COMPARATIVE STUDY OF THE ADSORPTION PERFORMANCE OF A MULTI-SORBENT BED (CARBOTRAP, CARBOPACK X, CARBOXEN 569) AND A RADIELLO® ADSORBENT TUBE FOR THE ANALYSIS OF VOCs

LABORATORI DEL CENTRE DE MEDI AMBIENT
(E.T.S. D'ENGINYERIA INDUSTRIAL BARCELONA)

E.Gallego[1], F. X. Roca[1], F. Perales[1], X. Guardino[2] and M. G. Rosell[2]

MINISTERIO DE TRABAJO E INMIGRACIÓN — INSTITUTO NACIONAL DE SEGURIDAD E HIGIENE EN EL TRABAJO

[1] Laboratori del Centre de Medi Ambient. Universitat Politècnica de Catalunya (LCMA-UPC). Avda. Diagonal, 647. E 08028 Barcelona

[2] Centro Nacional de Condiciones de Trabajo. INSHT. Dulcet 2-10. E 08034 Barcelona.

INTRODUCTION

Sensitive, selective, fast and reliable methodologies are needed to sample and analyse pollutants in ambient air. The sampling step is a critical part of ambient air analysis. Sampling strategy has to allow sample collection during a concrete period of time, giving the results as time-weighted average concentrations. In addition to that, the sampling strategy has to be easy and simple enough to permit a facile field sampling.

Both active and passive sampling strategies are suitable for determining low concentrations of pollutants in outdoor and indoor ambient air. Nowadays, passive sampling is being an increasingly used technique for ambient air measurements, specially in urban environments. In addition to that, the easy operability and low cost of passive samplers make them an ideal tool for long-time averaged pollution concentrations studies.

Good agreement correlations between passive and active samplings of pollutants have been found in several studies (Batterman et al., 2002; Yamamoto et al., 2002; McClenny et al., 2006; Strandberg et al., 2006). However, slight differences between concentrations have been found for some compounds (e.g. benzene, toluene and xylenes) due to atmospheric chemical reactions. Passive samples accumulate compounds during a large period of time (e.g. 7-10 days), whereas active sampling retains freshly emitted pollutants (Pilidis et al., 2005; Sunesson, 2007) .

In the present study, a comparison between the performance of two types of sampling strategies, active (multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569)) and passive (Radiello® diffusive sampler indicated for thermal desorption, filled with Carbograph 4), is done.

MATERIALS AND METHODS

Sampling

Daily duplicate 24 hour samples of multi-sorbent bed tubes were taken during a period of 14 days. On the other hand, during the same period of time, quadruplicate samples of Radiello® tubes were taken in 4 days, 3 days, 7 days and 14 days samples. The sampling was done indoors during the months of February-March 2010 in Tarragona city. Active sampling was done connecting the multi-sorbent bed tubes to an air collector pump sampler specially designed in the LCMA-UPC laboratory. The flow sampling rate was 70 ml min^{-1}.

Desorption and analysis

The analysis of VOCs was performed by Automatic Thermal Desorption (ATD) coupled with capillary Gas Chromatography (GC)/ Mass Spectrometry Detector (MSD), using a Perkin Elmer ATD 400 (Perkin Elmer, Boston, Massachusetts, USA) and a Thermo Quest Trace 2000 GC (ThermoQuest, San Jose, California, USA) fitted with a Thermo Quest Trace Finnigan MSD. VOCs standards were prepared in methanol and injected at 30˚C on the tubes under an inert Helium gas flow (100 ml min^{-1}) using a conventional gas chromatograph packed column injector (Ribes et al., 2007). The instrumental settings and operating conditions are shown in Table 1.

Table 1. - Instrumental settings and operating conditions.

TD		***GC***	
Desorption temp.:	300 ºC/370ºC	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 %		

Figure 1. Multi-sorbent bed tube

Figure 2. Radiello® tube

RESULTS AND DISCUSSION

Multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569)-Radiello® concentrations comparative

In Tables 2 and 3, the average concentrations for different periods both for multi-sorbent bed and radiello diffusive tubes are shown. Generally, only a few of the studied compounds do not show significant differences in the concentrations observed between the two different sampling methodologies, being higher the concentrations obtained with the Radiello® samplers (Figure 3). Daily variability of VOCs concentrations was observed through the multi-sorbent bed samples; hence, as Radiello® passive samplers represent the average concentration during a period of time, the daily variability may not be shown properly.

Table 2. Average ± standard deviation indoor air concentrations (µg m-3) for multi-sorbent bed tubes for each period sampled (*n* = 8 for 4 days periods; *n*= 6 for 3 days periods; *n*=14 for 7 days periods and *n*=28 for 14 days periods). Compounds are listed by elution order.

	Week 1			Week 2			Week 1+2
Compounds	**Days 1-4**	**Days 5-7**	**Days 1-7**	**Days 8-11**	**Days 12-14**	**Days 8-14**	**Days 1-14**
tert-Butyl methyl ether*	1.5 ± 0.6	1.2 ± 0.4	1.3 ± 0.5	1.4 ± 0.4	1.9 ± 0.4	1.6 ± 0.5	1.5 ± 0.5
n-Hexane*	18 ± 11	13 ± 2	16 ± 9	12 ± 6	20 ± 3	16 ± 6	16 ± 7
1,1,1-Trichloroethane*	0.02 ± 0.02	0.01 ± 0.01	0.02 ± 0.01	0.007 ± 0.002	0.02 ± 0.02	0.01 ± 0.01	0.01 ± 0.01
Cylcohexane	15 ± 11	6 ± 2	11 ± 10	4 ± 2	7 ± 6	5 ± 4	8 ± 8
Benzene*	8 ± 8	3 ± 1	6 ± 7	3 ± 2	4 ± 2	3 ± 2	4 ± 5
n-Heptane*	16 ± 13	10 ± 6	13 ± 11	6 ± 5	7 ± 3	6 ± 4	10 ± 9
Trichloroethylene*	0.02 ± 0.02	0.01 ± 0.01	0.02 ± 0.02	0.02 ± 0.02	0.008 ± 0.002	0.01 ± 0.02	0.02 ± 0.02
Toluene	105 ± 52	80 ± 47	94 ± 50	98 ± 40	83 ± 16	92 ± 32	93 ± 41
n-Octane	8 ± 5	5 ± 3	7 ± 5	7 ± 3	9 ± 3	8 ± 3	7 ± 4
Tetrachloroethylene*	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.04 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.1 ± 0.1
Butyl acetate*	0.6 ± 0.5	0.2 ± 0.2	0.4 ± 0.5	0.5 ± 0.3	0.77 ± 0.02	0.6 ± 0.3	0.5 ± 0.4
Ethylbenzene*	22 ± 16	9 ± 7	17 ± 15	11 ± 6	9 ± 4	10 ± 5	13 ± 11
n-Nonane*	2 ± 2	0.7 ± 0.4	2 ± 2	7 ± 7	1 ± 1	5 ± 6	3 ± 4
m+*p*-Xylene	87 ± 42	45 ± 28	69 ± 42	62 ± 21	57 ± 18	60 ± 20	64 ± 32
Styrene*	2 ± 1	0.7 ± 0.6	1 ± 1	0.9 ± 0.4	0.8 ± 0.4	0.9 ± 0.4	1.0 ± 0.7
o-Xylene*	26 ± 16	10 ± 7	19 ± 15	14 ± 6	14 ± 6	14 ± 6	17 ± 12
n-Decane	7 ± 2	4 ± 2	6 ± 3	4 ± 1	3 ± 2	4 ± 1	5 ± 2
1,2,4-Trimethylbenzene*	30 ± 13	12 ± 6	23 ± 14	14 ± 9	11 ± 5	13 ± 7	18 ± 12
p-Dichlorobenzene	2 ± 2	0.5 ± 0.3	2 ± 2	0.4 ± 0.2	0.2 ± 0.1	0.3 ± 0.2	1 ± 1
n-Undecane*	3 ± 2	0.8 ± 0.5	2 ± 2	0.8 ± 0.3	0.8 ± 0.3	0.8 ± 0.3	1 ± 1

Table 3. Average ± standard deviation indoor air concentrations (µg m-3) for Radiello® tubes for each period sampled (*n* = 4). Compounds are listed by elution order.

	Week 1			Week 2			Week 1+2
Compounds	**Days 1-4**	**Days 5-7**	**Days 1-7**	**Days 8-11**	**Days 12-14**	**Days 8-14**	**Days 1-14**
tert-Butyl methyl ether*	5 ± 1	2 ± 1	2.4 ± 0.1	3 ± 1	3 ± 1	3 ± 1	0.8 ± 0.2
n-Hexane*	23 ± 3	14 ± 2	19 ± 1	15 ± 4	19 ± 5	25 ± 2	20 ± 1
1,1,1-Trichloroethane*	0.7 ± 0.1	0.28 ± 0.04	0.67 ± 0.02	0.1 ± 0.1	0.2 ± 0.1	0.23 ± 0.04	0.19 ± 0.03
Cylcohexane	17 ± 2	8 ± 1	11.1 ± 0.4	4 ± 2	12 ± 3	13 ± 1	11.5 ± 0.4
Benzene*	15 ± 2	9 ± 2	10 ± 1	8 ± 2	9 ± 2	12 ± 1	6 ± 1
n-Heptane*	24 ± 2	19 ± 4	22 ± 1	12 ± 4	17 ± 3	24 ± 2	25 ± 1
Trichloroethylene*	0.07 ± 0.02	0.04 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	0.01 ± 0.01	0.032 ± 0.004	0.03 ± 0.01
Toluene	107 ± 4	86 ± 3	79 ± 1	109 ± 8	119 ± 7	105 ± 3	88 ± 2
n-Octane	10 ± 1	8 ± 1	8.5 ± 0.4	11 ± 2	9 ± 1	9 ± 1	5.8 ± 0.2
Tetrachloroethylene*	0.5 ± 0.1	0.2 ± 0.1	0.6 ± 0.1	0.10 ± 0.04	0.05 ± 0.02	0.18 ± 0.04	0.4 ± 0.1
Butyl acetate*	0.17 ± 0.03	0.08 ± 0.03	0.25 ± 0.01	0.13 ± 0.05	0.06 ± 0.03	0.25 ± 0.03	0.5 ± 0.1
Ethylbenzene*	38 ± 3	26 ± 5	24 ± 1	22 ± 5	20 ± 4	28 ± 2	31 ± 2
n-Nonane*	5 ± 1	3 ± 1	8 ± 1	11 ± 4	4 ± 1	13 ± 1	10 ± 2
m+*p*-Xylene	99 ± 5	63 ± 6	75 ± 2	75 ± 9	75 ± 6	84 ± 4	72 ± 5
Styrene*	8 ± 1	1.9 ± 0.3	2.49 ± 0.04	1.7 ± 0.2	1.8 ± 0.3	2.6 0.2±	2.1 ± 0.1
o-Xylene*	43 ± 3	24 ± 4	30 ± 1	30 ± 6	22 ± 4	35 ± 2	26 ± 1
n-Decane	8 ± 1	3 ± 1	6 ± 1	8 ± 3	5 ± 2	4 ± 1	6 ± 1
1,2,4-Trimethylbenzene*	37 ± 3	19 ± 5	31 ± 2	27 ± 8	21 ± 2	29 ± 3	34 ± 3
p-Dichlorobenzene	1.6 ± 0.3	0.7 ± 0.2	4.7 ± 0.4	0.8 ± 0.3	0.3 ± 0.1	1.0 ± 0.2	2 ± 1
n-Undecane*	5 ± 1	5 ±2	9 ± 2	4 ± 1	7 ± 2	6 ± 2	14 ± 7

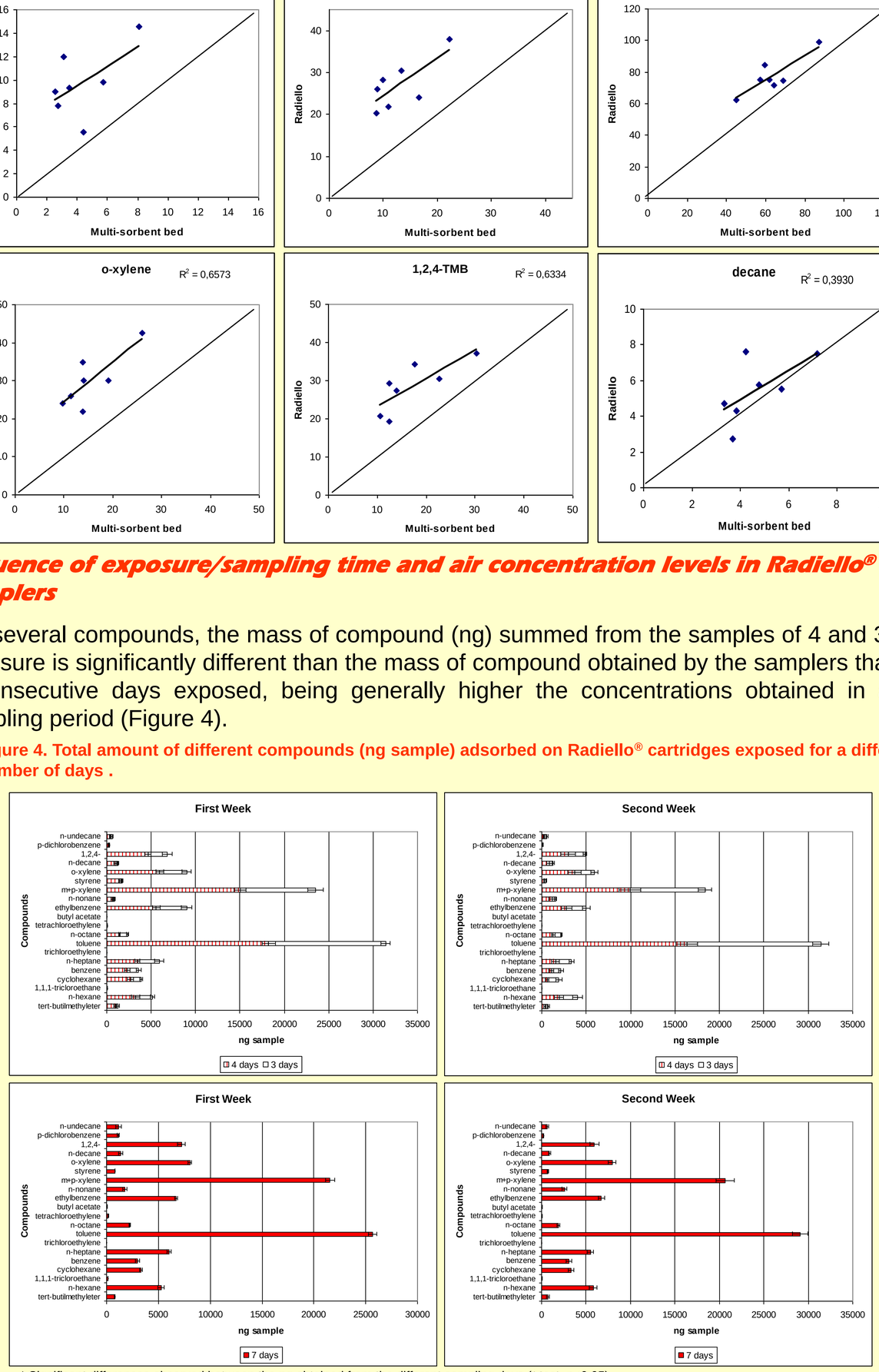
* Significant differences observed between the concentrations obtained from multi-sorbent bed and Radiello tubes for all samples (*t*-test, p<0.05).

Figure 3. Comparison of different compounds concentrations (µg m^{-3}) using multi-sorbent bed active tubes (Carbotrap, Carbopack X and Carboxen 569) and Radiello® passive tubes.

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

For several compounds, the mass of compound (ng) summed from the samples of 4 and 3 days of exposure is significantly different than the mass of compound obtained by the samplers that stayed 7 consecutive days exposed, being generally higher the concentrations obtained in a longer sampling period (Figure 4).

Figure 4. Total amount of different compounds (ng sample) adsorbed on Radiello® cartridges exposed for a different number of days .



* Significant differences observed between the ng obtained from the different sampling days (*t*-test, p<0.05).

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