambient and workplace air and have received much attention because of their potentially adverse effects on human health[1,2 3-7].

For assessing exposure to VOCs personal monitoring methods are preferable. Both passive and active sampling methods have long been used to collect VOCs. Passive sampling is more popular since it does not require a pump that needs regular verifications to avoid possible errors in flow-rate measurements, a large number of passive samplers can easily be deployed simultaneously, and wearer compliance is less of a problem than for samplers with pumps. Passive samplers are now available for a large number of target compounds, e.g., VOCs, aldehydes, ozone and nitrogen dioxide. However, in contrast to active samplers that need a pump, knowledge of the uptake rate for each target compound is essential for quantitative measurements with passive samplers. The uptake rate can be calculated if the diffusion coefficient of the compound is known[8], but this calculation can lead to some inconsistencies. Therefore, if possible, uptake rates should be determined experimentally followed by field testing.

Most applications for occupational applications utilize an adsorbent in a badge typesampler[9-11]. Following sampling, the trapped compounds are generally chemically desorbed and subsequently analyzed by gas chromatography (GC) or high performance liquid chromatography (HPLC). However, passive samplers that are desorbed thermally have gained wide acceptance in a variety of environmental applications[6,7,12-16]. Thermal desorption has several advantages over chemical desorption since it can recover most of the trapped target compounds, thereby greatly increasing sensitivity. Moreover it is both occupationally and environmentally friendly as it avoids the need for chemical solvents for desorption[17]. Although there are international standards for sampling workplace air using thermal desorption and GC analysis[18] thermal desorption samplers appear to have been underutilized in occupational applications. One reason for this may be a lack of comparative studies on sampler uptake rates under laboratory and field conditions.

Recently, we evaluated a variety of sampling variables and determined uptake rates of 1,3-butadiene and benzene in ambient air over 24 h and one-week exposures with SKC-Ultra and Radiello samplers, and validated the measurements[19, 20]. These were passive samplers fitted with the graphitized carbon black adsorbent Carbopack X. In continuation of these studies, here we compare the efficiency of thermal desorption passive samplers from three manufacturers: Perkin Elmer, SKC-Ultra and Radiello. The uptake rates for 1,3-butadiene and benzene were determined at three concentrations likely to be found in occupational air situations, over 4 h or 8 h in an exposure chamber. In addition, the samplers were tested at a petroleum refinery where the personnel were exposed to 1,3-butadiene and benzene.

Experimental

Standard gas and reference solutions

Two certified gas mixtures were used as standard reference. The first standard gas (Praxair, Belgium) consists of 1,3-butadiene (5.33 ppm ±2%) and benzene (4.79 ppm

±2%) in nitrogen and the second consists of 1,3-butadiene and benzene (both at 110 mol ppm ±3%) in nitrogen (AGA gas, Sweden). Standard samples were prepared by injecting the gas into Perkin Elmer tubes, using a gas tight syringe, under a flow of helium gas (approximately 15 mL min^{-1}), and were analysed in parallel with the samples to be analysed. A calibration curve was obtained for calculating the concentrations of the analytes in the samples. The calibration curve (typically 3-4 data points) was prepared aiming to cover the expected masses of the target compounds to be analysed. The calibration curve was linear within the range tested (0.20 ng – 20 µg on the tubes).

Samplers and sorbent material

One of each three types of passive sampler compatible with thermal desorption — tube type (Perkin Elmer, Wellesley, MA, USA), badge type (SKC Inc., PE, USA) and radial type (Radiello, Maugeri, Padova, Italy) — were used in this study. The Perkin Elmer sampler consists of a steel tube (90 mm x 6.3 mm outer diameter, 5.0 mm inner diameter) filled with about 300 mg adsorbent. The tubes were sealed with Swagelok fittings with Teflon inserts. During sampling, the tubes were equipped with Perkin Elmer diffusion caps. The SKC-Ultra is a badge sampler with a diffusion barrier 21 mm in diameter and 15 mm deep, containing about 600 mg adsorbent. The Radiello sampler (yellow diffusive body, number 120-2) consists of a stainless steel net coaxial cylindrical cartridge (60 mm long, 100 mesh hole size) filled with about 350 mg adsorbent housed in a cylindrical diffusive body made of polycarbonate and microporous polyethylene (50 mm long, 16 mm diameter). The SKC-Ultra and Radiello sampler handling protocols are described in detail elsewhere[19]. The adsorbent used in all samplers was Carbopack X 60/80 mesh (Supelco, Bellefonte, PA, USA). Before use all samplers were conditioned at 320ºC for 1 h under a flow of high purity nitrogen (c. 20 mL min^{-1}) using a TC-20 tube conditioner (Markes International Ltd.).

Exposure chamber providing workplace concentrations of 1,3-butadiene and benzene

Standard atmospheres of 1,3-butadiene and benzene were generated in chambers (a modified cylindrical reaction vessel) at VSL, Dutch Metrology Institute, Delft, The Netherlands to determine the samplers' uptake rates. The chamber is 55 cm high and made of glass with a contact part of teflon and an internal diameter of 15 cm. It is equipped with sensors for temperature and humidity and a sampler hanging system that is able to rotate and generate a linear air velocity from a couple of cm s^{-1} to m s^{-1}. The chamber is exposed to a laminar flow, between 10 and 20 L min^{-1}, of a standard atmosphere of 1,3 butadiene and benzene. The accuracy and stability of the generated atmosphere is monitored by an online GC sampling directly from the exposure chamber. Samplers were placed in the chamber for 4 h or 8 h at concentrations of about 10, 100, and 1000 µg m^{-3} (Tables S1 and S2). Five samplers of each type were exposed to each concentration and exposure time. The chambers were maintained at a temperature of 20°C, a relative humidity of 50% and wind speed of 0.5 m s^{-1}.

Field experiments

Field samples were collected on four occasions (designated F1 to F4) at a petroleum refinery located on the Swedish West coast from Dec 2007 to June 2008. On two of the occasions an indoor site was selected and on the other two outdoor sites (different sites in each case), to cover both high- and low-exposure conditions to the target compounds, as well as the likely presence of potentially interfering chemical species such as other VOCs and ozone. An overview of the field experimental conditions and environmental parameters on each of the occasions is presented in Table 1.

On each occasion, four passive samplers of each of the three types (Perkin Elmer, SKC-Ultra and Radiello) were exposed for 4 h or 8 h. The samplers were mounted inside a stainless-steel shelter (500 x 370 x 110 mm), suitable for both indoor and outdoor studies[20], which protected them from high velocity winds and precipitation while allowing enough air movement for sampling. The same shelter was thus used for both indoor and outdoor studies. The sampling rates obtained from the chamber experiments for each sampler type were used to calculate the air concentrations of the two target compounds. In parallel, air concentrations of the target compounds were measured using an active sampler fitted with a pump[16]. The inlet for the active sampling equipment was placed inside the shelter close to the passive samplers to ensure that the same atmosphere was sampled by all of the samplers. The pump container (NPL, National Physical Laboratory, Teddington, UK) was specially designed and housed a pair of Perkin Elmer tube samplers containing Carbopack X, and its operation is described elsewhere[16,19]. The measurements acquired with the active sampler were considered to reflect the true concentrations of target compounds. A Tinytag data logger (Gemini data loggers, Chichester, UK) was used to record the relative humidity (RH) and temperature. The wind speed was estimated from published meteorological data for the region.

Chemical analysis and quality control

An automated thermal desorption (ATD) unit (Markes Unity thermal desorber) coupled to a gas chromatograph (GC, Agilent 6890N) and a mass spectrometer (MS, Agilent 5973) was used to analyse the gases trapped in the samplers. In the GC the compounds were separated on a non-polar column (DB-5, 60 m, 0.32 mm ID, 0.25 µm film) with a 10°C min^{-1} temperature gradient after initially holding at 35°C for 5 min. The MS was operated in electron impact (EI) mode with selective ion monitoring (SIM: m/z ratios 54, 53 and 52 for 1,3-butadiene; 78, 77 and 63 for benzene).

Quality control (QC) samples at three pre-determined loading levels (5, 25 and 200 ng) of 1,3-butadiene and benzene were independently prepared at VSL, The Netherlands by pumping an accurately known volume of a standard atmosphere of benzene and 1,3-butadiene in dry air into sorbent tubes . The standard atmosphere was prepared by a two- or one-stage dilution using diffusion and dynamic blending techniques for the dosage of benzene and 1,3-butadiene, respectively. These QC samples were analysed in parallel with the samples from the chamber and field studies. The estimated amounts of the QCs did not deviate by more than 10% from the expected amounts for either compound, except for an 18% overestimation of 1,3-butadiene at 200 ng loading. The results for the QC samples were considered to be acceptable.

During all experiments, five blanks for each sampler type were processed in parallel with the samples to estimate the residual levels of the benzene and 1,3-butadiene. A correction factor was applied to account for the blank levels. The limit of detection

(LOD) for each sampler type was calculated as three times the standard deviation (SD) of the blanks. The samplers were stored in a refrigerator (ca 5ºC) and analysed within a week after reaching the laboratory.

Statistical methods

The acquired data were statistically analysed using SAS for Windows version 9.1 (SAS Statistical Software, SAS Institute, Cary, NC). Multiple linear regression analysis was used to test the influence of concentration, time, and dose (concentration x time) in the chamber tests (Proc GLM, SAS), for each of the substances and for the three different samplers separately. Significant differences refer to $P<0.05$ in two-tailed tests (if not presented). The agreement between results obtained from the passive and the active (NPL-pump) samplers in the field evaluation experiments was evaluated by calculating intra-class correlation coefficients (ICC), using the following equation:

$$\mathrm{ICC} = \sigma_b^2/(\sigma_w^2 + \sigma_b^2)$$

where $\sigma_b^2 =$ between-pair variance, and $\sigma_w^2 =$ within-pair variance (Proc NESTED, SAS). If the within-pair variance is small, the two methods will give almost identical results and the ICC will be close to one. In addition, the agreement between the passive and active samplers was evaluated using a graphical method presented by Bland and Altman[21] (Fig. 1).

Results and discussion

Experimental uptake rates in the exposure chamber

Thermal desorption passive samplers from Perkin Elmer (tube), SKC (badge) and Radiello (radial) were exposed to benzene and 1,3-butadiene at varying concentrations in an environmental exposure chamber. The sampling rates were estimated by multiple linear regression analysis of data obtained from quantitative GC analysis of trapped gases after thermal desorption and are presented in Table 2. The relative standard deviations (RSD) were also determined (Tables S1 and S2). The precision of the uptake rates of the gases by the samplers, expressed as RSDs, was generally good (<15%) for most measurements, and did not exceed 20% for any measurement (Tables S1 and S2).

Effects of concentration of target compounds, exposure time and loading on uptake rates of samplers in the exposure chamber

The multiple linear regression analysis detected no significant effects of concentration, sampling time, or dose on the uptake rate of benzene by the Perkin Elmer tubes (Table 2). For the other two samplers there was a significant influence of concentration, but not time or dose, with a much higher uptake rate at the highest concentration (1000 µg m^{-3}), but the same uptake rate at 10 and 100 µg m^{-3}. The uptake rate at the highest concentration was 24 % and 26 % higher for the SKC-Ultra sampler and the Radiello sampler, respectively, compared with lower exposure levels. For 1,3-butadiene the multiple regression analysis detected an overall effect of concentration for all samplers (Table 2). For the SKC-Ultra and Radiello samplers the sampling time was also a significant factor at the highest exposure level. The loadings of 1,3-butadiene desorbed from the Radiello sampler after 4 h and 8 h exposure at 1000 µg m^{-3} were very similar.

Our results indicate that the Radiello sampler becomes overloaded when exposed to the analytes, especially 1,3-butadiene, at 1000 µg m^{-3} for longer than 4 h. This could possibly be due to poor adsorption of weakly retained compounds such as 1,3-butadiene and/or their reverse diffusion, again due to weak bonding with the collection medium. For weakly retained compounds uptake rates are expected to vary with time. However, this effect was only observed for the high concentration loading with the Radiello sampler and (to a lesser extent) the SKC-Ultra sampler, but not with the Perkin Elmer sampler. SKC-Ultra and Radiello samplers will absorb larger amounts of 1,3-butadiene at a given exposure level and sampling time than the Perkin Elmer tube, thus they are more sensitive to higher loadings. In a previous environmental study[19] we found that the uptake rate for 1,3-butadiene was lower during a week-long sampling compared with 24 h sampling, presumably due to reverse diffusion, with both SKC-Ultra and Radiello samplers, although the effect was less pronounced with the former. We believe that 1,3-butadiene binds more weakly to the adsorbent than benzene. Thus the design of a sampler is an important feature for preventing reverse diffusion.

The sampler uptake rates presented in this study can be compared to the scientific literature and to uptake rates listed by the manufacturer. In health-related environmental surveys personal exposure is usually monitored with Perkin Elmer tubes over at least a week. The sampling rates for Perkin Elmer tubes containing the adsorbent Carbopack X used in this study were similar for both compounds to those reported for exposure times of one and two weeks using the same adsorbent[16,22,23] and to the results declared by the manufacturer (benzene ca 0.6 mL min^{-1} and 1,3-butadiene ca 0.7 mL min $^{-1}$) (www.markes.com). The Perkin Elmer tube appears to be efficient over broad ranges of both time and concentrations of the target compounds tested here, which is an important feature for its use in field work. It is advantageous in comparative studies if the same instrumentation and sampling methods can be used for ambient and workplace sampling.

The first study on a radial type sampler[24] containing activated charcoal and chemical desorption analysis reported an uptake rate (measured over 24 h) of 80 mL min^{-1} for benzene. In the present study, the rate for the yellow diffusion body Radiello sampler containing Carbopack X and thermal desorption analysis was about half of that cited rate. In contrast, at 10 or 100 μg m^{-3} concentrations (Table 2) the sampling rates obtained for this yellow type sampler were about 25% higher than those reported for the same sampler type during 24 h sampling of ambient air at a concentration of 10 μg m^{-3} [19] and also about 36% higher than those reported for the yellow type by the manufacturer for an 8 h to 7 day exposure time (27.8 mL min^{-1}) (www.radiello.it). A similar comparison for SKC-Ultra showed a 25% higher sampling rate in this study (Table 2) than those reported by Strandberg et al.,[19] and a theoretical calculation by the manufacturer (ca 16 mL min^{-1}) (SKC Inc., personal communication). The sampling rates for 1,3-butadiene with Radiello and SKC-Ultra samplers (Table 2) were 85% and 30% higher, respectively, than those reported previously for 24 h sampling at a concentration of 2 μg m^{-3} [19]. Interestingly, a theoretical calculation, however, showed a similar uptake (19.6 mL min^{-1}) for this compound on SKC-Ultra (SKC Inc., personal communication) compared to the present study (Table 2). There is no given sampling rate value by the manufacturer for 1,3-butadiene and Radiello. Thus, the SKC-Ultra sampler and (especially) the Radiello sampler appear to provide much less stable sampling rates with respect to concentrations than the Perkin Elmer sampler. Reverse diffusion may partially explain this divergence.

Field studies

Comparing passive and active sampling methods in a field test is an important means of examining the validity of measured uptake rates since variations in the field, such as changes in the concentrations of the target compounds, or interference by non-target chemical species, are difficult to reproduce in the laboratory. Such assessment of passive samplers is particularly important for their use in occupational situations. Petroleum refineries are generally large industrial installations and are sources of emissions of VOCs, including 1,3-butadiene and benzene, mainly originating from production processes, storage tanks and waste areas[3,4].

The concentrations of 1,3-butadiene and benzene at the refinery, estimated using the reference method (the NPL-pump) ranged from about 1 – 50 µg m^{-3} and 1 – 250 µg m^{-3}, respectively (Table 3). The concentrations in field studies F1 and F2 were lower, although higher than the typical concentrations encountered in the air in Sweden and the UK (0.1 – 1.7 µg m^{-3} for 1,3-butadiene, and 0.7 – 10 µg m^{-3} for benzene)[6,7,16,20,25]. The concentrations estimated in field studies F3 and F4 for both compounds were considerably higher, but still below the threshold limit values for Swedish working environments (1000 µg m^{-3} for 1,3-butadiene, and 1500 µg m^{-3} for benzene)[26]. Thus, the concentration ranges in this study correspond to low occupational exposure levels for both of these VOCs.

The mean concentrations of both compounds at the same sites, sampled over 4 h or 8 h of exposure, varied by factors of two to four for 1,3-butadiene and only negligibly for benzene (Table 3). It is possible that the concentrations had indeed varied during the measurement period but this was not always reflected in the mean values. When calculating the concentrations using data obtained from the passive samplers in the field experiments, the sampling rates determined in the chamber experiments for the lower concentrations (10 or 100 µg m^{-3}, as given in Table 2) have been used. A detailed description of the passive sampler results is given in Table S3.

ICC values for each type of sampler and the two target compounds were estimated using all measurements (four sampling occasions x four sampling sites x two sampling times; 32 sets of pair-wise comparisons in total) and separately for the 4 and 8 h sampling times (16 sets of pair-wise comparisons in each case) (Table 4, Fig. 1). The coherence between the passive samplers and the reference method (the NPL-pump) is fully acceptable for benzene for all samplers (ICC values ≥ 0.90), while for 1,3-butadiene only the Perkin Elmer sampler gave acceptable ICC values (~0.85) for an 8 h sampling time. The Perkin Elmer sampler tended to overestimate the benzene concentration of 1000 µg m^{-3} at 4 h but not 8 h of sampling (Fig. 1).

The LOD that can be achieved with passive samplers is a function of the sampling rate, sampling time, blank values of unexposed samplers, the reproducibility and sensitivity of the GC detector and the selectivity of the GC column[27]. The LODs for 1,3-butadiene and benzene were calculated as three-fold standard deviations of the values for sampler blanks (n=20) converted to a sampling interval of 8 h using the sampling rates at the lower concentrations from Table 2. Accordingly, the LODs of the Perkin Elmer, SKC-Ultra and Radiello samplers were 0.18, 0.12 and 0.030 µg m^{-3} for 1,3-butadiene, respectively, and 0.32, 0.75 and 0.054 µg m^{-3} for benzene, respectively. Blank values of the unexposed samplers for both compounds were lowest for the Perkin Elmer sampler, and successively higher for the Radiello and SKC-Ultra samplers. The reproducibility of the blanks, expressed as relative standard deviations, was good (<10%) for the Perkin Elmer and Radiello samplers, while for the SKC-Ultra sampler it was ca. 20% for 1,3-butadiene and ca. 30% for benzene (resulting in an even higher LOD for benzene than that of the Perkin Elmer sampler, despite a much higher uptake rate). Thus, due to the higher sampling rate and low blank values and spread of the blank results, the LOD values for both compounds were lowest for the Radiello sampler. However, the Perkin Elmer sampler also showed low LODs, despite its relatively low uptake rates. An advantage of the Perkin Elmer sampler is that the sample handling protocol after the precondition procedure is simpler than for the other two samplers, yielding low blank values.

The LODs of these three passive thermal desorption samplers were compared with those of chemical desorption samplers such as the 3M 3500 and SKC575-series samplers. From our own experience using these samplers for benzene, and a report on the 3M 3500 monitor for 1,3-butadiene[10], typical LODs of the chemical desorption samplers range from 20 – 50 µg m^{-3}. Thus, considerable reductions in the LOD, even down to concentration ranges corresponding to background concentrations, can be achieved with thermal desorption samplers after 4-8 h sampling.

Validity and limitations of the field study

The active sampling method (with the NPL-pump) was used as the reference method and the data it provided were considered to reflect the true concentrations. However, it should be mentioned that the active sampling method also has sources of error, and uncertainties of 13% and 12%, respectively, in measurements of 1,3-butadiene and benzene by the NPL-pump method have been estimated[16]. In the light of this and the moderate overall divergence of the results it may be premature to use the results of the present field studies to adjust the uptake rates experimentally determined in the laboratory.

High ambient temperatures may increase back diffusion of 1,3-butadiene[20]. The influence of the temperatures encountered in this field study (Table 1) is expected to be negligible[20], but in some occupational situations the temperatures may be much higher. Therefore, it is important to test the performance of the samplers in a given occupational environmental situation.

Regrettably (in the context of a validation study), none of the field measurements of the concentrations of the two compounds were higher than, or even close to, the Swedish threshold limits[26]. Field levels of >500 µg m^{-3} would have been desirable in order to validate the capacity of the samplers to measure higher concentrations accurately.

Conclusions

The uptake rates of the Perkin Elmer, SKC-Ultra and Radiello passive samplers, as determined from 4 h or 8 h exposures, appeared satisfactory for measuring benzene concentrations in occupational environments. Using these uptake rates the results obtained by the samplers were in good agreement with those obtained by the reference method in a field test. However, the uptake rates for 1,3-butadiene were more variable among the samplers. On the basis of uptake rates, only the Perkin Elmer sampler met the statistical criteria of accuracy for a full 8 h working shift in the field test.

The present study confirms conclusions from studies by other authors, that passive sampling represents a good alternative to traditional methods for assessing occupational exposure. Passive samplers are simple to use and thus amenable to large-scale personal sampling in various occupational situations. For the thermal desorption samplers evaluated here, the LODs of both compounds were low enough to detect environmental background concentrations within 4 h, which is a considerable improvement over chemical desorption monitors.

One limitation of the samplers is their inability to provide information on short-term (e.g. seconds to minutes) concentration peaks. For this an active (pumped) method cannot be replaced by passive methods. The development of passive samplers capable of providing short-term measurements would be a valuable future endeavour.

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References

1. U.S.-EPA: Health assessment of 1,3-butadiene. Office of Research and Development, Washington, DC. EPA/600/P-98/001, 2002.
2. J. Whysner, M.V. Reddy, P.M. Ross, M. Mohan, E.A. Lax, *Mutation Research*., 2004, **566**, 99-130.
3. P.D. Kalaboka, J. Hatzaianestis, J.G. Bartzis, P. Papagiannakopoulos P. *Atmos. Environ*., 2001, **35**, 753-760.
4. E. Cetin, M. Odabasi, R. Seyfioglu. *Sci. Total Environ*., 2003, **312**, 103-112.
5. T. Anttinen-Klemetti, R. Vaaranrinta, P. Mutanen, K. Peltonen. Int. Arch. Occup. Environ. Health., 2004, **77**, 288-292.
6. L. Modig, A.-L. Sunesson, J.-O. Levin, M. Sundgren, A. Hagenbjörk-Gustafsson, B. Forsberg. *J. Environ. Monit*., 2004, **6**, 1-8.
7. P. Gustafson, L. Barregard, B. Strandberg, G. Sällsten. *J. Environ. Monit*., 2006, **9**, 23-32.
8. C.R. Wilke and C.Y. Lee. *Ind. Engineering Chem*., 1955, **47**, 1253-1257.
9. J. Delcourt and J.-P. Sandino. Int. Arch. Occup. Environ. Health., 2001, **74**, 49-54.
10. T. Anttinen-Klemetti, R. Vaaranrinta, P. Mutanen, K. Peltonen. *Int. Arch. Occup. Environ. Health*., 2004, **77**, 288-292.
11. K. Bergemalm-Rynell, B. Strandberg, E. Andersson, G. Sällsten. *J. Environ. Monit*., 2008, **10**, 1172-1178.
12. A.R. Mastrogiacomo, E. Pierini, L. Sampaolo, F. Bruner. *Journal of Chromatography A*., 1998, 810, 131-139.
13. S. Batterman, T. Metts, P. Kalliokoski, E. Barnett. *J. Environ. Monit*., 2002, **4**, 361-370.

14. H. Hellén, H. Hakola, T. Laurila, V. Hiltunen, T. Koskentalo. *The Science of the Total Environment.*, 2002, **298**, 55-64.
15. U. Wideqvist, V. Vesely, C. Johansson, A. Potter, E. Brorström-Lundén, K. Sjöberg, T. Jonsson. *Atmos. Environ.*, 2003, **37**, 1963-1973.
16. N.A. Martin, D.J. Marlow, M.H. Henderson, B.A. Goody, P.G. Quincey. *Atmos. Environ.*, 2003, **37**, 871-879.
17. B. Tolnai, A. Gelencser, G. Barko, J. Hlavay. *Analyst.*, 1999, **124**, 1859-1863.
18. EN ISO 16017-2:2003.
19. B. Strandberg, A. –L. Sunesson, K. Olsson, J. –O. Levin, G. Ljungkvist, M. Sundgren, G. Sällsten, L. Barregard L *Atmos. Environ.*, 2005, **39**, 4101-4110.
20. B. Strandberg, A. L. Sunesson, M. Sundgren, J. O. Levin, G. Sällsten, L. Barregard. *Atmos. Environ.*, 2006, **40**, 7686-7695.
21. M.J. Bland, D.G. Altman. *Lancet.*, 1986, **8**, 307-310.
22. N.A. Martin, P. Duckworth, M.H. Henderson, D.J. Marlow, B.A. Goody. *The Diffusive Monitor.*, 2003, **14**, 4-6.
23. J. O. Levin, A. L. Sunesson, M. Sundgren, B. Strandberg. Presented in part at the 5th International Symposium on Modern Principles of Air Monitoring, Loen, Norway, June, 2005.
24. V. Cocheo, C. Boaretto, P. Sacco. *American Industrial Hygiene Association Journal.*, 1996, **57**, 897-904.
25. N.A. Martin, P. Duckworth, M.H. Henderson, N.R.W. Swann, S.T. Granshaw, R.P. Lipscombe, B.A. Goody. *Atmos. Environ.*, 2005, **39**, 1069-1077.
26. Arbetsmiljöverkets AFS 2011:18, hygieniska gränsvärden, 16th of December, 2011, Sweden

27. J. Begerow, E. Jermann, T. Keles. *Fresenius J Anal Chem.*, 1999, **363**, 399-403.

Table 1. Overview of sites and environmental conditions in the field experiments.

Sampling sites	Expected pollutant situation	Relative humidity (%)	Temperature (°C)	Wind speed* (m s^{-1})
F1-indoors	Low-medium	47	21	<1
F2-outdoors	Low-medium possible increase of 1,3-butadiene	78	4	<1
F3-outdoors	Low-medium possible increase of benzene	42	11	<1
F4-indoors	Medium-High expected increase of both compounds	45	17	<1

*Estimated value using published meteorological data for the region.

Table 2. Sampling rates (mL min^{-1}) of benzene and 1,3-butadiene by passive samplers from three manufacturers, estimated by multiple linear regression analysis of data obtained in exposure chamber experiments with the indicated concentrations and sampling times.

Compound	**Perkin-Elmer**	**SKC-Ultra**	**Radiello**
Benzene			
10,100 µg m^{-3} , 4 and 8 h	0.61	20.0	37.9
1000 µg m^{-3}, 4 or 8 h	0.61	31.1[a]	52.3[a]
1, 3-butadiene			
10, 100 µg m^{-3}	0.59	19.5	41.7
1000 µg m^{-3}, 4 h	0.83[a]	26.6[a]	41.7
1000 µg m^{-3}, 8 h	0.83[a]	22.2[a,b]	20.6[c,d]

[a] $p<0.001$ for comparisons with lower concentrations, [b] $p=0.038$ for comparison with 4 h exposure time, [c] $p<0.001$ in comparison both with lower exposure levels and the shorter sampling time (4 h), [d] should not be used in practice.

Table 3. Average concentrations of 1,3-butadiene and benzene (µg m^{-3}) determined by active sampling (NPL-pump) after 4 h or 8 h of exposure at four sampling sites at the refinery.

Sampling sites	**1,3-butadiene**		**Benzene**	
	4 h	**8 h**	**4 h**	**8 h**
F1	1.1	3.9	2.7	3.7
F2	1.3	2.7	1.1	1.4
F3	13	14	36	37
F4	50	33	260	200

Table 4. Estimated intra class correlation coefficients (ICC) for measurements of benzene and 1,3-butadiene obtained with the active sampler (NPL-pump) versus each of the three passive samplers in the field experiments[a].

Sampler	Benzene			1,3-butadiene		
	4 h and 8 h[a]	8 h	4 h	4 h and 8 h[a]	8 h	4 h
Perkin Elmer	0.95	0.99	0.93	0.84	0.85	0.84
SKC-Ultra	0.94	0.90	0.97	0.71	0.54	0.77
Radiello	0.99	0.99	0.98	0.19	-[b]	0.31

[a] N= 32; pair-wise comparisons for all measurements (four sampling occasions x four sampling sites x two sampling times) and separately for the 4 and 8 h sampling times (16 sets of pair-wise comparisons in each case), [b] negative estimate of the between-pair variance.

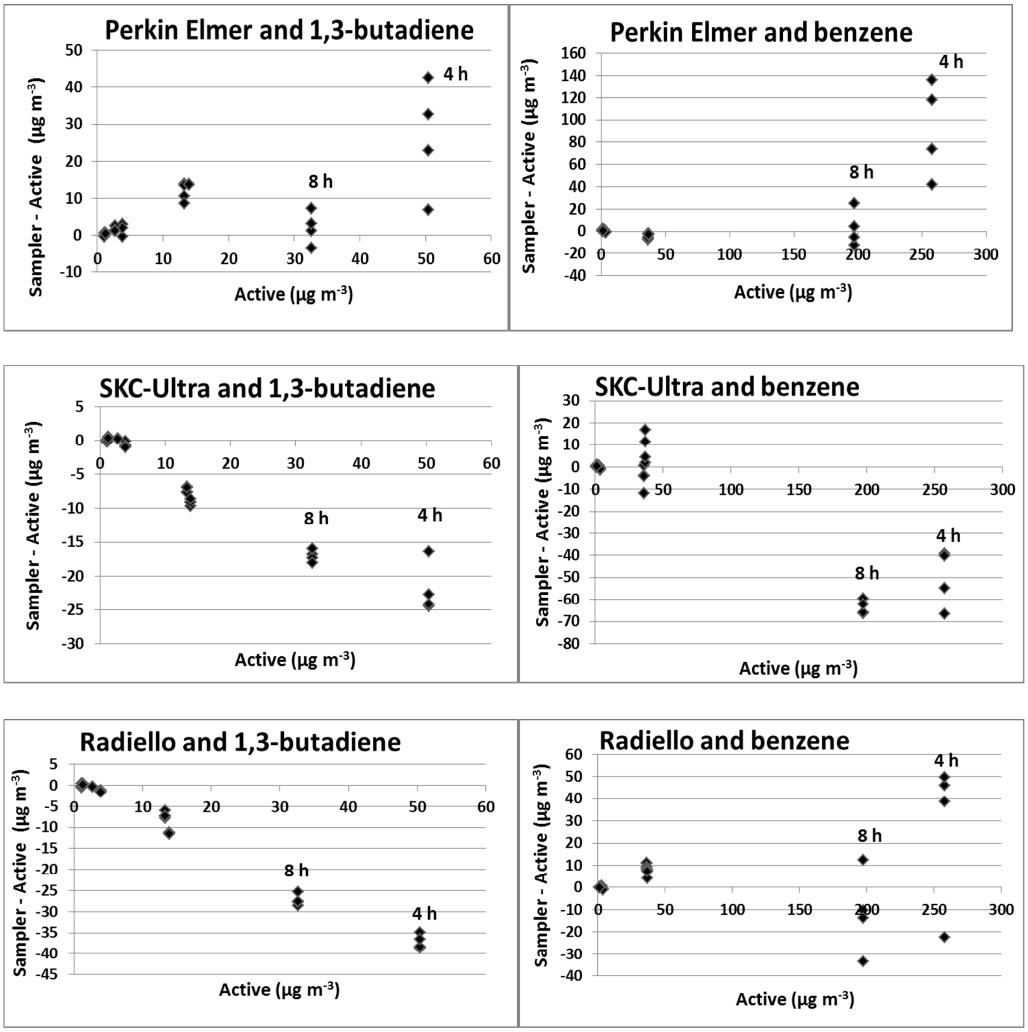

Figure 1. The agreement between measurements by each of the passive samplers and the active sampler (NPL-pump) of 1,3-butadiene and benzene after 4 h or 8 h exposure times in the field study, depicted using a graphical method by Bland and Altman[21]. The 4 h and 8 h exposure results indicated in the figure are for the F4 sampling site; for the other sites, particularly the F1 and F3 sites, the differences between the 4 h and 8 h sampling results are so small that the data points are tightly clustered (Table 3).

Table of contents entry text:

Thermal desorption passive samplers filled with Carbopack X adsorbent can be used to measure benzene in occupational air conditions.

Colour graphic:

Volatile organic compounds (VOCs) such as 1,3-butadiene and benzene are common pollutants in ambient and workplace air and have received much attention because of their adverse effects on human health. For assessing exposure to VOCs personal monitoring methods based on passive sampling are preferable. Most occupational applications utilize chemically desorption techniques followed by GC analysis. Thermal desorption has several advantages over chemical desorption. Although there are international standards for sampling workplace air using thermal desorption these samplers appear to have been underutilized. One reason for this may be a lack of comparative studies on efficiency and sampler uptake rates under laboratory and field conditions.