Electronic Supplementary Material

New applications of the mathematical model of a permeation passive sampler: uptake rate correction and storage stability

Faten Salim,[a] Tadeusz Górecki*[a] and Marios Ioannidis[b]

[a.] *University of Waterloo, Department of Chemistry, 200 University Avenue West, Waterloo, ON, Canada N2L 3G1.*
[b.] *University of Waterloo, Department of Chemical Engineering, 200 University Avenue West, Waterloo, ON, Canada N2L 3G1.*
** Correspondig author. Email: tgorecki@uwaterloo.ca, Tel: +1 519 888 4567.*

Experimental

Waterloo Membrane Sampler (WMS)

The WMS (Figure S1-a) was prepared by filling a glass chromatographic vial with a certain amount of the adsorbent material. The PDMS membrane, cut into the size of the vial opening, was then fixed in place at the vial's mouth using a polytetrafluoroethylene (PTFE) washer and an aluminium crimp cap. Two sizes of chromatographic vials, with different sampling areas, were used in this evaluation: a regular 2-ml vial (C223682C, Chromatographic Specialties Inc., Brockville, ON, Canada) filled with approximately 250 mg of the adsorbent, and a 300-µL microvial (round bottom microvial, C2211051, Chromatographic Specialties Inc.) filled with approximately 93 mg of the adsorbent. The sorbent used was Carbopack B™, which is a non-porous adsorbent made of graphitized carbon black obtained from Supelco, Sigma-Aldrich (Oakville, Ontario, Canada). The process of fabrication of the PDMS membrane is described elsewhere.[1] The thickness of the membrane was controlled through weight. The membranes were always cut using the same die for a given sampler geometry, hence their surface areas were constant and reproducible. The target weight of the membrane for the 2-mL WMS was 8.0 ± 0.5 mg to obtain a 100-µm thick membrane, and 16.0 ± 0.5 mg to obtain a 200-µm thick membrane. The PTFE washers for this size of the sampler were of the dimensions 0.040" × 0.440" × 0.216" (thickness × OD × ID) (virgin PTFE, purchased from Penn Fibre Plastics, Bensalem, PA, US). The target weight of the PDMS membrane for the microvial WMS was 3.7 ±

0.2 mg to obtain a 100-µm thick membrane, and the PTFE washers used for this version were of the dimensions 0.040" × 0.281" × 0.188" (thickness × OD × ID), purchased from the same vendor.

Experimental procedure

Uptake rate prediction method

In the setup used for the experimental evaluation, purified nitrogen gas flowed at a rate of 896 mL/min controlled by a mass flow controller. The nitrogen flow was passed through an analyte vapor generator, which consisted of a flow-through vessel containing a custom-made permeation vapor source. To control the vapor concentration, the vessel was placed inside a GC oven used as a tool for controlling the temperature and, therefore, controlling the vapor concentration. The standard gas was then passed through a thermostated chamber consisting of a 10-liter cylindrical glass jar with a circulation fan inserted through the center of the top cover. Holes were drilled in the top cover to insert the samplers. They were kept closed before and during the exposure. The temperature was controlled by wrapping the glass jar with Tygon tubing connected to a water circulation thermostat and insulating it with an insulating jacket. The concentration was measured actively either by direct injection of a 1 ml sample of the standard gas, drawn using a gas-tight syringe, into the GC in splitless mode, or by passing 10 ml of the standard gas through a sorption tube packed with Carbopack B using a gas-tight syringe. In the latter method, the sorption tube was analyzed in the same manner as the sorbent of the passive sampler (WMS). In all the experiments, the sorbent from the WMS was transferred after the exposure into a pre-cleaned thermal desorption tube and was sandwiched between two layers of thermally cleaned glass wool. The packed tube was transferred afterwards to a thermal desorption unit connected to a GC-MS system for analysis.

Additional experiments were conducted by exposing the WMS to an atmosphere containing trichloroethylene (TCE) vapour using the experimental setup described above. TCE vapour was obtained by passing nitrogen gas through a vessel containing a TCE permeation source (the chemical purchased from Sigma-Aldrich, Canada Co. Oakville, Ontario). Active samples of the TCE vapour were collected by drawing the vapour through a sorption tube

packed with 200 mg of Anasorb 747 (SKC Inc., USA) using AirCheck® sampling pump (XR5000, from SKC Inc.). Anasorb 747 was transferred for analysis to a 4 mL glass vial with an open-top screw cap and a PTFE/Silicone septum (purchased from Fisher Scientific, Ottawa, Ontario). The vial was placed in an ice bath while adding 1 ml of carbon disulfide (purchased from Sigma-Aldrich) for desorption. Keeping the vial sealed, it was subsequently left for 40 min at ambient temperature with intermittent shaking. An aliquot of the extract was then transferred to a 2 mL crimp top chromatographic vial with a 100 µL glass insert (purchased from Chromatographic Specialties Inc.). Analysis was performed using an Agilent 6890 GC- 5973 MS system in all experiments in this paper. Direct solvent injection was used to inject the carbon disulfide extract aliquots using a 7683 Agilent autosampler with a tray of 100-sample capacity and a Hewlett Packard 3683 injector. The inlet was set to 290 °C with a 1:10 split ratio. The oven temperature program started at 90 °C, which was held for two minutes before it was increased to a final temperature of 280 °C at a rate of 30 °C/min (no hold). Selected Ion Monitoring (SIM) was used targeting the ions with m/z of 95, 130, and 60.

Evaluation of the post-sampling period

Calibration

A 1-µl aliquot of each standard was spiked into a bed of approximately 250 mg of Carbopack B packed in between two layers of glass wool in a sorption tube. The tubes with the standards were analysed using the same method used to analyse the sorbent from the WMS. Standards of 29 VOCs in methanol, in one set of the experiments, were spiked into a flow of helium through the sorbent bed at a flow rate of 78 ml/min for one minute.

Chemicals

All standards were prepared in methanol, HPLC grade (≥99.9%), purchased from Sigma-Aldrich (Oakville, Ontario, Canada). All chemicals used in this evaluation were of a ≥ 99 % purity and were also purchased from Sigma-Aldrich. These chemicals included benzene, anhydrous toluene, trichloroethylene, tetrachloroethylene, 11-dichloroethane, *cis*-1,2-dichloroethylene, chloroform, 1,1,1-trichloroethane, 1,2-dichloropropane, 1,1,2-trichloroethane, dibromochloromethane, 1,2-dibromomethane, chlorobenzene, ethylbenzene, *p*-xylene (anhydrous), *o*-xylene, 1,1,2,2-tetrachloroethane, 1,2,3-trichloropropane, propylbenzene, *tert*-

butylbenzene, *sec*-butylbenzene, 1,2-dichlorobenzene, 1,3-dichlorbenzene, 1,4-dichlorobenzene, 1,2,3-trichlorobenzene, isopropylbenzene (cumene), 1,2,4-trimethylbenzene (pseudocumene), 1,2,4-trichlorobenzene, and naphthalene. Two pressurized cylinders containing mixtures of VOCs were used. The first cylinder was obtained from Air Liquide (Plumsteadville, PA, USA), while the second cylinder contained a mixture of 29 VOCs custom-made in pressurized nitrogen.

Experimental setup

The experimental setup used to expose the samplers to an atmosphere with a single analyte was similar to that presented in Ref. 2 and is illustrated in Figure S3. In this setup, nitrogen gas was purified by passing it through an activated charcoal bed before it reached a mass flow controller (MKS, Andover, MA, 0-100 mL/min, model # 1179A12CR1BV--S). This controller was connected to an MKS 4-channel readout system (Andover, MA, Type 247) to set and monitor the flow rate. The nitrogen gas was then directed through an analyte vapor generator at a rate of 100 mL/min. The vapor generator consisted of a flow-through vessel containing a vapor source, which was either a custom-made PTFE permeation tube filled with the pure analyte, or a diffusion source prepared by filling a chromatographic vial with a neat analyte and sealing it with an open-top cap equipped with a Teflon/Silicon septum penetrated by a deactivated fused silica capillary acting as a diffusion barrier. The length and the diameter of the capillary varied depending on the desired concentration and the volatility of the analyte. The flow-through vessel was placed inside a GC oven as a method of controlling the vapor concentration via controlling the temperature. The standard gas was then passed through an approximately 4-m long copper tube of a 1/8" OD before it entered the exposure cell. A 1 L, 3-neck, round-bottom flask was used as the exposure cell, with the standard gas entering the cell through one side neck and flowing to the other side neck. The standard gas was then directed to the fume hood using a flexible tube. The WMS were inserted through the top neck into the exposure cell and hanged using thin fishing lines. The top cap was kept closed at all times and only opened shortly during sampler insertion and removal. To evaluate the concentration of the standard gas, active samples were collected by switching a three-way valve, connected before the exposure cell, to allow the standard gas to flow through a sorption tube packed with

Carbopack B for a controlled time. The other end of the sorption tubes was connected to a bubble flow meter to measure the flow.

For the experiments in which the samplers were exposed to an atmosphere of a mixture of VOCs, a similar setup was used except that a cylinder containing a pressurized standard gas mixture of VOCs in nitrogen was used as a vapour source. The flow of this standard gas was controlled using a mass flow controller (MKS, range 50 SCCM) connected to the 4-channel readout system. The standard gas mixture flowed through a stainless steel three-way connector to be diluted with nitrogen gas flowing at a controlled flow rate, as explained earlier. The diluted standard gas entered the exposure cell in the manner explained above. In one set of experiments, the standard gas mixture, containing seven VOCs, flowed at a rate of 9.8 ml/min. This standard gas was diluted with nitrogen gas flowing at a rate of 82 ml/min. In the other set of experiments, the standard gas mixture, containing a mixture of 29 VOCs, flowed at a rate of 20.8 ml/min to be diluted with the nitrogen gas flowing at a rate of 81 ml/min.

Instruments

Initial experiments were conducted by exposing the microvial-based WMS to a vapor of a single VOC in nitrogen. In these experiments, a manual Dynatherm thermal desorption (TD) unit (model 9300 ACEM, CDS Analytical, Oxford, PA, USA) was used for sorbent analysis. This TD unit was equipped with a single glass sorbent tube, 8 mm OD × 6 mm ID × 114 mm length, with a glass frit. In later experiments, in which the regular 2 ml vial WMS were exposed to mixtures of VOCs, an automated Perkin Elmer thermal desorption unit (ATD 400) was used for desorption. The TD unit was equipped with stainless steel desorption tubes, 6.35 mm OD and 90 mm long. The TD unit in both cases was connected to an Agilent 6890 GC-5973 MS system. The Dynatherm TD unit was connected to the GC-MS system through a heated transfer line inserted into the GC injector, whereas the heated transfer line of the Perkin Elmer TD unit was connected to the column of the GC using a press-tight universal connector (Restek, Bellefonte, PA, USA). An Rxi®-624Sil MS capillary column was used in the GC (60 m × 0.32 mm ID × 1.8 µm film thickness) purchased from Restek (Bellefonte, PA). Helium was used as the carrier gas. Data acquisition and processing were achieved using ChemStation software (Enhanced ChemStation

G1701CA, Version C.00.00 21-Dec-1999, Agilent Technologies). This software was also employed for calibration and quantification using multi-point calibration curve.

TD-GC-MS methods

In all the experiments using the Dynatherm TD unit, the sorption tube was thermally desorbed at 330 °C for 7 min with the focusing trap held at ambient temperature. Tube cooling for 1 min followed desorption before heating the focusing trap to 300 °C for 5 min. Tubes with the standards were desorbed after a solvent drying step lasting 1 min. The GC inlet was set to 250 °C with a split ratio of 1:10 and a 1 mL/min carrier gas flow through the column. The parameters in the Perkin Elmer TD unit were set as follows: the tube was first purged with helium for one minute. The desorption temperature was 330 °C, which was held for five minutes, and the trapping temperature was -16 °C, which was held for 5 min. No split was applied and the desorption flow was set to 22.7 ml/min. The carrier gas pressure was set to 120 kPA. Table S2 details the GC-MS methods in the three sets of experiments, in which toluene, p-xylene, and 1,2,4-trichlorobenzene were sampled and analyzed separately.

In the following sets of experiments, the WMS was used to sample a mixture of VOCs starting with a mixture of seven VOCs followed by a more complex mixture containing 29 VOCs. Pekin Elmer TD unit, used in these experiments, was operated using the method explained above. For the first mixture (seven VOCs), the composition, GC oven temperature program and MS SIM method are described in Table S3, while data for the latter mixture (29 VOCs) are presented in Table S4.

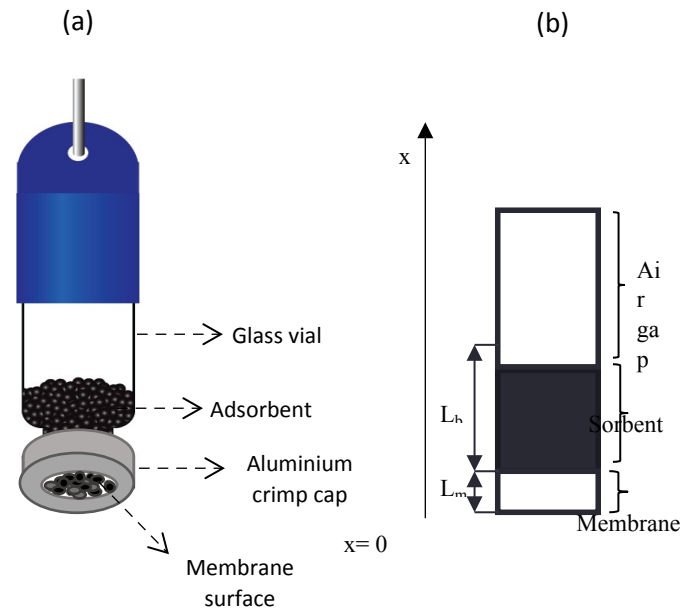

Figure S1: The Waterloo Membrane Sampler (WMS) (a), and the conceptual representation of the WMS used in the model (b) (based on ref.[2]).

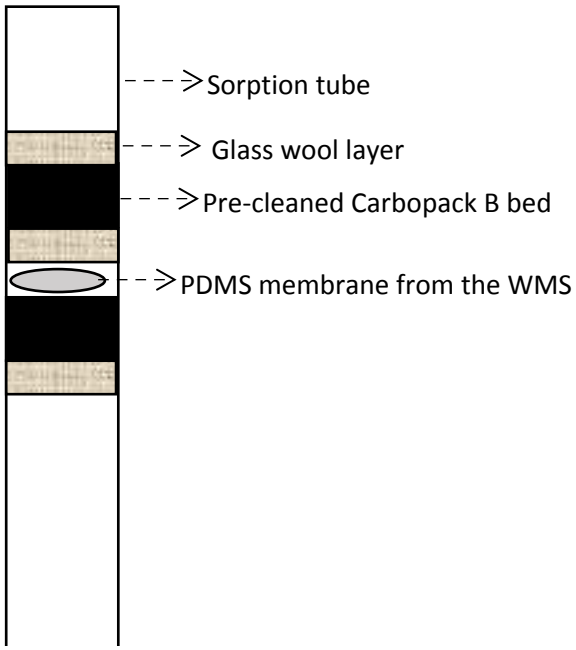

Figure S2: Schematic diagram of the WMS membrane prepared for analysis in a thermal desorption tube

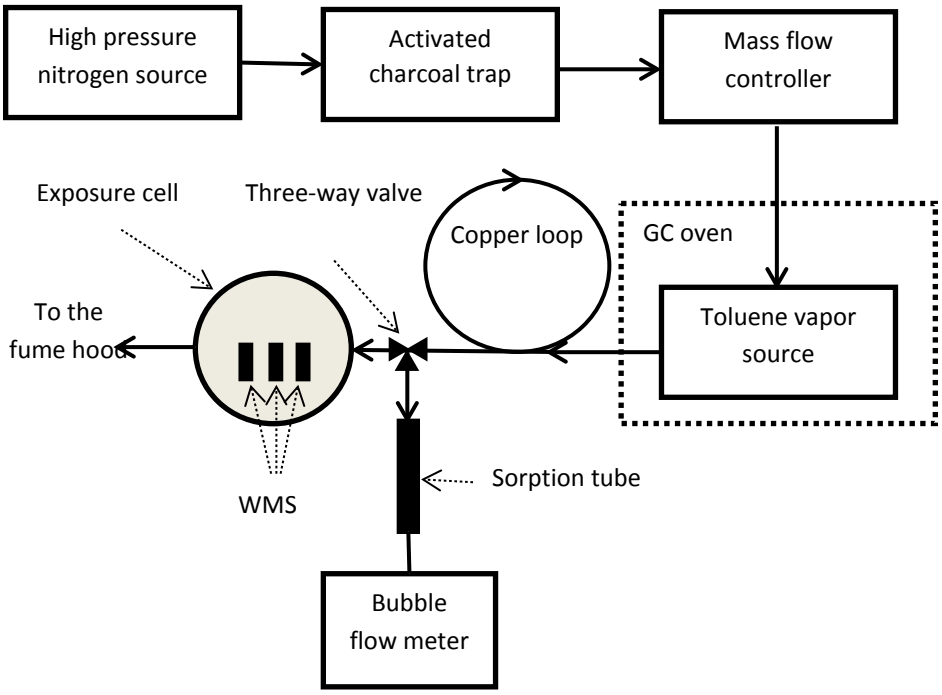

Figure S3: Apparatus used in experimental evaluation [2]

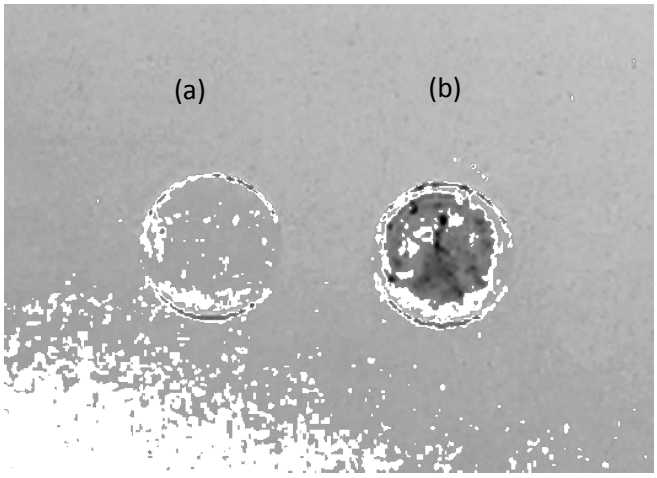

Figure S4: An image of the PDMS membrane before sampling (a) and after sampling (b) when Carbopack B was used as the adsorbent

Table S1: Values of parameters used in the uptake rate prediction method

Symbol	Description	Value	
	Compound	Toluene	TCE
L_m	Membrane thickness (m)	1×10^{-4}	1×10^{-4} & 2×10^{-4}
L_b	Sorbent bed thickness (m)	1.4×10^{-2}	
A_m	Membrane sampling area (m^2)	34.5×10^{-6}	
D_m	Diffusion coefficient in the membrane (m^2/sec)	1.07×10^{-10}(ref.[3-7])*	4.81×10^{-10}(ref.[8,9])*
K	Partition coefficient between air and the membrane material (dimensionless)	843 (ref.[10, 11])*	621 (ref.[12])
D_a	Diffusion coefficient in air (m^2/sec)	8.5×10^{-6}(ref.[13])	8.75×10^{-6}(ref.[14])
D_{eff}	Effective diffusion coefficient in the sorbent bed (m^2/sec)	2.11×10^{-6}	2.17×10^{-6}
ε	Sorbent bed porosity (dimensionless)	0.40	
τ	Tortuosity (dimensionless)	1.61	
α	Specific surface area (m^2/m^3)	$11226 \times 10^{+4}$	
k_c	Mass transfer coefficient (m/sec)	0.0198	0.0204
d	Sorbent particle diameter (m)	2.135×10^{-4}	
a	Parameter for the isotherm $C^* = a \times q^b$	7.67×10^{-6}(ref.[15])	9.78×10^{-6}
b	Parameter for the isotherm $C^* = a \times q^b$	1.566 (ref.[15])	1.60

**An average value from the references listed*

Table S2: GC-MS method used in the initial experiments with a single analyte sampled from a nitrogen atmosphere

Experiment number	Analyte	GC oven Program		MS mode	Ions/Scan range (m/z)
1	Toluene	Initial temperature	90 °C	SIM	65, 91
		Hold	5 min		
		Next ramp	50 °C/min		
		Next temperature	300 °C		
		Hold	1 min		
2	*p*-xylene	Initial temperature	90 °C	Scan	50-550
		Hold	2 min		
		Next ramp	30 °C/min		
		Next temperature	300 °C		
		Hold	7 min		
3	1,2,4-trichlorobenzene	Initial temperature	90 °C	Scan	50-550
		Hold	2 min		
		Next ramp	30 °C/min		
		Next temperature	300 °C		
		Hold	7 min		

Table S3: GC-MS method used in the analysis of the samples containing a mixture of seven analytes

GC oven Program		Compound	Ions (m/z)
Initial temperature	35 °C	Trichloroethylene	95, 130, 60
Hold	2 min	Tetrachloroethylene	166, 131, 194
Next ramp	30 °C/min	1,2,4-Trimethylbenzene	105, 120
Next temperature	300 °C	1,4-dichlorobenzene	146, 111, 75
Hold	3.5 min	1,2-Dichlorobenzene	146, 111, 75
		1,2,4-Trichlorobenzene	180, 145, 109

Table S4: GC-MS method used in the analysis of the samples containing a mixture of 29 analytes

GC oven Program		Compound	Ions (m/z)
Initial temperature	35 °C	1,1-Dichloroethane	63, 83
Hold	5 min	cis-1,2-Dichloroethylene	61, 96
Next ramp	4 °C/min	Chloroform	83
Next temperature	280 °C	1,1,1-Trichloroethane	97, 61
Hold	10 min	Benzene	78, 77
		1,2-Dichloroethane	62, 64
		Trichloroethylene	95, 130
		1,2-Dichloropropane	63, 76
		Toluene	91, 92
		1,1,2-Trichloroethane	97, 83
		Tetrachloroethylene	166, 131
		Dibromochloromethane	129
		1,2-Dibromoethane	107
		Chlorobenzene	112, 77
		Ethylbenzene	91, 106
		p-Xylene	91, 106
		o-Xylene	91, 106
		Isopropylbenzene	105, 120
		1,1,2,2-Tetrachloroethane	83
		1,2,3-Trichloropropane	75, 110
		Propylbenzene	91
		tert-Butylbenzene	119, 91, 134
		1,2,4-Trimethylbenzene	105, 120
		sec-Butylbenzene	105, 134
		1,2-Dichlorobenzene	146, 111, 75
		1,4-Dichlorobenzene	146, 111, 75
		1,3-Dichlorobenzene	146, 111, 75
		1,2,4-Trichlorobenzene	182, 180, 145
		1,2,3-Trichlorobenzene	182, 180, 145

Table S5: Amounts of analytes detected in the adsorbent and percent amounts detected in the membrane after different storage times (uncertainties represent 95 % confidence intervals).

Analyte	Exposure concentration (mg/m^3)	Exposure time (hour)	**Storage time (hour)**	**0.08**		**2**		**4**		**24**		**48**		**72**	
				Amount (µg)	***Fraction (%)***	**Amount (µg)**	***Fraction (%)***	**Amount (µg)**	***Fraction (%)***	**Amount (µg)**	***Fraction (%)***	**Amount (µg)**	***Fraction (%)***	**Amount (µg)**	***Fraction (%)***
Toluene	9.07	2	**Amount detected in the sorbent (µg)/ *Fraction detected in the membrane (%)***	1.3 ± 0.3	*0.35 ± 0.20*	1.3 ± 0.3	*0.04 ± 0.15*	1.3 ± 0.2	*0.07 ± 0.0.19*	1.3 ± 0.2	*0.01 ± 0.18*	1.37 ± 0.06	*0.11 ± 0.28*	1.4 ± 0.3	*0.03 ± 0.06*
	77.6	1		6.8 ± 0.4	*0.26 ± 0.18*	7.0 ± 0.7	*0.22 ± 0.26*	7 ± 5	*0.02 ± 0.00*	6.5 ± 0.3	*0.27 ± 0.13*	7.3 ± 0.9	*0.09 ± 0.14*	7.0 ± 1.0	*0.10 ± 0.19*
1,2,4-Trichlorobenzene	20.7	1		4 ± 1	*1.8 ± 3.3*	4.35 ± 0.40	*0.29 ± 0.80*	4 ± 1	*0.01 ± 0.04*	4.2 ± 0.3	*0.0 ± 0.0*	4.9 ± 0.4	*0.0 ± 0.0*	4.2 ± 0.5	*0.21 ± 0.89*
	7.6	1		1.2 ± 0.6	*2.5 ± 6.2*	1.6 ± 0.6	*0.84 ± 0.33*	1.5 ± 0.6	*0.24 ± 0.53*	2 ± 1	*0.6 ± 1.5*	1.6 ± 0.9	*0.04 ± 0.12*	2 ± 1	*1.0 ± 3.7*
***p*-Xylene**	33.5	1		4 ± 1	*0.30 ± 0.16*	4.2 ± 0.5	*0.18 ± 0.06*	4.3 ± 0.8	*0.18 ± 0.04*	4.0 ± 0.3	*0.17 ± 0.06*	4.0 ± 0.4	*0.16 ± 0.03*	4 ± 1	*0.15 ± 0.02*
	88.6	1	**Storage time (hours)**	**0.08**		**2**		**4**		**27**		**49**		**94**	
				Amount (µg)	***Fraction (%)***	**Amount (µg)**	***Fraction (%)***	**Amount (µg)**	***Fraction (%)***	**Amount (µg)**	***Fraction (%)***	**Amount (µg)**	***Fraction (%)***	**Amount (µg)**	***Fraction (%)***
			Amount detected in the sorbent (µg)/ *Fraction detected in the membrane (%)*	12 ± 8	*0.45 ± 0.27*	15 ± 9	*0.09 ± 0.40*	13 ± 2	*0.03 ± 0.05*	15 ± 1	*0.025 ± 0.009*	14 ± 6	*0.04 ± 0.09*	11 ± 5	*0.05 ± 0.07*

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