

# Development of a miniaturized diffusive sampler for true breathing-zone sampling and thermal desorption gas chromatographic analysis

Roger Lindahl,<sup>\*a</sup> Jan-Olof Levin<sup>ab</sup> and Margit Sundgren<sup>b</sup>

Received 29th January 2009, Accepted 29th April 2009

First published as an Advance Article on the web 27th May 2009

DOI: 10.1039/b901926j

Exposure measurements should be performed as close as possible to the nose and mouth for a more correct assessment of exposure. User-friendly sampling equipment, with a minimum of handling before, during and after measurement, should not affect ordinary work. In diffusive (passive) sampling, no extra equipment as sampling pumps is needed, making the measurements more acceptable to the user. The diffusive samplers are normally attached on a shoulder, on a breast-pocket or on the lapel. There are, however, difficulties if true breathing-zone sampling is to be performed, since available diffusive samplers normally cannot be arranged close to the nose/mouth. The purpose of this work was to study the performance of a miniaturized tube type diffusive sampler attached to a headset for true breathing-zone sampling. The basis for this miniaturization was the Perkin Elmer ATD tube. Both the size of the tube and the amount of adsorbent was decreased for the miniaturized sampler. A special tube holder to be used with a headset was designed for the mini tube. The mini tube is thermally desorbed inside a standard PE tube. The new sampler was evaluated for the determination of styrene, both in laboratory experiments and in field measurements. As reference method, diffusive sampling with standard Perkin Elmer tubes, thermal desorption and gas chromatographic (GC) analysis was used. The sampling rate was determined to  $0.356 \text{ mL min}^{-1}$  (CV 9.6%) and was not significantly affected by concentration, sampling time or relative humidity.

## Introduction

Hazard identification and evaluation is necessary in order to prevent illness due to chemical exposure in the work environment. Data from exposure assessments is also used in epidemiology and toxicology studies. One important tool for controlling and reducing occupational health risks is exposure assessment by personal measurement of airborne chemical hazards. Such exposure measurements should be performed as close as possible to the nose and mouth. The “breathing zone” is generally assumed to be within 30 cm from nose and mouth.<sup>1,2</sup> There are, however, differences in contaminant concentrations at different points over the head<sup>3</sup> and upper torso. These differences may be dramatic, especially for exposures from point sources.<sup>1</sup> Measurements more close to the nose/mouth give a better estimate of the exposure.

Another important issue concerning exposure measurement methods is worker acceptability. The sampling equipment should be small and with low weight in order not to affect ordinary work. It is also important that the equipment is user-friendly, with a minimum of handling before, during and after measurement. In diffusive (passive) sampling, no extra equipment as sampling pumps, tubes *etc.*, is needed, making personal measurements more acceptable to the wearer. The easy handling of many diffusive sampling devices make them possible to use also by the workers themselves.<sup>4</sup> A diffusive sampler is normally attached to a shoulder, to a breast-pocket or to the lapel.

Normally, this type of sampling is not true “breathing zone” sampling, since there are difficulties in sampling close to the mouth. Available diffusive samplers are not suitable due to size and/or weight and there are no accessories for this purpose available.

The purpose of this work was to study the performance of a miniaturized diffusive sampler especially designed to be attached to a headset. The arrangement allows true breathing-zone sampling only centimetres away from the mouth. The basis for the miniaturization is a diffusive sampler of tube type, the Perkin Elmer tube.<sup>5</sup> Both the size of the sampler and the amount of adsorbent was decreased for the miniaturized sampler. The new sampler was evaluated for the determination of styrene both at controlled conditions in the laboratory and in field measurements. As reference method, diffusive sampling with Perkin Elmer tubes, thermal desorption, and gas chromatographic (GC) analysis was used.

## Methods and materials

### Chemicals and adsorbents

Styrene (99%, Aldrich) was used for dynamic generation of test atmospheres, and methanol (Merck, p.a.) was used as solvent for standards for thermal desorption analyses. The adsorbent was Tenax TA, 60–80 mesh (Perkin Elmer Inc., Wellesley, MA).

### Reference diffusive sampling method

As reference method, diffusive sampling with Perkin Elmer ATD tubes (Perkin Elmer Inc., Wellesley, MA) was used.

<sup>a</sup>Umeå University, Department of Chemistry, SE-901 87 Umeå, Sweden. E-mail: roger.lindahl@chem.umu.se

<sup>b</sup>Fenix Environmental, SE- 907 19 Umeå, Sweden

Approximately 60 mm of the adsorbent Tenax TA was packed into ATD stainless-steel tubes, 90 mm × 6.3 mm O.D. × 5.0 mm I.D. The distance between adsorbent and orifice of the sampler was 14 mm. The tubes with Tenax TA were conditioned for two hours at 320 °C followed by 30 minutes at 335 °C with 100 mL min<sup>-1</sup> nitrogen gas flow (Markes Sample tube conditioning/dry purge model TC-20). The tubes were sealed with Swagelok fittings with PTFE inserts (Swagelok Co., Solon, OH). During sampling, the tubes were equipped with Perkin Elmer diffusion caps. The uptake rate for styrene with Tenax TA is 0.463 mL min<sup>-1</sup> (20 °C).<sup>6</sup>

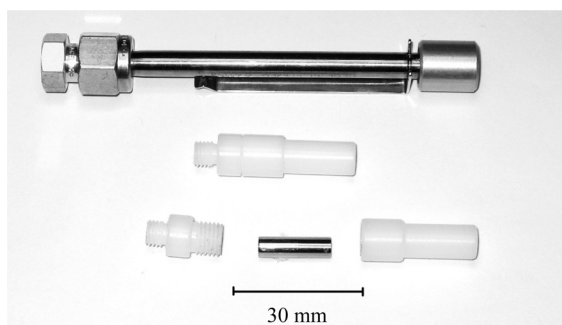
### Miniaturized diffusive samplers

The miniaturized sampler (Mini sampler) consisted of an insert made of stainless steel (outer diameter of 4.9 mm, inner diameter of 4.0 mm and length 17 mm) and a holder made of POM (polyoxymethylene), shown in Fig. 1. Tenax TA was packet in the tube and kept in place by stainless steel grids. The POM holder was cylindrical, with a length of 38 mm, outer diameter of 8 and 10 mm and an inner diameter of 4.0 mm, same as the insert tube, for the diffusion part. The total diffusion path length was 12 mm.

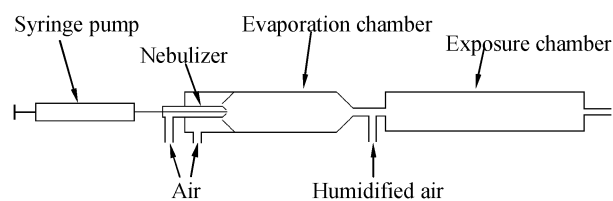
The Mini insert tube was placed inside an empty ATD tube during conditioning and analysis, using the same conditions as for the standard ATD tubes. The standard ATD tube had an inner diameter of 5.0 mm, and was modified with an inside constriction in order to minimize gas flow between the tubes. The Mini insert (OD 4.9 mm) was positioned inside the ATD tube against the constriction during conditioning and analysis

### Generation of styrene

Standard atmospheres of styrene were dynamically generated according to Fig. 2. Styrene was slowly injected into a stream of humidified air by means of a motor-driven microinjection pump (Carnegie Medicin CMA/100, Stockholm, Sweden). A 5 mL or a 250 µL gas-tight syringe (Hamilton #1005 or SGE 250R-GT) was used for the injection, depending on concentration and sampling time. The needle was connected to a fused silica capillary, which was inserted into a nebulizer (Meinhard nebulizer TR-30-A7, J.E. Meinhard Associates). The air flow rate through the nebulizer was 0.9 L min<sup>-1</sup>. The aerosol from the nebulizer was mixed with air (5 L min<sup>-1</sup>) and evaporated into an evaporation chamber. The air mixture was further diluted and



**Fig. 1** Mini diffusive sampler assembled and in parts and at top Perkin Elmer ATD Diffusive sampler.



**Fig. 2** Equipment for generation of styrene atmosphere.

transported to an exposure chamber made of Teflon, 900 × 80 × 60 mm. The total air flow through the exposure chamber was 40 L/min, giving a wind velocity of 0.3 m s<sup>-1</sup> in the chamber. The air was controlled with respect to relative humidity by passing clean air through one to four gas-dispersion bottles. The generation equipment and exposure chamber has been previously reported.<sup>7,8</sup>

### Laboratory validation

The laboratory evaluation was performed mainly according to the standard EN 838:1995 8. In each experiment six ATD diffusive samplers and six MiniATD samplers were exposed simultaneously in the exposure chamber. The effect of concentration, sampling time and relative humidity on the sampling rate was studied using a factorial design.

Back diffusion was studied by exposing two sets of six Mini-ATD samplers to styrene at 90 mg/m<sup>3</sup> and 80% RH for 30 min. After 30 min one set of six tubes were capped with Swagelok caps and the other set was further exposed to air at 80% RH free from styrene for another 7.5 h.

To ensure that the Swagelok caps were completely tight (capping efficiency), six diffusive samplers were capped with Swagelok caps with PTFE ferrules at both ends, one end capped hand-tight and one using keys. The tubes were placed in a 90 mg m<sup>-3</sup> styrene atmosphere (80% RH) for 8 hours.

The storage was tested by exposing twelve MiniATD samplers and twelve ATD samplers to 90 mg m<sup>-3</sup> styrene atmosphere at 80% RH for 8 hours. Six samplers of each type were analysed immediately after exposure. The others were capped and stored for 14 days at room temperature before analysis.

### Sample analysis

The diffusive samples were analysed by thermal desorption-gas chromatography/masspectrometry (GC/MS Agilent 1530N/masspectrometry Agilent 5973 with MSD Chemstation Software, type G1701DA). The adsorbent tubes were desorbed in an automatic thermal desorption injector (ATD 400, Perkin Elmer). The tubes were desorbed at 220 °C for 5 min with a desorption flow of 70 mL/min. Helium was used as carrier gas and the pressure on the injector and column was 30 psi. The temperature of the valve of the ATD 400 and of the line between the injector and the gas chromatograph was 200 °C. The cold trap was packed with Tenax TA (Chrompack, 60–80 mesh) and silanized glass wool (Supelco). The cold trap was kept at -30 °C during the tube desorption and the sample was thereafter desorbed from the cold trap by heating to 250 °C for 5 min. No inlet split was used and the outlet split was 150 mL min<sup>-1</sup>. The gas chromatographic separations were performed with a fused silica column

(HP Ultra 2, 50 m × 0.2 mm I.D., coated with cross-linked 5% phenylmethylsilicone, 0.33 μm). The mass spectrometer was operated in the full scan mode between 50 to 150 mass units. The MS Quad was kept at 150 °C and the MS source at 230 °C. The temperature program for the separations was 100 °C for 1 min, followed by a temperature rise of 10 °C min<sup>-1</sup> up to 200 °C, which was maintained for 1 min. The data from the analyses was recorded, integrated and quantified by MSD Chemstation D.02.00.275. Reference standards for quantification of samples analysed by thermal desorption-gas chromatography-mass spectrometry were obtained by injecting styrene in various concentrations in methanol into ATD tubes packed with Tenax TA. The tubes were placed in a stream of helium (100 mL min<sup>-1</sup>) and 1.0 μL of the standard solution was applied at the stainless steel gauze in the tube. Helium was blown through the tubes for 1 min in order to transfer the substances to the adsorbent and for removal of most of the solvent. The standards were analysed under the same conditions as the samples. The detection limit was determined to 0.05 μg, corresponding to 0.3 mg m<sup>-3</sup> for an eight hour sampling period.

### Head-set for personal sampling

In order to achieve true breathing zone sampling a special head-set was utilized. It consists of one or two flexible tubes fitted to a head-set that goes behind the ears and back of the head. It gives the possibility to attach sampling heads near the mouth. A standard sampling pump can be attached to the tubes, making it possible to use pumped samplers like adsorbent tubes as well. The head-set is shown in Fig. 3.

### Field sampling

The two sampling methods were compared at a reinforced plastic factory where styrene was used. Stationary sampling was performed with sample sets at two locations in the factory. Each sample set consisted of six ATD and six Mini samplers placed within an area of 20 × 15 cm. Sampling times were about 6 hours. Paired personal sampling with the two methods was performed at the same factory on 6 workers with different work tasks. Mini samplers were used with head-set or attached to the breast pocket with a clip. Sampling times were about 6 hours except for one worker with a sampling time of 60 minutes.



Fig. 3 Head-set for breathing-zone sampling with Mini diffusive sampler.

## Results and discussion

### Laboratory validation

The Mini sampler was validated according to the protocol proposed in the European standard EN 838.<sup>9</sup> Effects of sampling time, concentration, and relative humidity on sampling rate were studied. The results from the experiments are shown in Table 1. The mean sampling rate was determined to 0.356 mL min<sup>-1</sup>, with a coefficient of variation of 9.6%.

There was no negative effect from back diffusion, as the back diffusion test resulted in a sampling rate of 0.343 mL min<sup>-1</sup> (CV 7.9%, N = 6), not statistically significant (5%) different from the mean sampling rate.

It is important that there is no leakage into capped samplers. This was tested by exposing capped samplers to 180 mg m<sup>-3</sup> of styrene for 8 hours. No detectable amounts of styrene could be measured in the samplers after the exposure. As the detection limit was 0.05 μg, this corresponds to a capping efficiency of >99.8%.

Storage after exposure for 1 and 14 days at room temperature resulted in a sampling rates of 0.377 mL min<sup>-1</sup> (CV 7.5%, N = 6) and 0.394 mL min<sup>-1</sup> (CV 6.1%, N = 6). There was not a statistically significant (5%) difference between these sampling rates, and the determined mean sampling rate of 0.356 mL min<sup>-1</sup> (Table 1).

The ACGIH occupational time-weighted exposure limit value (TWA) of 20 ppm<sup>10</sup> corresponds to 86 mg m<sup>-3</sup>. The limit of detection (LOD), three times the standard deviation (σ) of the blank,<sup>11</sup> was determined to 0.05 μg, corresponding to 0.3 mg m<sup>-3</sup> for an eight hour sampling period. This means that the LOQ (limit of quantification, ten times σ) is about one percentage of the TWA value.

### Field validation

Paired personal sampling was performed at a reinforced plastic factory. The mean results from the Mini sampler was 94.8% of the ATD results, as can be seen in Table 2. The two methods showed a good agreement with a correlation coefficient of 0.9987 ( $y = 0.9744x - 0.0528$ ).

The mini sampler was compared to the ATD sampler in field tests at the reinforced plastic factory. Two sets of ATD and Mini samplers for stationary sampling were placed at different locations at the factory. The determined uptake rate of 0.356 mL min<sup>-1</sup> was used for the MiniATD sampler and 0.463 mL min<sup>-1</sup> for the standard Perkin Elmer ATD sampler. The deviation between the two methods was less than 6%, as can be seen in Table 3.

### Theoretical uptake rates

The theory of diffusive sampling is based on Fick's first law of diffusion, which with the assumption that the concentration on the surface of the collector, *i.e.* the adsorbent layer, is zero, results in the following equation,<sup>13</sup>

$$\frac{m}{t} = \frac{DA}{L} C = SC$$

**Table 1** Sampling rate of the Mini diffusive sampler at various styrene concentrations, relative humidities, and sampling times. RH: relative humidity, CV: coefficient of variation, N: number of determinations

Sampling time min	RH %	Conc mg m <sup>-3</sup>	CV	Sampling rate mL min <sup>-1</sup>	CV	N
30	80	208	1.5%	0.368	8.9%	6
30	80	239	2.0%	0.337	3.3%	6
30	20	207	3.3%	0.376	8.0%	6
30	20	251	1.7%	0.347	2.4%	6
30	80	13	8.3%	0.303	3.4%	6
30	20	14	4.9%	0.319	4.1%	6
30	20	190	1.0%	0.312	3.6%	6
30	20	265	11%	0.392	3.0%	11
30	20	219	3.7%	0.402	4.7%	12
90	20	9	5.9%	0.304	5.0%	5
120	20	167	3.4%	0.352	3.4	6
404	80	87	2.9%	0.377	4.5%	6
480	20	84	2.5%	0.371	2.9%	6
480	80	12	0.9%	0.354	2.0%	6
480	20	11	2.1%	0.342	3.3%	6
240	50	96	0.8%	0.364	4.1%	6
All experiments			Mean	0.356	9.6%	106

**Table 2** Personal sampling of styrene with ATD and Mini sampling methods. Mini sampler results are given as a percentage of the ATD results. The “Corner of the mouth” results are compared with the simultaneous sampling with ATD placed at the breast-pocket

Worker	Sampler position	ATD mg m <sup>-3</sup>	Mini mg m <sup>-3</sup>	Mini/ATD
A	Breast-pocket	16.2	15.6	96%
A	Corner of the mouth		14.7	91%
B	Breast-pocket	4.37	4.18	96%
B	Corner of the mouth		4.05	93%
C	Breast-pocket	1.80	1.79	100%
D	Breast-pocket	8.75	8.75	100%
E	Breast-pocket	3.10	2.69	87%
F	Breast-pocket	3.54	3.45	97%
	Mean			95%

where  $m$  = mass transported,  $t$  = time,  $D$  = diffusion coefficient,  $A$  = cross sectional area of diffusion path,  $L$  = length of diffusion path,  $C$  = ambient concentration of contaminant,  $S = DA/L$  = sampling rate for the contaminant.

Using this equation, theoretical sampling rates for the miniaturized sampler were calculated according to Table 4. Benzene and toluene have been included in these calculations due to similar chemical properties. There is a difference between the calculated and determined sampling rates for the ATD sampler, shown as Cal/ISO value in Table 4. This may be due to a theoretical, not measured diffusion coefficient and/or conditions that are not ideal, *i.e.* a stagnant air layer close to the sampler orifice or due to non-ideal adsorption directly at the adsorbent layer. The boundary layer has, for one diffusive sampler, been shown to contribute with about 30% of the sampling rate.<sup>14</sup> The boundary layer effect is probably the major factor for the difference between theoretical and determined sampling rates for styrene, as the adsorbent used in this study (Tenax TA) has been considered as “ideal” for the adsorption/thermal desorption of styrene.<sup>15</sup> The Cal/ISO values have been used to calculate corrected sampling rates for the miniaturized sampler. The theoretically calculated corrected sampling rate for determination of styrene with the Mini sampler is 0.346 mL min<sup>-1</sup>, as can be seen in Table 4. This theoretical value deviates from the experimentally

determined sampling rate of 0.356 mL min<sup>-1</sup>, shown in Table 1, with only 3%.

## Summary and conclusions

A new miniaturized system for personal air sampling focused on diffusive sampling was developed and evaluated. The basis for this miniaturization was the standard sampling tube for automatic thermal desorption (Perkin Elmer ATD tube). Both the size of the tube and the amount of adsorbent was decreased for the miniaturized sampler. A special tube holder to be used with a headset was designed for the mini tube. The mini tube is thermally desorbed inside a standard Perkin Elmer tube. The

**Table 3** Stationary sampling of styrene comparing ATD and Mini diffusive sampling methods with sample sets at two locations in a reinforced plastic factory. CV: coefficient of variation, N: number of determinations

		mg m <sup>-3</sup>	CV	N	Mini/ATD
Set 1	ATD	2.52	2.8%	6	
	Mini	2.37	2.1%	5	94.0%
Set 2	ATD	5.95	7.0%	6	
	Mini	5.64	4.9%	6	94.8%

**Table 4** Calculated sampling rates for Mini diffusive sampler

Compound	Diffusion coeff. <sup>a</sup> cm <sup>2</sup> s <sup>-1</sup>	ATD Sampl rate Calc (Cal) <sup>b</sup> mL min <sup>-1</sup>	ATD Sampl rate EN ISO (ISO) <sup>c</sup> mL min <sup>-1</sup>	ATD ISO/Cal <sup>d</sup> mL min <sup>-1</sup>	Mini Sampl rate Calc <sup>e</sup> mL min <sup>-1</sup>	Mini Sampl rate Corr <sup>f</sup> mL min <sup>-1</sup>
Benzene	0.0798	0.681	0.401	0.589	0.508	0.299
Toluene	0.0731	0.624	0.437	0.700	0.466	0.326
Styrene	0.0680	0.580	0.463	0.798	0.433	0.346

<sup>a</sup> Diffusion coefficient calculated according to Fuller, Schettler and Giddings (FSG).<sup>12</sup> <sup>b</sup> Sampling rate calculated from FSG diffusion coefficient and physical properties of the ATD sampler (diffusion length 14 mm and inner diameter 5 mm). <sup>c</sup> Sampling rates according to EN ISO 16017-2:2003.<sup>5</sup> <sup>d</sup> EN ISO 16017-2:2003 sampling rate (ISO) divided with calculated sampling rate (Cal). <sup>e</sup> Sampling rate calculated from FSG diffusion coefficient and physical properties of the Mini sampler (diffusion length 12 mm and inner diameter 4 mm). <sup>f</sup> Calculated sampling rates corrected with the corresponding ISO/Cal-value.

new sampler was evaluated for the determination of styrene, both in laboratory experiments and in field measurements. As reference method, diffusive sampling with standard Perkin Elmer tubes, thermal desorption and gas chromatographic (GC) analysis was used. The sampling rate was determined to 0.356 mL min<sup>-1</sup> (CV 9.6%) and was not significantly affected by concentration, sampling time or relative humidity. The field sampling tests showed good agreement between the two methods. Based on the results for styrene, sampling rates for benzene and toluene was calculated from diffusion coefficients and sampler geometry. The detection limit was determined to 0.3 mg m<sup>-3</sup> for an eight hour sampling period.

The new sampling system will facilitate true breathing-zone sampling only centimetres away from the mouth.

## References

- 1 M. Harper, *J. Environ. Monit.*, 2004, **6**, 404–412.
- 2 G. Lidén and J. Surakka, *Ann. Occup. Hyg.*, 2009, **53**, 99–116.
- 3 A. T. Simpson, *Ann. Occup. Hyg.*, 2005, **49**, 439–442.
- 4 J.-O. Levin, *Occupational Health Review*, 2002, Feb, 14–16.
- 5 MDHS 80, *MDHS Methods for the determination of hazardous substances.*, Health and Safety Executive, 1995.
- 6 *CEN European committee for standardization*, Brussels, Editon edn., 2003.
- 7 R. Lindahl, J.-O. Levin and M. Mårtensson, *Analyst*, 1996, **121**, 1177–1181.
- 8 J.-O. Levin, R. Lindahl and K. Andersson, *Environmental Science and Technology*, 1986, **20**, 1273–1276.
- 9 *CEN European committee for standardization*, Brussels, Editon edn., 1995.
- 10 American Conference of Governmental Industrial Hygienists (ACGIH), in *2006 TLVs and BEIs*, Cincinnati (OH), Editon edn., 2006.
- 11 H. K. Lawrence, W. Crummett, J. J. Deegan, R. A. Libby, J. K. Taylor and G. Wentler, *Anal. Chem.*, 1983, **55**, 2210–2218.
- 12 E. N. Fuller, P. D. Schettler and J. C. Giddings, *Industrial and Engineering Chemistry*, 1966, **58**, 19–27.
- 13 V. E. Rose and J. L. Perkins, *Am. Ind. Hyg. Assoc. J.*, 1982, **43**, 605–621.
- 14 D. W. Underhill and C. E. Feigley, *Anal. Chem.*, 1991, **63**, 1011–1013.
- 15 N. van den Hoed and M. T. H. Halmans, *Am. Ind. Hyg. Assoc. J.*, 1987, **48**, 364–373.