Evaluation of Radello Diffuive Sampler Indicated for Thermal Desorption VOCs in Ambient Air

Evaluation of Radiello diffusive sampler indicated for thermal desorption for measuring VOCs in ambient air

E. Gallego[1], F.J. Roca[1], F.J. Perales[1], X. Guardino[2]

[1]Laboratori del Centre de Medi Ambient. Universitat Politècnica de Catalunya (LCMA-UPC). Avda. Diagonal, 647. E 08028 Barcelona. Phone: 34934016683, Fax: 34934017150, e-mail: Lcma.info@upc.edu

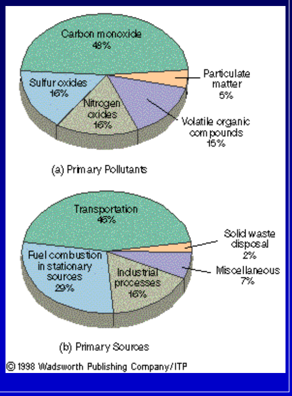
[2]Centro Nacional de Condiciones de Trabajo. INSHT. C/Dulcet, 2-10. E 08034 Barcelona. Phone: 34932800102, Fax: 34932803642, e-mail: cnctinsht@mtin.es

BACKGROUND

Odour episodes and environmental air quality are topics of worldwide concern.

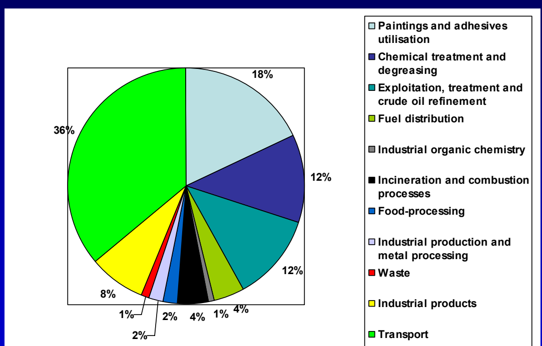
VOCs are responsible for odorous annoyance of varying degrees of nuisance and represent a threat to human health (irritation of mucous membranes, psychological stress and long-term toxic reactions) and comfort.

Sensitive, selective, fast and reliable methodologies are needed to sample and analyse pollutants in ambient air.



Laboratori del Centre de Medi Ambient- UPC

Most important VOC sources

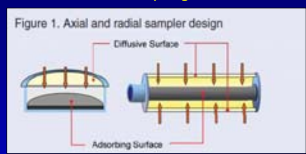


Source: Slovak Environmental Agency

Laboratori del Centre de Medi Ambient- UPC

Active sampling has been a traditional sampling technique used to determine pollutants in air; however, passive sampling is being an increasingly used technique for ambient air measurements, specially in urban environments

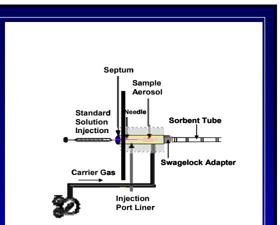
Active sampling | **Passive sampling**

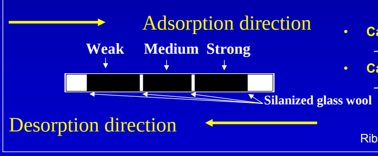


Laboratori del Centre de Medi Ambient- UPC

MATERIALS AND METHODS

Active sampling





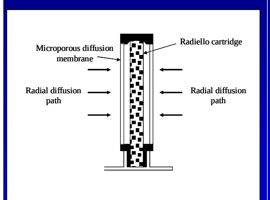
- Carbotrap (24/40 mesh, 70mg)
  - Weak sorption strength, hydrophobic
- Carbopack X (40/60 mesh, 100 mg)
  - Medium sorption strength
- Carboxen 569 (20/45 mesh, 90 mg)
  - High sorption strength

Ribes et al., 2007, J. Chr.A., 1140 (44-55)

Laboratori del Centre de Medi Ambient- UPC

Passive sampling

- Adsorbent cartridges filled with 350 mg Carbograph 4 (40/60 mesh) (Code 145)
- Yellow Radiello diffusive bodies (code 120-2)

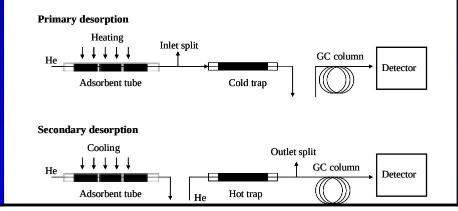


Laboratori del Centre de Medi Ambient- UPC

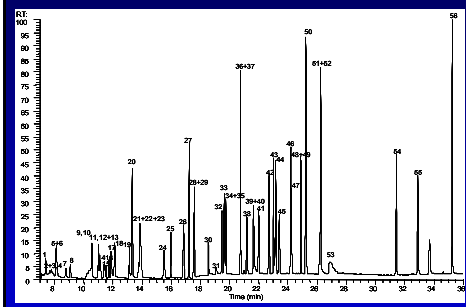
Thermal desorption

Instrumental settings and operating conditions.

TD		***GC***	
Desorption temp.:	300 ºC	Capillary column:	DB-624 (60 m x 0.25 mm x 1.4 µm)
Desorption time:	10 min	Temperature program:	40 ºC (1 min), 6 ºC/min until 230 ºC (5min)
Transfer line:	200 ºC	Carrier gas:	He (19.1 psi)
Cold trap sorbent	Tenax TA + Carbotrap	***MS***	
Cold trap low:	-30 ºC	Interface:	250 ºC
Cold trap high:	300 ºC	Ionization source:	200 ºC
Desorption flow rate:	He (50 ml/min)	Ionization mode:	Electron impact
Inlet split:	4 ml/min	Electron energy:	70 eV
Outlet split:	7 ml/min	Mass range	20 - 300 amu
Split ratio:	12 %		



MS analysis



Ethanol	1
Propanal	2
Acetone	3
Carbon disulfide	4
Methyl acetate	5
Isopropanol	6
Tert-butylmethylether	7
n-Hexane	8
Butanal	9
Ethyl acetate	10
Chloroform	11
Methylethylketone	12
Tetrahydrofuran	13
1,1,1-Trichloroethane	14
Cyclohexane	15
Carbon tetrachloride	16
Isobutanol	17
Benzene	18
1-Butanol	19
Trichloroethylene	20
Methylcyclohexane	21
Pentanal	22
Methyl methacrylate	23
Methylisobutylketone	24
Toluene	25
1,1,2-Trichloroethane	26
Tetrachloroethylene	27
Butyl acetate	28
Hexanal	29
N,N-Dimethylformamide	30
N-Methylformamida	31
Ethylbenzene	32
n-Nonane	33
m-Xylene	34
p-Xylene	35
o-Xylene	36
Styrene	37
Heptanal	38
2-Butoxyethanol	39
α-Pinene	40
Cyclohexanone	41
Propylbenzene	42
n-Decane	43
1,3,5-Trimethylbenzene	44
β-Pinene	45
1,2,4-Trimethylbenzene	46
Benzaldehyde	47
Isocyanatocyclohexane	48
Limonene	49
p-Dichlorobenzene	50
n-Undecane	51
Phenol	52
1-Octanol	53
Naphthalene	54
Isothiocyanatocyclohexane	55
2-Methylnaphthalene	56
1-Methylnaphthalene	57

Laboratori del Centre de Medi Ambient- UPC

Sampling strategy

Two main aspects of passive sampling strategy using Radiello passive samplers are discussed:

- a comparative between two types of sampling strategies, active and passive
- an evaluation of the effect of passive sampling exposition time

Sampling was done in three locations of Catalonia (Spain 2008): La Canonja, Constantí and Sant Adrià del Besós.

Active-Passive comparative (12 different places):

- active 24-hour samples (sampling flows between 80-120 ml min^{-1}).
- passive sampling with sampling periods ranging between 3 and 17 days

Sampling exposure time (only in La Canonja and Constantí):

- at each sampling location two Radiello samplers were exposed during 1 week (7 days). At the same time, one sampler was exposed during 4 days, replaced at the end of the 4th day for a new sampler that was exposed 3 days, leading to a total of 7 days of exposure.

Laboratori del Centre de Medi Ambient- UPC

RESULTS

Comparison of adsorbents used

-Only compounds with uptake rate values available (www.sigma-aldrich.com/radiello) were quantified in the passive Radiello samplers, even though much more compounds could be identified qualitatively.

-The comparison between active and passive samplings could only be referred to these compounds (Table 1).

-There were no significant differences in concentrations obtained between the two kinds of adsorbent tubes for:

- trichloroethylene (*t* test, $p \leq 0.05$)
- toluene (*t* test, $p \leq 0.05$)
- 1,2,4-trimethylbenzene (*t* test, $p \leq 0.05$)
- *p*-dichlorobenzene (*t* test, $p \leq 0.05$)
- *m*+*p*-xylene (*t* test, $p \leq 0.01$)
- BTEX (*t* test, $p \leq 0.05$)

-Hexane, tetrachloroethylene, butyl acetate, 1-metoxy-2-propanol, 2-ethylhexanol, benzene, ethylbenzene and *o*-xylene presented significant differences between the two adsorbents.

Laboratori del Centre de Medi Ambient- UPC

Table 1. Minimum and maximum, average concentrations (µg m^{-3}) and standard deviation values obtained for the studied compounds for both multi-sorbent tubes and Radiello tubes

	Min. Value		Max. Value		Average ± SD		Ratio
Compound	Multi-sorbent	Radiello	Multi-sorbent	Radiello	Multi-sorbent	Radiello	Multi-sorbent/Radiello
n-hexane	0.39	0.49	11.25	4.38	2.63 ± 2.74	1.56 ± 1.02	1.7
Trichloroethylene*	0.04	0.02	1.56	1.84	0.31 ± 0.44	0.41 ± 0.54	0.8
Tetrachloroethylene	0.13	0.51	5.69	22.08	1.09 ± 1.55	3.64 ± 6.35	0.3
Butyl acetate	0.16	0.33	5.28	5.15	0.94 ± 1.14	2.00 ± 1.38	0.5
1-metoxi-2-propanol	0.11	4.14	5.01	19.13	0.84 ± 1.06	11.10 ± 4.72	0.1
2-ethylhexanol	0.27	1.28	26.24	13.94	3.53 ± 5.92	5.65 ± 4.94	0.6
p-dichlorobenzene*	0.02	0.01	0.21	0.21	0.08 ± 0.06	0.09 ± 0.06	0.9
1,2,4-trimethylbenzene*	0.08	0.06	1.94	2.54	0.60 ± 0.76	0.68 ± 0.99	0.9
Toluene*	4.72	7.54	71.52	72.40	26.60 ± 22.58	32.59 ± 22.03	0.8
Benzene	0.11	0.42	1.93	3.94	0.58 ± 0.56	1.46 ± 1.06	0.4
m+*p*-xylene**	2.63	2.47	92.86	125.36	21.14 ± 29.94	32.33± 40.53	0.7
o-xylene	0.47	1.27	2.68	8.63	1.01 ± 0.73	4.20 ± 2.09	0.6
Ethylbenzene	0.65	1.65	34.49	49.87	7.10 ± 11.50	12.30 ± 17.13	0.6
BTEX*, a	8.58	6.30	157.61	186.12	48.26 ± 50.54	50.71 ± 60.17	1.0

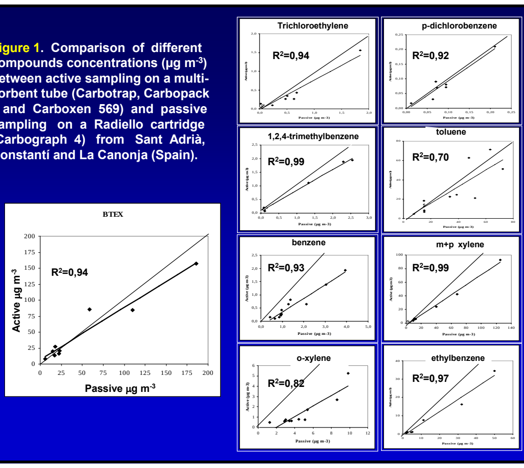
*Not statistical differences between the average values from multi-sorbent and radiello tubes were found, *t*-test, $p \leq 0.05$.
** Not statistical differences between the average values from multi-sorbent and radiello tubes were found, *t*-test, $p \leq 0.01$.
[a]BTEX = benzene + toluene + ethylbenzene + sum of xylenes

Comparison of sampling strategy (passive and active)

- Good agreement is observed between active and passive samplings for different types of compounds (Figure 1): being all studied correlations significant (Pearson correlation, $p \leq 0.01$).
- The correlation coefficients range from 0.70 to 0.99.
- Obtained passive concentrations are generally higher than active concentrations.
- Some compounds, such as benzene and *o*-xylene express relevant differences between active and passive sampling strategies.
- Passive samples represent the average of 3 to 17 days' VOCs concentrations, although active samples represent the average of 24-hour's VOCs concentrations during a particular day.
- In other studies, differences between concentrations in simultaneous active and passive strategies have also been found for benzene, toluene and xylenes, mainly due to atmospheric chemical reactions (Pilidis et al. 2005, Sunesson 2007).

Laboratori del Centre de Medi Ambient- UPC

Figure 1. Comparison of different compounds concentrations (µg m[-3]) between active sampling on a multi-sorbent tube (Carbotrap, Carbopack X and Carboxen 569) and passive sampling on a Radiello cartridge (Carbograph 4) from Sant Adrià, Constantí and La Canonja (Spain).



Influence of exposure/sampling time and air concentration levels in Radiello passive samplers

- In several studies it has been observed that in early stages of sampling, uptake rates are higher and, above a certain threshold limit, they decrease to a constant level.

- Uptake rate is regulated by the concentration gradient established between the surface of the adsorbent and the entrance of the diffusion zone of the sampling device.

- Air pollutant concentrations have also been found to be an important factor in uptake rates decrease, usually depending on the heaviness and volatility of the compound.

- In the present study, for tetrachloroethylene and toluene, the mass of compound summed from the samples of 4 and 3 days of exposure is higher than the mass of compound obtained by the samplers that stayed 7 consecutive days exposed (Table 2, Figure 3).

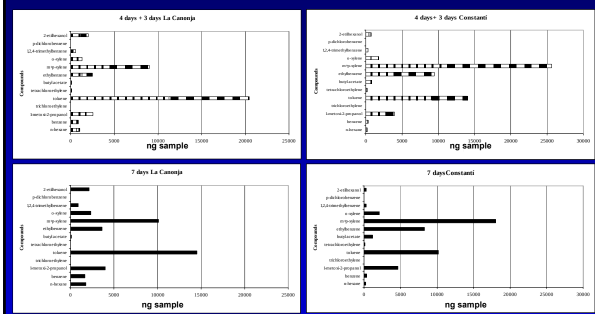
Laboratori del Centre de Medi Ambient- UPC

Table 2. Amount of sampled compound (ng in sample) coming from the samplings of 4+3 days and 7 consecutive days, and ratio between the two amounts.

	La Canonja			Constantí		
Compounds	4 + 3 days (ng sample)	7 days (ng sample)	4+3 days/7 days ratio	4 + 3 days (ng sample)	7 days (ng sample)	4+3 days/7 days ratio
2-etilhexanol	2004.6	2105.7 ± 458.5	1.0	719.2	324.4 ± 56.7	2.3
p-dichlorobenzene	48.0	41.7 ± 9.6	1.2	5.5	2.6 ± 0.7	2.2
1,2,4 trimethylbenzene	554.9	903.7 ± 184.4	0.6	309.6	290.1 ± 107.3	1.1
o-xylene	1274.4	2329.4 ± 351.6	0.6	1760.7	2126.4 ± 9.2	0.8
m+p-xylene	9005.9	10113.4 ± 759.9	0.9	25609.6	18051.9 ± 60.1	1.4
Ethylbenzene	2484.9	3628.3 ± 491.3	0.7	9451.9	8280.5 ± 23.2	1.1
butyl acetate	109.1	109.5 ± 37.9	1.1	829.7	1147.1 ± 162.3	0.7
Tetrachloroethylene	129.6	70.4 ± 7.7	1.9	199.3	128.5 ± 15.9	1.6
Toluene	20413.0	14505.7 ± 889.1	1.4	13989.9	10186.2 ± 637.1	1.4
Trichloroethylene	6.0	7.4 ± 3.0	0.9	15.4	14.7 ± 1.2	1.1
1-metoxi-2-propanol	2544.4	3978.1 ± 1409.8	0.7	3947.3	4660.0 ± 611.4	0.9
Benzene	901.0	1654.7 ± 529.6	0.6	335.6	358.9 ± 69.0	1.0
n-hexane	1011.8	1750.9 ± 430.6	0.6	206.0	235.7 ± 29.8	0.9

Laboratori del Centre de Medi Ambient- UPC

Figure 2 Total amount of different compounds (ng sample) adsorbed on Radiello cartridges exposed for a different number of days in La Canonja and Constantí (Spain) between 27-09-2008 and 4-10-2008.



Laboratori del Centre de Medi Ambient- UPC

Table 4. Ambient air concentrations (µg m[-3]) in La Canonja and Constantí (Spain) for 4 days, 3 days and 7 days, between 27-09-2008 and 4-10-2008.

	La Canonja (µg m[-3])			Constantí (µg m[-3])		
Compounds	4 d	3 d	7 d	4 d	3 d	7 d
2-etilhexanol	13.93	13.62	14.50 ± 3.16	5.54	4.32	2.27 ± 0.40
p-dichlorobenzene	0.19	0.24	0.19 ± 0.04	0.03	0.01	0.01 ± 0.003
1,2,4-trimethylbenzene	2.29	2.79	4.06 ± 0.83	2.29	0.22	1.32 ± 0.49
o-xylene	4.90	5.39	9.32 ± 1.41	5.14	9.84	8.63 ± 0.04
m+p-xylene	28.56	40.10	37.44 ± 2.81	74.38	125.36	67.80 ± 0.23
ethylbenzene	8.35	11.18	13.90 ± 1.88	26.94	49.87	32.19 ± 0.09
butyl acetate	0.45	0.42	0.44 ± 0.15	4.88	1.35	4.68 ± 0.66
Tetrachloroethylene	0.46	0.56	0.27 ± 0.03	0.64	0.98	0.51 ± 0.06
Toluene	63.19	72.40	47.61 ± 2.92	52.27	38.81	33.92 ± 2.12
Trichloroethylene	0.02	0.02	0.03 ± 0.001	0.07	0.04	0.05 ± 0.004
1-metoxi-2-propanol	10.58	7.77	14.73 ± 5.22	17.90	10.64	17.50 ± 2.30
Benzene	3.94	2.13	5.86 ± 1.88	1.37	0.98	1.29 ± 0.25
n-hexane	4.38	3.24	6.76 ± 1.66	0.84	0.76	0.92 ± 0.12

Laboratori del Centre de Medi Ambient- UPC

Table 5. Ratios between 4 and 7 days and between 3 and 7 days concentrations in La Canonja and Constantí (Spain), between 27-09-2008 and 4-10-2008.

	La Canonja (µg m[-3])		Constantí (µg m[-3])	
Compounds	4 d/7 d ratio	3 d/7 d ratio	4 d/7 d ratio	3 d/7 d ratio
2-etilhexanol	1.0	0.9	2.4	1.9
p-dichlorobenzene	1.0	1.3	3.0	1.0
1,2,4-trimethylbenzene	0.6	0.7	1.7	0.2
o-xylene	0.5	0.6	0.6	1.1
m+p-xylene	0.8	1.1	1.1	1.9
ethylbenzene	0.6	0.8	0.8	1.6
butyl acetate	1.0	1.0	1.0	0.3
tetrachloroethylene	1.7	2.1	1.3	1.9
toluene	1.3	1.5	1.5	1.2
trichloroethylene	0.7	0.7	1.4	0.8
1-metoxi-2-propanol	0.7	0.5	1.0	0.6
benzene	0.7	0.4	1.1	0.8
n-hexane	0.7	0.5	0.9	0.8

Laboratori del Centre de Medi Ambient- UPC

REMARKS

- One of the key aspects regarding air monitoring is to determine the suitability of the methodology chosen.

-The comparison between validated active air multi-sorbent tubes and Radiello diffusive samplers show no significant differences between the two methodologies for several compounds studied.

-For the Radiello passive sampler, relevant differences have not been observed between the sum of two shorter sampling periods (4 days + 3 days) and a longer sampling period (7 days).

-The Radiello diffusive sampler provides satisfactory quantitative measurements and is suitable for the determination of several VOCs in ambient air.

-Radiello passive sampler coupled with ATD-GC/MS is a simple to use, sensible and cheap method to assess ambient air concentrations of VOCs.

-More research has to be done to enhance the results obtained in this study.

Laboratori del Centre de Medi Ambient- UPC