

# Field evaluation of thermal and chemical desorption BTEX radial diffusive sampler radiello<sup>®</sup> compared with active (pumped) samplers for ambient air measurements

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The performance of two types of radiello<sup>®</sup> diffusive samplers, filled with a thermally desorbable adsorbent (graphitised carbon Carbograph 4<sup>TM</sup>) and with a solvent desorbable adsorbent (activated charcoal), respectively, have been evaluated for the monitoring of BTEX in ambient air, by comparison with active (pumped) samplers. A two year survey was carried out in Padua, a medium-sized town, in a traffic site, close to a busy crossroad. The concentrations of BTEX were measured for 15 campaigns, during which four series of radial diffusive samplers were exposed for 2 day, 7 day, 10 day and 14 day time periods, respectively. Every series of chemical desorption samplers included three replicates; thermal desorption samplers included six replicates, three of them filled with freshly conditioned cartridges and three filled with regenerated cartridges. No significant difference in the levels measured either by new or by regenerated cartridges has been found. During three campaigns (summer 2004, winter and spring 2005) two active (pumped) samplers were added for each sampling period. The diffusive uptake rates have been calculated and modelled under various conditions of concentration, temperature and exposure time. The effects of the environmental factors on the performances of both solvent and thermally desorbable samplers have been evaluated. The repeatability of the whole measurement process (sampling and analysis) was calculated for every sampling duration. The comparison of concentration levels measured by diffusive and active sampling methods shows correlation coefficients  $R \geq 0.98$  ( $p < 0.01$ ) for all the compounds. The uncertainty of the diffusive sampling method under field conditions, using active sampling as the reference method, has been assessed according to the ISO 13752 requirements. On field relative expanded uncertainty for benzene has been found below 20%.

## Introduction

Chronic exposure to benzene can result in haematotoxic, genotoxic and carcinogenic effects, such as leukopenia, anaemia, induction of chromosomal aberrations and leukaemia.

The main exposure route is inhalation; cigarette smoke and evaporation or combustion of automotive fuels and industrial emissions are the main sources. Other substituted monoaromatic compounds such as toluene and xylenes, have chronic and acute effects on the central nervous system, but do not show carcinogenic effects.

The need for collecting data representative of urban or workplace air pollution is all-important in order to monitor the population or workers' exposure and to identify episodes where threshold levels are exceeded. Currently, data in urban environments are obtained at fixed sites of air quality monitoring

networks by automated continuous gas chromatographic analyzers.

A complementary approach is offered by diffusive sampling that does not involve the use of heavy and encumbering pumping systems, does not need an electrical power supply, does not require supervision, is noiseless and can be accomplished by everybody, everywhere and with very low costs.

The radiello<sup>®</sup> diffusive sampler is already used on a large scale for monitoring BTEX concentration levels in urban air,<sup>1–4</sup> in the air of dwellings<sup>5,6</sup> or offices<sup>7</sup> and for measuring personal exposure.<sup>8–11</sup>

In this paper we present the results of a long-term field study of the performance of the diffusive sampler radiello<sup>®</sup> for the measurement of atmospheric BTEX, using both the solvent desorption and the thermal desorption sampler configuration.<sup>12</sup>

While many experiments have already been performed in order to test the sampler performances under laboratory conditions at controlled environmental parameter levels (concentration, air temperature, relative humidity, pressure, etc.)<sup>12–14</sup> this study investigates the effects of environmental factors under field

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conditions, according to the requirements of the standards EN 13528 Parts 1 and 2.<sup>15</sup>

Models have been developed to describe the variations of the diffusive uptake rate as a function of the environmental parameters. Expanded uncertainty has been evaluated according to the ISO GUM<sup>16</sup> and ISO 13752<sup>17</sup> for field tests.

Furthermore, we tested the effect of repeated regeneration cycles on the performance of the thermally desorbable radiello® sampler.

## Experimental

### Materials

BTEX were sampled by two configurations of the radiello® diffusive sampler (Fondazione Salvatore Maugeri, Padova, Italy): the solvent desorbable sampler and the thermally desorbable one. The latter contains a stainless steel net cylinder, 60 mm length, 4.8 mm od, with  $3 \times 8 \mu\text{m}$  mesh opening, packed with  $350 \pm 10 \text{ mg}$  of 35–50 mesh particle size graphitised carbon black Carbograph 4,  $128.9 \text{ m}^2 \text{ g}^{-1}$  Langmuir specific surface;<sup>16</sup> the adsorbing cylinder is inserted in a microporous polyethylene diffusive membrane.<sup>12</sup> The solvent desorbable sampler contains a 60 mm length, 5.8 mm od, with 100 mesh openings, packed with  $530 \pm 30 \text{ mg}$  of 35–50 mesh particle size activated charcoal. BTEX are trapped by adsorption and recovered by carbon disulfide displacement.

Driven by the concentration gradient existing between the free air outside the diffusive membrane and the stainless steel net cylinder containing the adsorbent (from now on referred to as the ‘adsorbing cartridge’), the compounds diffuse through the membrane towards the cartridge where they are adsorbed either by the graphitised carbon black (in thermally desorbable sampler) or by the activated charcoal (in the solvent desorbable sampler).

The BTEX concentrations  $C$  in  $\mu\text{g m}^{-3}$  are calculated by the following equation,<sup>19</sup> which is derived from Fick’s first law:

$$C = \frac{m_d - m_b}{R_u t} 10^6 \quad (1)$$

where  $m_d$  is the adsorbed mass ( $\mu\text{g}$ ) of the analyte found in the cartridge,  $m_b$  the mass ( $\mu\text{g}$ ) of the analyte on a non-exposed cartridge (blank),  $R_u$  the diffusive uptake rate of the analyte ( $\text{ml min}^{-1}$ ) and  $t$  is the exposure time (min).

Parallel measurements have been carried out by active (pumped) sampling, drawing air through sorbent tubes filled with 400 and 200 mg activated charcoal (Di. Elle, Albignasego, Italy), at flow-rates ranging from 20 to  $100 \text{ ml min}^{-1}$ . Flow-rates were

measured every day by means of a calibrated 100 ml bubble flow meter, with 1, 10 and 100 ml reading marks.

### Field measurements

A two year survey was carried out in Padua, a medium sized town (211 000 inhabitants over a  $94 \text{ km}^2$  area). The measurement site is close to a busy crossroad: the street width is 20 m and side buildings have 2–3 floors.

The concentrations of BTEX were measured for twelve campaigns, from August 2003 to July 2004. During each monitoring campaign, a total of 36 samples (24 thermally desorbable and 12 solvent desorbable) were exposed for 2 day, 7 day, 10 day and 14 day time periods, according to the scheme shown in Table 1. Among thermally desorbable samples, one half included freshly conditioned adsorbing cartridges, while the remaining cartridges underwent a number of thermal regeneration cycles after exposure (from now on referred to as ‘regenerated cartridges’).

Average temperatures have been measured by a thermometer data-logger with  $\pm 1.0^\circ\text{C}$  accuracy.

The aim of the first 12 campaigns was to assess the repeatability of field measurements and to check for any difference in the performances of fresh and regenerated cartridges.

Furthermore, three series of parallel measurements, with diffusive and active samplers, were carried out in summer 2004, winter and spring 2005. During these campaigns four series of six thermally desorbable diffusive samples (no more distinction between fresh and regenerated cartridges), six solvent desorbable and two active samples were taken for 2 day, 7 day, 10 day and 14 day time periods. These data have been used to estimate the effect of environmental parameters on the radiello®’s diffusive uptake rates and to estimate the field measurement uncertainty following the method described by ISO 13752.<sup>17</sup>

### Analytical methods

**Analysis of BTEX by thermal desorption.** The adsorbing cartridges were fitted into empty stainless steel standard thermal desorption tubes (6.35 mm od, 5 mm id, 90 mm long), then loaded on the tray of the automated thermal desorber (Turbo-Matrix ATD, Perkin Elmer, Norwalk, CT, USA). The automated thermal desorber was operated in the two-stage desorbing mode; the cold trap was filled with Tenax TA, 60–80 mesh particle size.

The GC system (Autosystem XL, Perkin Elmer, Norwalk, CT, USA) was equipped with a 50 m column (J&W PONA, 0.2 mm

**Table 1** Sampling scheme of each monitoring campaign

Exposure duration	Solvent desorbable samples (no. of replicates)	‘Fresh’ thermally desorbable samples (no. of replicates)	‘Regenerated’ thermally desorbable samples (no. of replicates)
2 days	3	3	3
7 days	3	3	3
10 days	3	3	3
14 days	3	3	3
Total no. of replicate samples	12	12	12

**Table 2** Analytical conditions

Automated thermal desorber	GC system
Carrier gas: nitrogen	Carrier gas: nitrogen (27 psi)
Primary desorption: 320 °C, 10 min	Column temperature program: 35 °C, 1 min
Total primary desorption flow-rate: 85 ml min <sup>-1</sup>	6 °C min <sup>-1</sup> to 110 °C
Inlet split flow-rate: 50 ml min <sup>-1</sup>	20 °C min <sup>-1</sup> to 220 °C; 2 min
Outlet split flow-rate: 20 ml min <sup>-1</sup>	Total run time: 22 min
Overall split ratio: 1 : 75	FID temperature: 250 °C
Valve temperature: 150 °C	
Cold trap temperature: 2 °C	
Secondary desorption temperature: 290 °C for 1 min	
Transfer line temperature: 200 °C	

id, 0.5 µm film thickness) and a flame ionisation detector (FID). Analytical conditions are given in Table 2.

The calibration was performed by injecting 1 µl of each of four standard BTEX solutions (in the range 0.044–8.8 mg ml<sup>-1</sup> of each analyte) onto blank adsorbing cartridges, through a GC injection port (kept at 200 °C). The cartridge was flushed by a 60 ml min<sup>-1</sup> N<sub>2</sub> stream during injection and purged for 2 min.

**Analysis of BTEX by solvent desorption.** The extraction is accomplished by introducing 2 ml of low-benzene content CS<sub>2</sub> and 100 µl of internal standard solution (2-fluorotoluene) directly in the radiello® glass storage tube without drawing out the cartridge. After 30 min, the CS<sub>2</sub> solution is injected in the gas chromatograph.

The analytical conditions are the same both for radiello® and for active samples. The GC system (6890N, Agilent Technologies, Wilmington, DE, USA) was equipped with a 50 m column (J&W-PONA, 0.2 mm id, 0.5 µm film thickness) and a FID detector. Analytical conditions are given in Table 3.

The calibration was performed by the phase equilibrium technique, adding to new, unexposed cartridges accurately measured 2 ml aliquots of a series of calibration solutions, ranging from 0.11 to 17.6 µg ml<sup>-1</sup> of each compound (except toluene, ranging from 0.22 to 34.7 µg ml<sup>-1</sup>), prepared by serial dilutions.

**Table 3** Analytical conditions

GC system
Injection volume: 3 µl
Injector temperature: 260 °C
Split ratio: 20 : 1
Carrier gas: nitrogen (25 psi)
Column temperature program: 35 °C, 5 min; 5 °C min <sup>-1</sup> , –90 °C; 90 °C, 3 min; 10 °C min <sup>-1</sup> , –150 °C; 20 °C min <sup>-1</sup> , –250 °C; 3 min
Total run time: 33 min FID temperature: 250 °C

## Results and discussion

### Comparison between new and regenerated thermal desorbable cartridges

In principle, the thermal desorption cartridges have to be conditioned prior to use, by heating them under a flow of inert gas. In general, it is recommended to condition thermal desorption tubes at a temperature above the analytical desorption temperature.<sup>18</sup> Therefore, the thermal desorption cartridges were re-conditioned after each analysis, keeping them at 350 °C for at least 24 h under nitrogen flow.

Moreover, graphitised charcoal is a fragile material that exhibits a tendency to turn to dust under mechanical stress during the use. The repeated desorption and reconditioning cycles produce little amounts of fine dust, which cannot be retained by the stainless steel net cylinder. The loss of adsorbent might introduce an additional uncertainty in the sampler performances that needs to be investigated. For that reason, the manufacturer suggests to discard the cartridges after a maximum of 20 desorption-reconditioning cycles.

Twelve on-field tests were carried out during which four series (2 day, 7 day, 10 day and 14 day time periods) of six thermal desorption diffusive samplers (three with new and three with regenerated cartridges) and three solvent desorption samplers were exposed, in parallel, to urban air. A total of 432 diffusion samplers were exposed under various conditions of temperature, concentration levels and exposure times.

Regenerated cartridges were chosen as near as possible to the maximum number of regenerating cycles recommended by the manufacturer (*i.e.* 20).

For all the compounds we compared, the concentrations were measured with the new and the regenerated cartridges. Table 4 shows the correlation coefficients and the linear regression model between the concentrations measured by new and regenerated cartridges; all the model parameters are significant at a 99% confidence level ( $p < 0.01$ ).

For all the compounds, no statistically significant differences at a 95% confidence level have been found between the average values measured with new and regenerated cartridges; therefore the performances of the samplers for thermal desorption does not depend on the 'age' of the samplers. As a consequence, the two sets of new and regenerated cartridges have been grouped to form a single set of six samplers to be compared with solvent desorption diffusive and active samplers.

### Blank values and detection limits

For each campaign a set of five unexposed samplers were analyzed to determine the blank values, giving a total of

**Table 4** Comparison between concentrations (µg m<sup>-3</sup>) measured with new and regenerated cartridges

Compound	R <sup>2</sup>	Linear regression model
Benzene	0.997	Regenerated = 0.997 new
Toluene	0.994	Regenerated = 0.992 new
Ethylbenzene	0.996	Regenerated = 0.988 new
<i>m</i> and <i>p</i> -xylenes	0.996	Regenerated = 0.990 new
<i>o</i> -Xylene	0.995	Regenerated = 0.996 new

60 blanks. Blank cartridges were shipped together with the cartridges which were inserted into the samplers exposed on-site, then they were brought back to the laboratory. Throughout the whole 14 day sampling period the blank cartridges were kept inside their glass tubes, well capped. As such, blank cartridges may be affected by any possible source of noise (transport, temperature abrupt changes, sun irradiation, highly polluted storage environments, and so on).

According to EN 13528-2 the limit of detection (LOD) is expressed as three times the standard deviation of the blank values, while the limit of quantitation (LOQ) is 10 times the standard deviation of the blank values.<sup>15</sup> We calculated the LOD and LOQ values in  $\mu\text{g m}^{-3}$  on the basis of the uptake rates estimated in the following (see section: 'Influence of concentration level, exposure time and air temperature'), considering a 7 day sampling period at 25 °C.

Mean blank levels (in ng), relative standard deviations, LOD and LOQ values of each compound for the thermally desorbable radiello® are listed in Table 5.

### Repeatability of the radiello® diffusive samplers

The repeatability of measurements has been estimated by calculating the percent relative standard deviation (%RSD) and the mean percent relative standard deviation (%MRSD) for all data for a given sampling duration. The %MRSD values for every exposure times are shown in Table 6 (thermally desorbable samplers) and in Table 7 (solvent desorbable samplers).

The repeatability is always lower than 10% and it is independent of the sampling duration, at the 95% confidence level, for all the compounds.

### Influence of concentration level, exposure time and air temperature

Three tests were performed in order to estimate the effect of concentration levels, exposure time and air temperature on the uptake rates of the samplers. During these tests we took the values measured by active (pumped) sampling as the reference values.

The environmental parameters covered a wide range of conditions: average temperatures from 2.2 °C to 28.4 °C, concentration levels from 2.4 to 14.3  $\mu\text{g m}^{-3}$  for benzene, from 9.1 to 48.1  $\mu\text{g m}^{-3}$  for toluene, from 1.9 to 9.1  $\mu\text{g m}^{-3}$  for ethylbenzene and from 8.9 to 45.0  $\mu\text{g m}^{-3}$  for xylenes (all isomers), exposure times from 1 to 14 days.

For each campaign four sets (2 day, 7 day, 10 day and 14 day time periods) of three radiello® samplers of both types (thermally and solvent desorbable) were exposed at the same site together with four sets of two active (pumped) samplers. The experimental

**Table 6** Repeatability of the radiello® thermal desorption samplers

Compound	%MRSD			
	2 days	4 days	7 days	14 days
Benzene	7.5	9.4	6.7	4.6
Toluene	8.0	9.1	8.6	7.8
Ethylbenzene	7.8	9.2	8.8	8.1
<i>m</i> and <i>p</i> -xylenes	8.6	9.4	8.9	8.1
<i>o</i> -Xylene	9.4	9.2	9.0	8.3

**Table 7** Repeatability of the radiello® solvent desorption samplers

Compound	%MRSD			
	2 days	4 days	7 days	14 days
Benzene	4.9	5.1	3.7	2.9
Toluene	4.7	5.0	3.4	3.0
Ethylbenzene	5.8	5.3	4.3	3.4
<i>m</i> and <i>p</i> -xylenes	6.3	5.4	3.7	3.4
<i>o</i> -Xylene	6.0	5.6	4.0	3.2

diffusive uptake rates were calculated by measuring the masses of each compound found into the cartridges, following the equation below, which is derived from eqn (1):

$$R_u = \frac{m_d - m_b}{Ct} 10^6 \quad (2)$$

where  $C$  is the mean concentration value measured with the two active samplers.

A multiple linear regression analysis (stepwise backward) has been performed on the experimentally calculated diffusive uptake rates in order to identify the parameters which significantly affect the sampler performances and to look for mathematical models suitable of describing the dependency of diffusive uptake rates on these parameters.

For all the compounds and for both thermally and solvent desorbable samplers the diffusive uptake rate was found to depend on not more than one parameter. Table 8 and Table 9 gather the models obtained for thermally and solvent desorbable BTEX radiello® samplers, respectively. In these tables  $d$  is the exposure duration (in days),  $T$  is the average air temperature (in °C) and  $I$  is the mean concentration (in  $\mu\text{g m}^{-3}$ ):

The results show that the air temperature is the only parameter which influences the diffusive uptake rate of toluene, ethylbenzene and xylenes. The positive dependency of the diffusive uptake rate on the air temperature is well known in the literature.<sup>20,21</sup> Diffusive uptake rate is a function of the diffusion

**Table 5** Solvent desorbable radiello®: Mean blank levels, LODs and LOQs

Compound	Mean blank/ng	STD (%)	LOD/ $\mu\text{g m}^{-3}$	LOQ/ $\mu\text{g m}^{-3}$
Benzene	25	57.6	0.05	0.18
Toluene	25	57.6	0.06	0.19
Ethylbenzene	25	57.6	0.06	0.19
<i>m</i> and <i>p</i> -xylenes	25	57.6	0.06	0.20
<i>o</i> -Xylene	25	57.6	0.06	0.21



**Table 8** Uptake rate models for thermally desorbable radiello® for BTEX<sup>a</sup>

Compound	Sampling rates model/ml min <sup>-1</sup>	P-value/slope	Temperature effect/% °C <sup>-1</sup>
Benzene	$U = 34.8 - 0.60\ d$	0.030	-1.7*
Toluene	$U = 28.3 + 0.17\ T$	<b>0.060</b>	0.5
Ethylbenzene	$U = 24.4 + 0.40\ T$	0.048	1.2
<i>m</i> and <i>p</i> -xylenes	$U = 25.4 + 0.31\ T$	0.026	0.9
<i>o</i> -Xylene	$U = 24.6 + 0.26\ T$	0.025	0.8

<sup>a</sup> \*: % day<sup>-1</sup>; bold: regression not statistically significant at 95% confidence level.

**Table 9** Uptake rate models for solvent desorbable radiello® for BTEX<sup>a</sup>

Compound	Sampling rates model/ml min <sup>-1</sup>	P-value/slope	Temperature effect/% °C <sup>-1</sup>
Benzene	$U = 83.1 - 1.08\ C$	0.030	-1.3*
Toluene	$U = 60.2 + 0.48\ T$	0.030	0.7
Ethylbenzene	$U = 55.8 + 0.64\ T$	0.011	0.9
<i>m</i> and <i>p</i> -xylenes	$U = 54.1 + 0.57\ T$	0.005	0.8
<i>o</i> -Xylene	$U = 52.1 + 0.60\ T$	0.043	0.9

<sup>a</sup> \*: % (μg m<sup>-3</sup>)<sup>-1</sup>.

coefficient (*D*), which increases as the air temperature increases, according to:

$$R_{uT} = R_{u25} \left( \frac{273 + T}{298} \right)^n \quad (3)$$

where  $R_{uT}$  is the diffusive uptake rate value at the mean air temperature *T* (in °C),  $R_{u25}$  is the diffusive uptake rate value at the nominal temperature of 25 °C and *n* = 1.5.

Eqn (3) describes an increase of uptake rates of about 0.5% °C<sup>-1</sup> that is in good agreement with the experimental uptake rate increases found also by other authors under laboratory conditions for toluene, ethylbenzene and xylenes thermally desorbed.<sup>20</sup> For those compounds, our results seems to indicate a stronger increase of uptake rates when air temperature increases (0.5 ÷ 1.2% °C<sup>-1</sup> for thermally desorbable sampler, 0.7 ÷ 0.9% °C<sup>-1</sup> for solvent desorbable sampler). It should be noted that in our field study the air temperature underwent large fluctuations, following the natural night-and-day temperature cycles, while it is kept constant, together with the concentrations, during laboratory tests.

The uptake rate of benzene shows different behaviours for thermally and solvent desorbable samplers.

For thermally desorbable samplers, the uptake rate depends only on the exposure duration (-1.7% day<sup>-1</sup>), while neither temperature nor concentration levels seem to affect the sampler performances. Such a behaviour might be explained, at some extent, by the nature of the sorbent. As previously described, thermally desorbable cartridges are filled with a graphitised carbon black (Carbograph 4), characterized by a medium-strength adsorbing surface and with a relatively weak adsorbing power. The recovery of adsorbed compounds is based onto the different shape of adsorption isotherms at different temperatures.

Due to the weakness of the sorbent, heavier compounds (like toluene, ethylbenzene and xylenes) will eventually displace the more volatile ones (like benzene), giving rise to the back diffusion.<sup>22,23</sup> As the exposure duration goes on, this phenomenon makes the uptake rate to decrease with exposure time.

For solvent desorbable cartridges, the benzene uptake rate depends only on the concentration levels (-1.3% (μg m<sup>-3</sup>)<sup>-1</sup>). The

sorbent used in solvent desorption sampler (activated charcoal) is much stronger than graphitised carbon. Thus, we might explain that slightly negative dependency by the higher volatility of benzene and, consequently, a less favourable adsorption equilibrium, with respect to the heavier aromatic compounds.

#### Comparison between active (pumped) samplers and radiello® samplers

On the basis of the modelled sampling rates quoted in Tables 8 and 9 and using eqn (1) we calculated the average air concentration levels for each compound and for each campaign.

Fig. 1 shows all the BTEX data obtained with thermally desorbable radiello® samplers *versus* those measured with solvent desorbable radiello® samplers during all 15 campaigns, independently on the sampling duration. All the parameters of linear regressions indicated in Fig. 1 are significant at 99% confidence level.

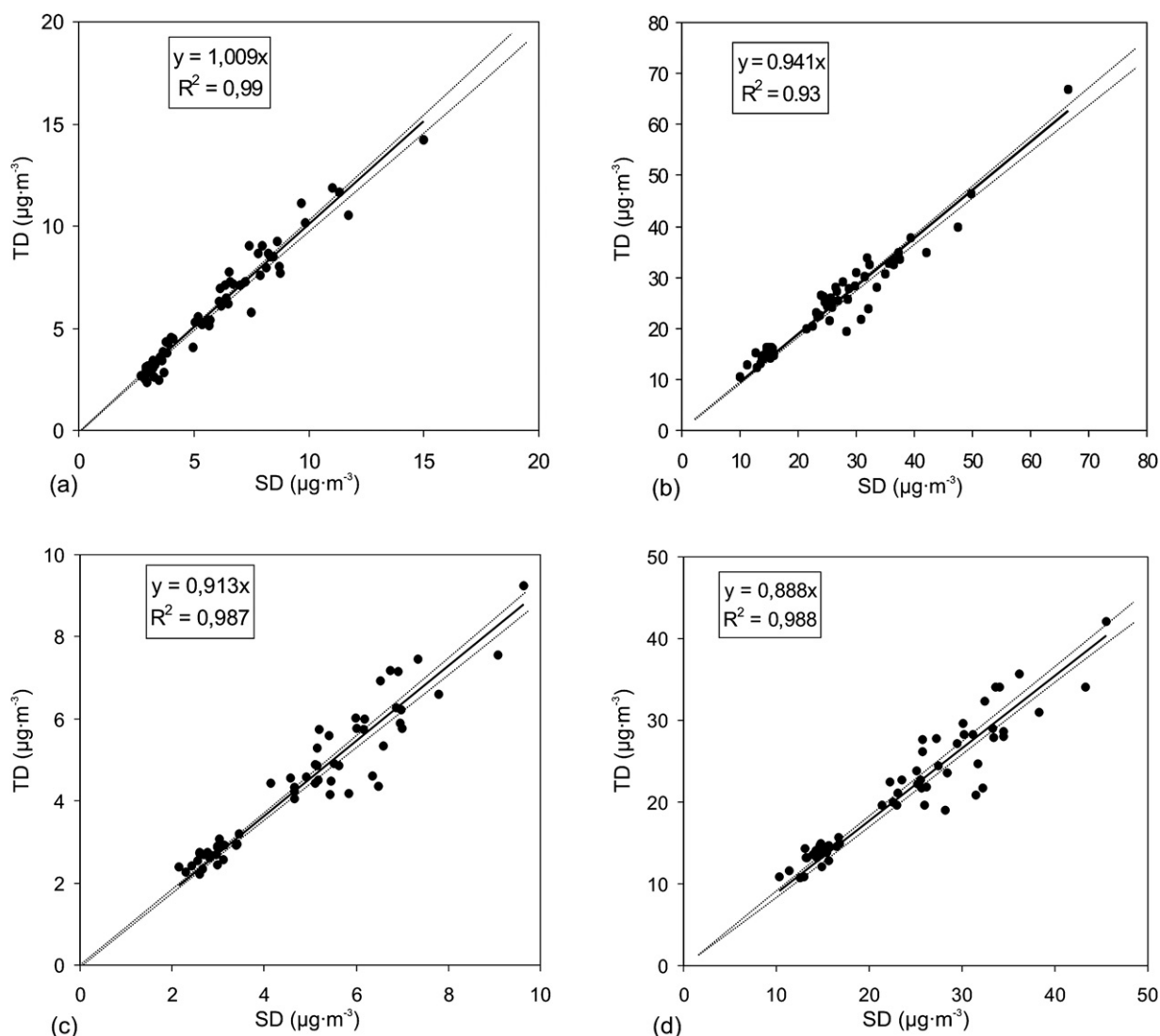
The agreement between thermally and solvent desorbable samplers is very good, especially for benzene (*R*<sup>2</sup> = 0.99). The slopes of the regression lines indicate that for toluene, ethylbenzene and xylenes thermally desorbable radiello® gives rise to an underestimation of about 6%, 9% and 11%, respectively, with respect to solvent desorbable samplers.

In Fig. 2 all the BTEX data obtained with thermally and solvent desorbable radiello® are matched *versus* those measured with active samplers during the last three campaigns. Slopes of the linear regressions (at 99% confidence levels) are gathered in Table 10.

The agreement between the radiello® diffusive sampling and the active sampling method is excellent, especially considering that the active sampling method (the reference method) has not a negligible experimental error.

#### Expanded uncertainty of BTEX determination under field conditions

The ISO 13752 standard has been used to evaluate the uncertainty of the radiello® BTEX measurements under field



**Fig. 1** BTEX concentrations measured with thermally desorbable radiello® versus solvent desorbable radiello® concentrations: (a) benzene, (b) toluene, (c) ethylbenzene, (d) xylenes. Linear regression and 95% confidence limits.

conditions using the active (pumped) sampling method as reference. In this standard the values of the reference method ( $x$ -method) are assumed to be 'true values' while the method (radiello®) whose uncertainty is under investigation ( $y$ -method) is assumed to be the 'test method'. All differences between the measurements carried out with test and reference methods are attributed to measurement deviation of the test method. As the uncertainty of the reference method is not taken into account by the statistical procedures described in the standard, this approach could lead to an overestimation of the uncertainty of the test method. Thus, all the uncertainties that will be attributed to the test method can be assumed as an overestimation of the true ones.

Twelve pairs ( $N = 12$ ) of measured values  $[(x_1, y_1), (x_2, y_2), \dots, (x_N, y_N)]$  have been obtained from parallel on-field measurements, both for thermal and solvent desorbable radiello®.

It is assumed that there is a linear relationship between the  $X$  and  $Y$  variables estimated by:

$$\hat{y} = b_0 + b_1x \quad (4)$$

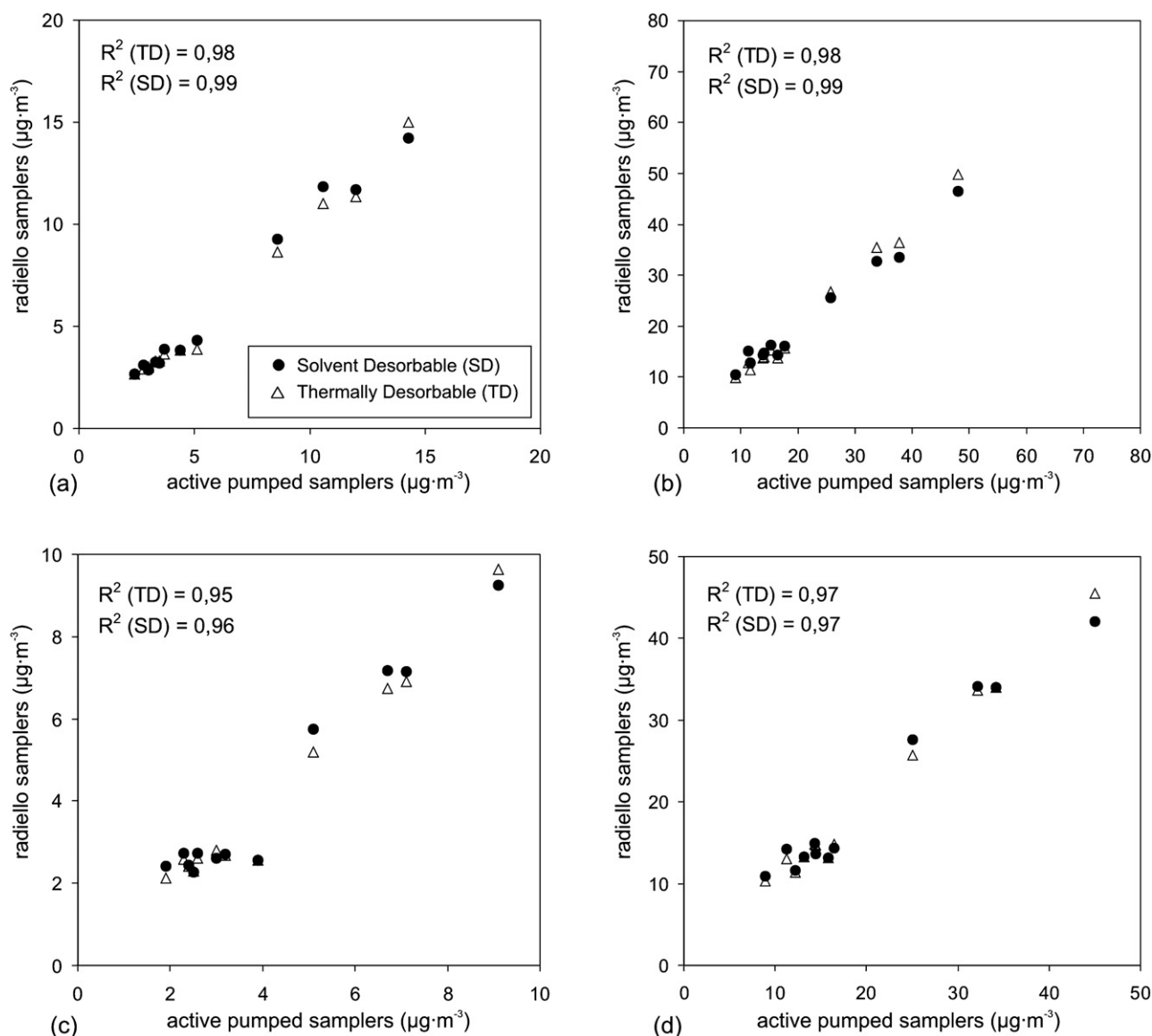
where  $x$  is the value of the reference method,  $\hat{y}$  is the predicted value of the model equation and  $b_0$  and  $b_1$  are the regression parameters.

The general variance function of the test method accounts not only for the variability of intercept and slope of the regression function but also for the statistical noise, and it is expressed as:

$$s^2 = a_0^2 + a_1^2x + a_2^2x^2 \quad (5)$$

The coefficients of the model ( $b_0, b_1, a_0, a_1, a_2$ ) are estimated iteratively on the criterion of maximum logarithmic likelihood ( $l$ ) as an indicator of best fit. The logarithmic likelihood is calculated as follows:

$$l = \sum_{i=1}^N \left( -\ln(s_i) - \frac{1}{2} \ln(2\pi) - \frac{(y_i - \hat{y}_i)^2}{2s_i^2} \right) \quad (6)$$



**Fig. 2** BTEX concentrations measured with thermally desorbable and solvent desorbable radiello® versus active (pumped) samplers: (a) benzene, (b) toluene, (c) ethylbenzene, (d) xylenes.

**Table 10** Slopes of linear regressions of radiello® versus active sampling data (99% confidence level)

Compound	Slope/thermally desorb. vs. active	Slope/solvent desorb. vs. active
Benzene	$1.03 \pm 0.04$	$1.03 \pm 0.04$
Toluene	$0.88 \pm 0.04$	$1.03 \pm 0.04$
Ethylbenzene	$1.05 \pm 0.07$	$1.04 \pm 0.06$
Xylenes	$0.95 \pm 0.05$	$1.01 \pm 0.04$

The maximum values of  $l$  are calculated iteratively by changing  $b_0$ ,  $b_1$ ,  $a_0$ ,  $a_1$ ,  $a_2$  using an optimization procedure that is described in a spreadsheet template annexed to the ISO 13752 (Annex A)<sup>17</sup>.

Systematic deviation (bias) of the test method is estimated by:

$$\Delta y = b_0 + (b_1 - 1)x \quad (7)$$

only when  $b_0$  and/or  $b_1$  are statistically different from their ideal values (at 95% confidence level) respectively equal to 0 and 1. The coefficients  $b_0$  and  $b_1$  are significantly different from their ideal values respectively if:

$$|b_0| - 2s_{b_0} > 0 \quad (8)$$

and

$$|b_1 - 1| - 2s_{b_1} > 0 \quad (9)$$

where  $s_{b_0}$  and  $s_{b_1}$  are the standard deviations of the regression coefficients.

The expanded uncertainty  $U$  of the test method with a coverage factor of 2 (*i.e.* at 95% confidence level) is given by:

$$U = 2\sqrt{s^2 + (\Delta y)^2} \quad (10)$$

**Table 11** Estimation of measurement uncertainties of the thermally desorbable radiello® using the active (pumped) method as reference (ISO 13752)

Compound	Model parameters	Concentration/ $\mu\text{g m}^{-3}$	$U(p = 0.95)/\mu\text{g m}^{-3}$	$U(p = 0.95) (\%)$
Benzene	$b_0 \pm s_{b0} = 0.028 \pm 0.233$	2.4	0.44	18.2
	$b_1 \pm s_{b1} = 0.991 \pm 0.059$	14.3	2.60	18.2
	$a_0 = 0.000$			
	$a_1 = 0.00003$			
	$a_2 = 0.091$			
Toluene	$b_0 \pm s_{b0} = 2.788 \pm 0.881$	9.1	3.64	40.0
	$b_1 \pm s_{b1} = 0.851 \pm 0.047$	48.1	9.14	19.0
	$a_0 = 0.000$			
	$a_1 = 0.35358$			
	$a_2 = 0.000$			
Ethylbenzene	$b_0 \pm s_{b0} = 0.031 \pm 0.322$	1.9	0.78	41.0
	$b_1 \pm s_{b1} = 0.992 \pm 0.087$	9.1	1.70	18.7
	$a_0 = 0.000$			
	$a_1 = 0.28227$			
	$a_2 = 0.000$			
<i>m</i> and <i>p</i> -xylene	$b_0 \pm s_{b0} = 0.219 \pm 0.823$	6.9	1.92	27.8
	$b_1 \pm s_{b1} = 0.980 \pm 0.062$	32.9	4.19	12.7
	$a_0 = 0.000$			
	$a_1 = 0.36557$			
	$a_2 = 0.000$			
<i>o</i> -Xylene	$b_0 \pm s_{b0} = 1.214 \pm 1.141$	2.0	1.57	78.4
	$b_1 \pm s_{b1} = 0.943 \pm 0.063$	12.1	2.57	21.2
	$a_0 = 0.000$			
	$a_1 = 0.44471$			
	$a_2 = 0.000$			

If both  $b_0$  and  $b_1$  are not statistically different from their ideal values, the expanded uncertainty is given by:

$$U = 2\sqrt{s^2} = 2s \quad (11)$$

Model parameters and expanded uncertainties are given on Table 11 (thermally desorbable radiello®) and Table 12 (solvent desorbable radiello®). Expanded uncertainties are calculated at the lowest and the highest concentration levels measured for each compound during the on-field campaigns.

In only two cases (toluene and *o*-xylene sampled with thermally desorbable radiello®) the slope  $b_1$  and the intercept  $b_0$  were statistically different from their ideal values, suggesting the existence of a systematic deviation (bias). For all other compounds the expanded uncertainty is dominated by the contribution of the variance function, whereas the bias is negligible.

Relative expanded uncertainties for benzene, both for thermally and solvent desorbable samplers, are independent on the

**Table 12** Estimation of measurement uncertainties of the solvent desorbable radiello® using the active (pumped) method as reference (ISO 13752)

Compound	Model parameters	Concentration/ $\mu\text{g m}^{-3}$	$U(p = 0.95)/\mu\text{g m}^{-3}$	$U(p = 0.95) (\%)$
Benzene	$b_0 \pm s_{b0} = 0.181 \pm 0.224$	2.4	0.42	17.4
	$b_1 \pm s_{b1} = 0.936 \pm 0.057$	14.3	2.49	17.4
	$a_0 = 0.000$			
	$a_1 = 0.000$			
	$a_2 = 0.081$			
Toluene	$b_0 \pm s_{b0} = -0.097 \pm 0.781$	9.1	1.89	20.8
	$b_1 \pm s_{b1} = 1.006 \pm 0.042$	48.1	4.33	9.0
	$a_0 = 0.000$			
	$a_1 = 0.31344$			
	$a_2 = 0.000$			
Ethylbenzene	$b_0 \pm s_{b0} = -0.053 \pm 0.266$	1.9	0.64	33.9
	$b_1 \pm s_{b1} = 0.987 \pm 0.072$	9.1	1.41	15.5
	$a_0 = 0.000$			
	$a_1 = 0.23361$			
	$a_2 = 0.000$			
<i>m</i> and <i>p</i> -xylene	$b_0 \pm s_{b0} = -0.053 \pm 0.519$	6.9	1.21	17.5
	$b_1 \pm s_{b1} = 1.006 \pm 0.039$	32.9	2.64	8.0
	$a_0 = 0.000$			
	$a_1 = 0.23045$			
	$a_2 = 0.000$			
<i>o</i> -Xylene	$b_0 \pm s_{b0} = 0.327 \pm 0.823$	2.0	0.72	36.2
	$b_1 \pm s_{b1} = 0.990 \pm 0.046$	12.1	1.78	14.7
	$a_0 = 0.000$			
	$a_1 = 0.32053$			
	$a_2 = 0.000$			



**Table 13** Comparison between measurement uncertainties under laboratory and on-field conditions (thermally desorbable radiello®)

Compound	Concentration / $\mu\text{g m}^{-3}$	$U\%$ laboratory conditions <sup>a</sup>	$U\%$ on-field conditions <sup>b</sup>
Benzene	5.27	19	18
Toluene	19.38	19	14
Ethylbenzene	3.92	30	29
<i>m</i> and <i>p</i> -xylenes	7.95	31	26
<i>o</i> -Xylene	4.65	27	27

<sup>a</sup> Source: Pennequin-Cardinal *et al.*<sup>20</sup> <sup>b</sup> Values extrapolated using eqn (4), (7), (10).

concentration level and they are always below the 30% at  $3.5 \mu\text{g m}^{-3}$  and 25% at higher concentrations required by the Annex VI of the 2000/69/EC European Daughter Directive on the maximum allowed uncertainty for benzene measurements.

The uncertainties found for benzene are comparable with the repeatability percent deviations (Tables 6 and 7) found with parallel measurements of replicate radiello® samplers, suggesting that the main factor contributing to the uncertainty of the method seems to be the random contribution (precision). For all the other compounds relative expanded uncertainty increases at lower concentration levels.

The on-field measurement uncertainties found following the treatment of the ISO 13752<sup>17</sup> agree with those found by other authors under laboratory conditions. A comparison between the uncertainties of the thermally desorbable sampler calculated in this work with those found by Pennequin-Cardinal under laboratory conditions is reported in Table 13.<sup>13</sup>

The agreement between the two different approaches is excellent. The relative expanded uncertainties were estimated by Pennequin-Cardinal for an exposure time of 7 days under laboratory conditions according to the method presented in the ISO GUM.<sup>16</sup> Our results show uncertainty values less than or equal to those found by Pennequin-Cardinal, even if we used measurements taken with different exposure times (from 2 to 14 days). This agrees with the results gathered on Tables 8 and 9, where the uptake rate of the samplers was found to be independent on the exposure time, with the exception of benzene for the thermally desorbable sampler. Anyway, the benzene uptake rate used in the calculations of uncertainty was corrected for the effect of the exposure duration, according to the model in Table 8.

## Conclusion

Radiello® diffusive samplers suitable for both thermal and solvent desorption have been tested during 15 on-field sampling campaigns, from August 2003 to April 2005, using active (pumped) samplers as a parallel reference method.

No statistically significant difference was found between new and regenerated cartridges used in thermally desorbable samplers.

The repeatability of measurements is always lower than 10%, for both thermally and solvent desorbable samplers, and it is independent on the sampling duration, at the 95% confidence level, for all the compounds.

Three tests were performed in order to estimate the effect of concentration, exposure time and air temperature on the uptake rates of the samplers using pumped adsorption on activated charcoal and solvent desorption as the reference method.

Benzene uptake rate for thermally desorbable radiello®, filled with graphitised charcoal (Carbograph 4), depends only on exposure time ( $-1.7\% \text{ day}^{-1}$ ), while neither temperature nor concentration seem to influence the uptake rate. For solvent desorbable radiello®, filled with activated charcoal, the uptake rate of benzene depends only on concentration level ( $-1.3\% (\mu\text{g m}^{-3})^{-1}$ ).

For toluene and the others mononuclear aromatics, both for thermally and solvent desorbable samplers, the only influencing parameter is the air temperature. For these compounds, the positive dependency of uptake rates with the temperature is largely explained by the fact, well reported in literature, that the diffusion coefficient in air  $D$ , depends on temperature following the relationship  $D \propto T^{3/2}$ .

Finally, ISO 13752 standard has been used to evaluate the uncertainty of the BTEX measurements under field conditions using the active (pumped) sampling method as reference. Expanded uncertainties for benzene, both for thermally and solvent desorbable samplers, largely meet the requirements of the Annex VI of the 2000/69/EC European Daughter Directive on the maximum allowed uncertainty for benzene measurements (25% at 1 LV).

According to these results, radiello® samplers, both for thermal and solvent desorption, seem to be an adequate and cost effective tool for on-field BTEX measurements.

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