Supporting Information

Fully Automated Online Dynamic In-Tube Extraction for Continuous Sampling of Volatile Organic Compounds in Air

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Reagents and materials

Dimethyl sulfide (≥99%), hexanal (98%), furfural (99%), octanal (99%), nonanal (≥95%), decanal (≥98%), 2-methylimidazole (99.9%), methyl isobutyl ketone (98.5%), delta-3-carene (90%), ethylbenzene (99%), isoprene (99%), 2-butanone (≥99.5%), dimethylformamide (99.9%), polyvinyl pyrrolidone (M_w=1 300 000), acetaldehyde (≥99.5%), carbon disulfide (≥99%), 2-ethyl-1-hexanol (≥99.6%), p-xylene (99%), p-cymene (99%), 1-butanol (99.8%), 2-methyl-1-butanol (≥98.0%), polyacrylonitrile (M_w=150 000), decafluorobiphenyl (99%) and acetonitrile (HPLC grade) were purchased from Sigma-Aldrich (St. Louis, USA). Acetone (≥99%), ethanol (100%) and toluene (HPLC grade) were from VWR Chemicals (Pennsylvania, USA). 1-Propanol (HPLC grade) was from Rathburn Chemicals Ltd (Walkerburn, Scotland). Sodium chloride (NaCl) (99.6%) and methanol (LC/MS grade) were from Fisher Scientific (Loughborough, Leicestershire, UK). Heptanal (>95%), longifolene (≥99%), tridecane (GC grade), tetradecane (GC grade), alpha-pinene (≥98%), benzaldehyde (≥99%) and 3-pentanone (99%) were from Fluka (The Netherlands). Tetrahydrofuran (≥99.9%) and ethyl acetate (≥99.7%) were from Honeywell (Honeywell GmbH, Seelze, Germany) and cyclohexane was from Hopkin&Williams Ltd (London, UK). Hexylcyclohexane (>98%), tert-butyl ethyl ether (>95%), 1,4-dimethyl cyclohexane (>98%), 1-undecene (>99.5%) and 4-methyl-1-hexene (>99%) were from Tokyo Chemical Industry Ltd (Tokyo, Japan). Allyl methyl sulfide (98%), methyl propyl sulfide (99%) and 2-pentylfuran (98%) were from Alfa Aesar (Karlsruhe, Germany). Acetophenone was from The British Drug Houses Ltd (Poole, England) and $Zn(NO_3)_2{\cdot}4H_2O$ was from Merck (98.5%).

Individual stock solutions were 1000 μg mL^{-1} in methanol and stored at -20 °C. The standard solution was prepared by mixing the individual stock solutions and diluted by ultrapure water (Millipore DirectQ-UV, Billerica, MA, USA) to 1 μg mL^{-1} and stored in the refrigerator at +4 °C. Fresh standard solutions were prepared every day. The 20 mL headspace vials were purchased from Agilent Technologies (Germany).

Instruments and GC-MS analysis

The GC-MS analysis was carried out with an Agilent 6890N gas chromatograph coupled with an Agilent 5975C mass selective detector (Agilent Technologies, Palo Alto, USA). An InertCap™ for Amines capillary column (30 m length with 0.25 mm i.d., GL Sciences, Tokyo, Japan) was utilized for the chromatographic separation. The GC-MS conditions for the analysis were as follows: oven temperature was programmed from 40 °C (held for 2 min) to 250 °C (held for 10 min) at a rate of 20 °C min^{-1}; injector, transfer line, ion source and quadrupole temperatures were 250, 250, 230 and 150 °C, respectively. Splitless injection was used for all experiments. Electron ionization (EI) mode (70 eV) was utilized (m/z, 15-350). Helium (99.996%, AGA, Espoo, Finland) was used as the carrier gas at a constant flow rate of 1.2 mL min^{-1}.

ITEXs packed with Tenax TA/Carbosieve S-III, Tenax GR, Tenax TA, Carbosieve S-III and Carboxen 1000, and the PAL RTC auto-sampler were kindly provided by CTC Analytics AG (Zwingen, Switzerland). Blank ITEXs were from BGB Analytik AG (Zurich, Switzerland). The surface morphologies of the nanofibers were studied by scanning electron microscopy (SEM) (Hitachi, model S-4800, Japan) and a 4 nm Au/Pd layer was sputtered onto the nanofibers in advance. The average diameters of nanofibers were determined by Image J software from the SEM images by measuring 100 individual nanofibers in each sample. Thermogravimetric analysis (TGA) was carried out at a ramp rate of 10 °C min^{-1} under the nitrogen flow with a Mettler Toledo Stare system equipped with a TGA 850 thermobalance.

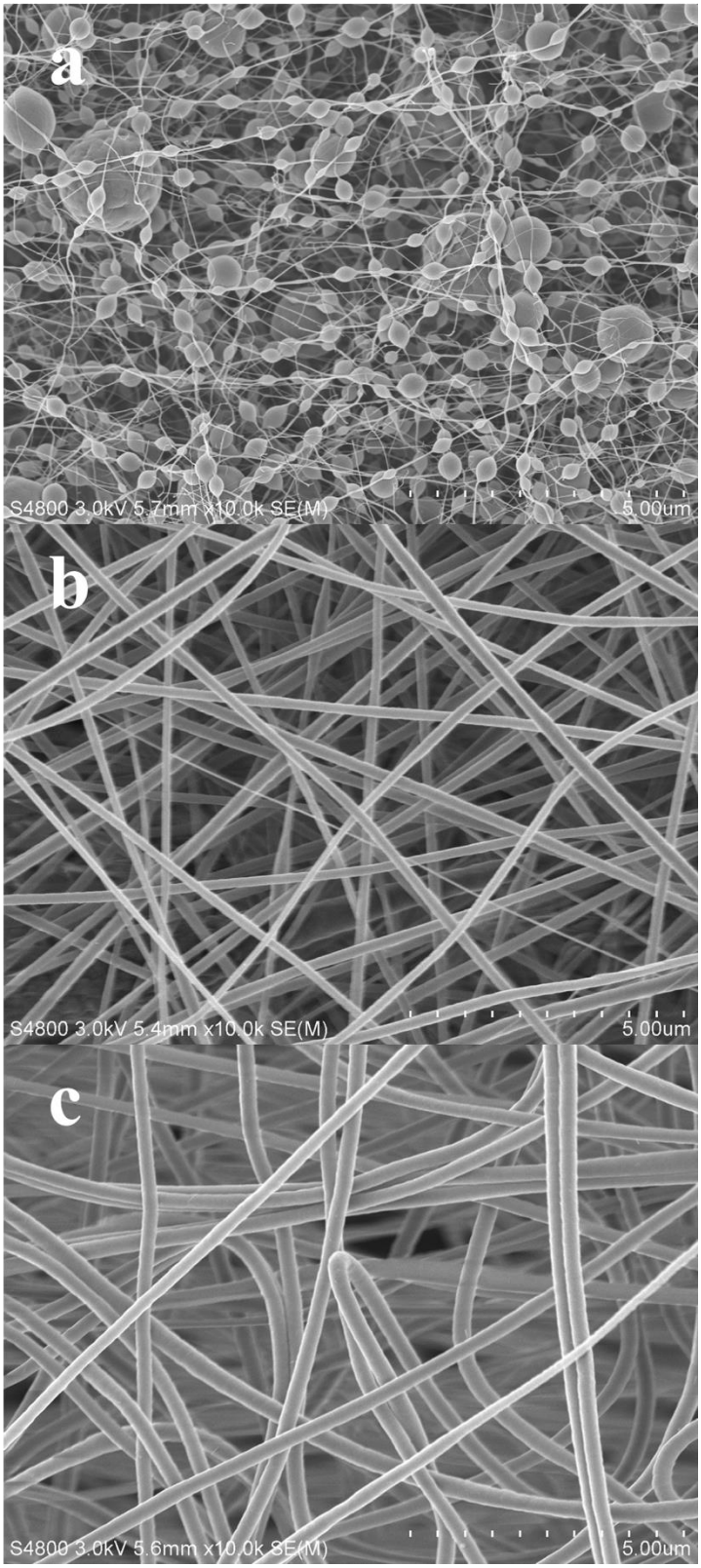


Figure S-1. SEM images of a) 5%, b) 7.5% and c) 10% PAN nanofibers.

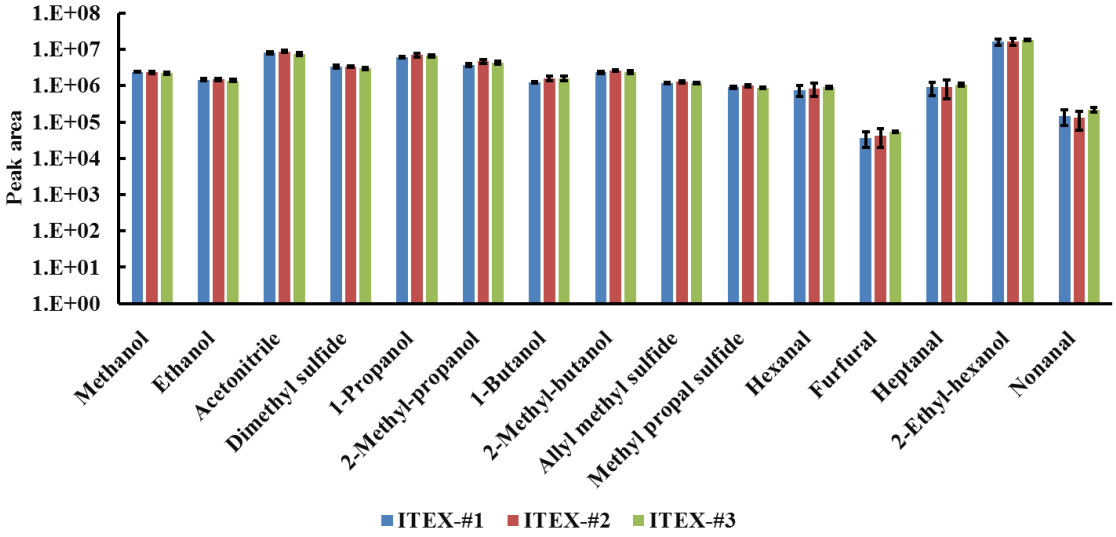
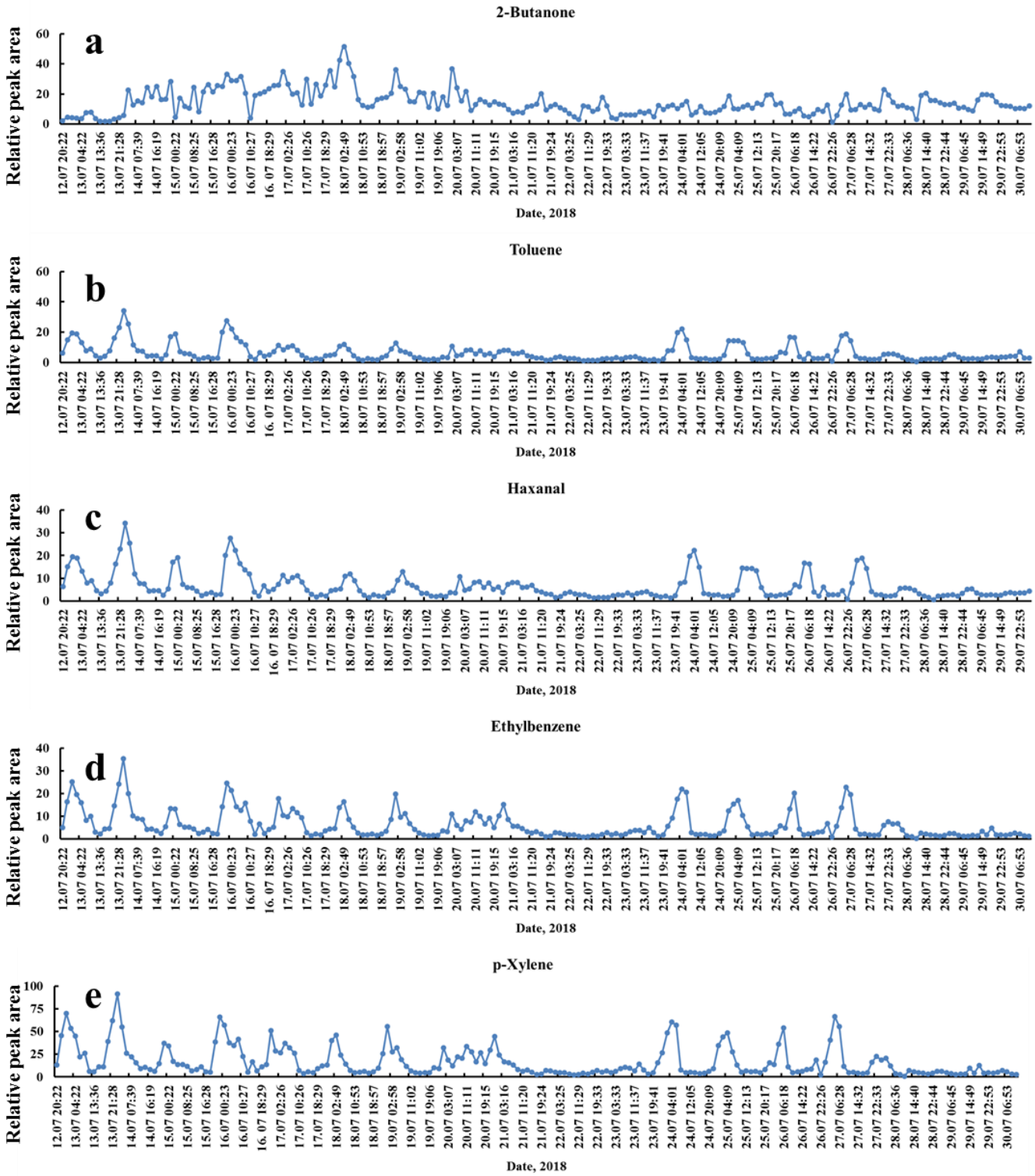
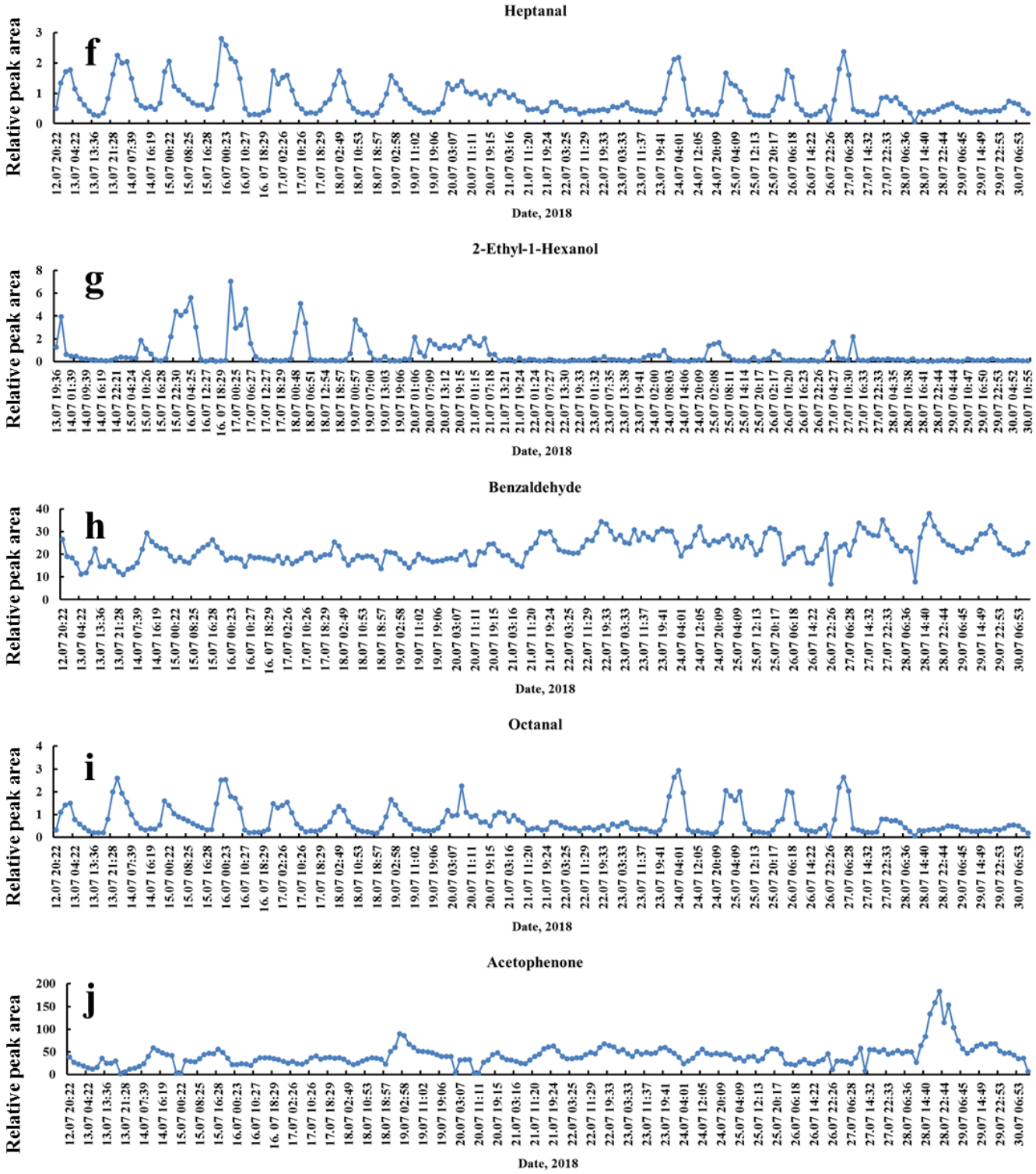


Figure S-2. Reproducibility test of 10%PAN-ITEX (N=3).


2-Butanone
a
Relative peak area
Date, 2018
Toluene
b
Relative peak area
Date, 2018
Haxanal
c
Relative peak area
Date, 2018
Ethylbenzene
d
Relative peak area
Date, 2018
p-Xylene
e
Relative peak area
Date, 2018


Heptanal
f
Relative peak area
Date, 2018
2-Ethyl-1-Hexanol
g
Relative peak area
Date, 2018
Benzaldehyde
h
Relative peak area
Date, 2018
Octanal
i
Relative peak area
Date, 2018
Acetophenone
j
Relative peak area
Date, 2018

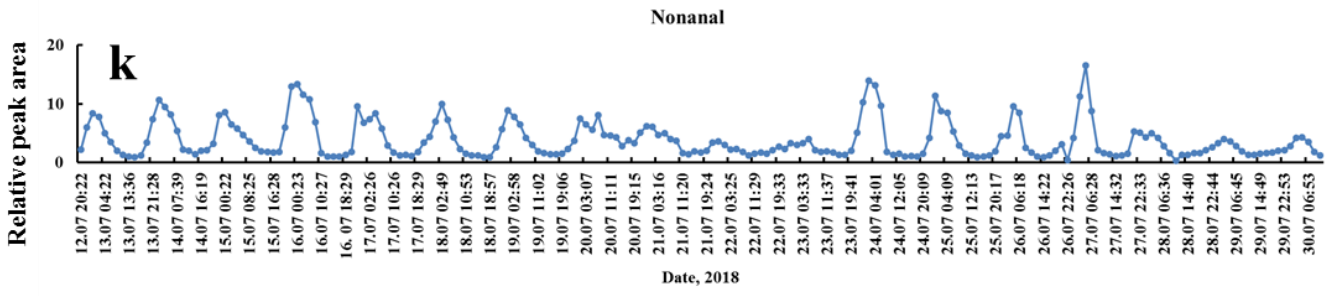
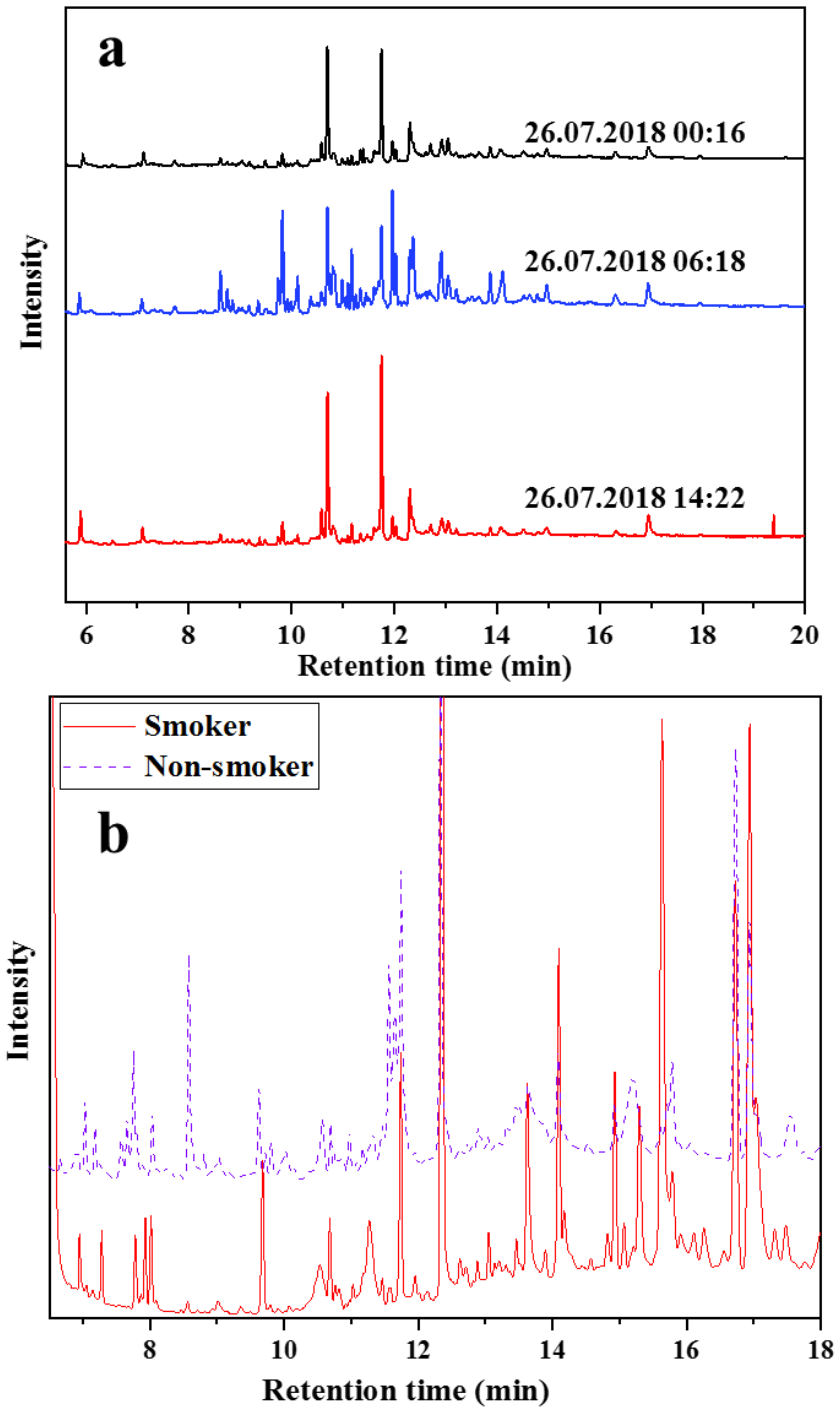


Figure S-3a-k. Variation of VOC concentrations in atmospheric air of Kumpula Campus in July, 2018. Y axis is the relative peak area of analyte (relative to ISTD).


a
26.07.2018 00:16
26.07.2018 06:18
26.07.2018 14:22
Intensity
6
8
10
12
14
16
18
20
Retention time (min)
Smoker
Non-smoker
b
Intensity
8
10
12
14
16
18
Retention time (min)

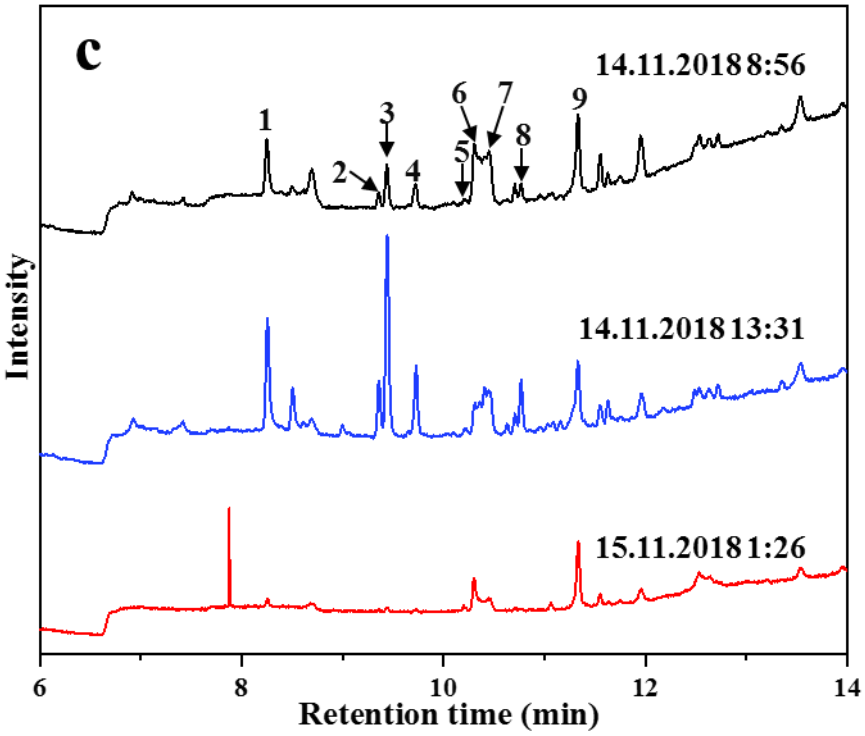


Figure S-4. Chromatograms of a) atmospheric air (July, 2018), b) exhaled air and c) atmospheric air (November, 2018) by 10% PAN ITEX-GC-MS method. The numbers marked in c) are (1) toluene, (2) ethylbenzene, (3) p-xylene, (4) o-xylene, (5) phenol, (6) benzaldehyde, (7) 1,2,3-trimethylbezene, (8) 1,2,4-trimethylbenzene and (9) acetophenone.

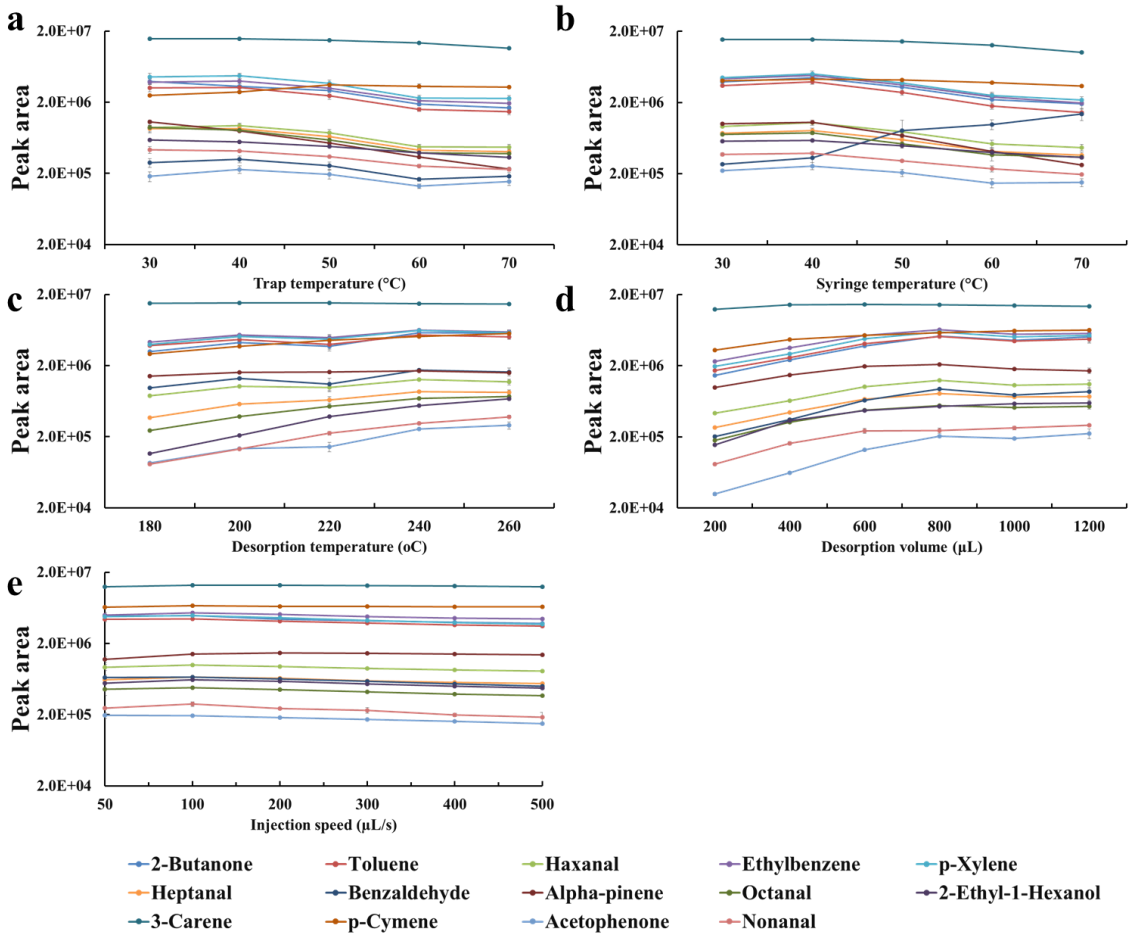


Figure S-5. Optimization of extraction and desorption conditions of 10% PAN-ITEX. a) ITEX trap temperature, b) syringe temperature, c) desorption temperature, d) desorption volume and e) injection speed of the desorption gas.

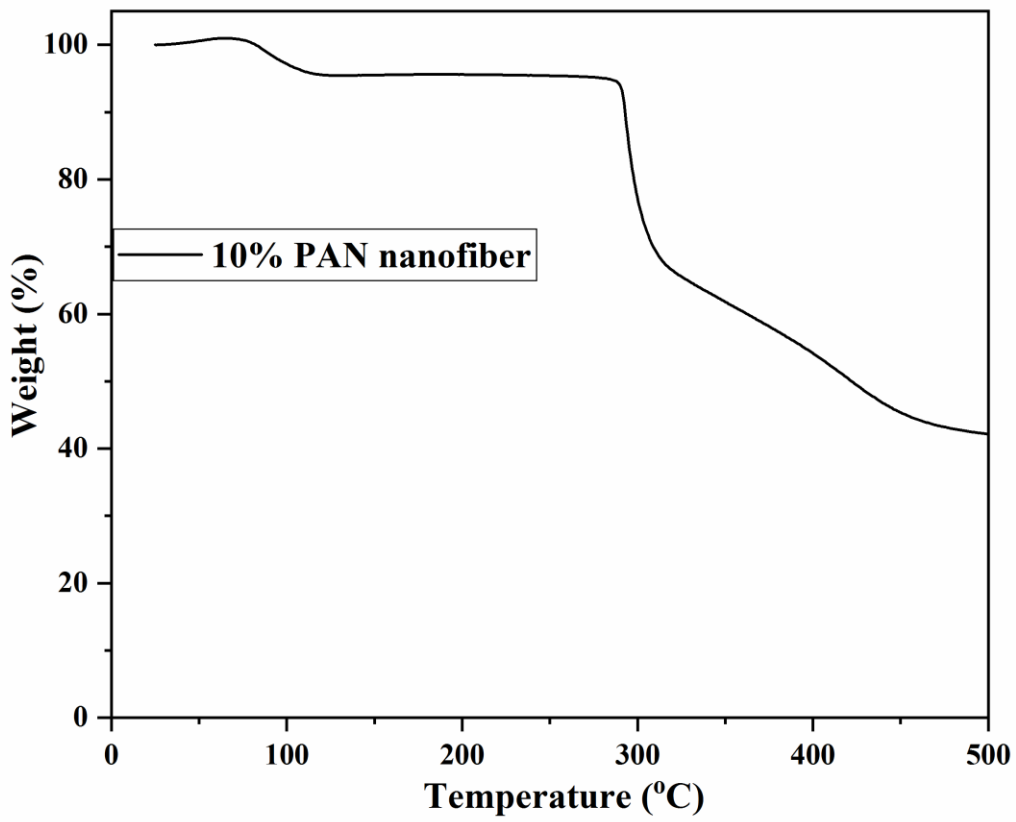


Figure S-6. Thermogravimetric analysis pattern of 10% PAN nanofiber.

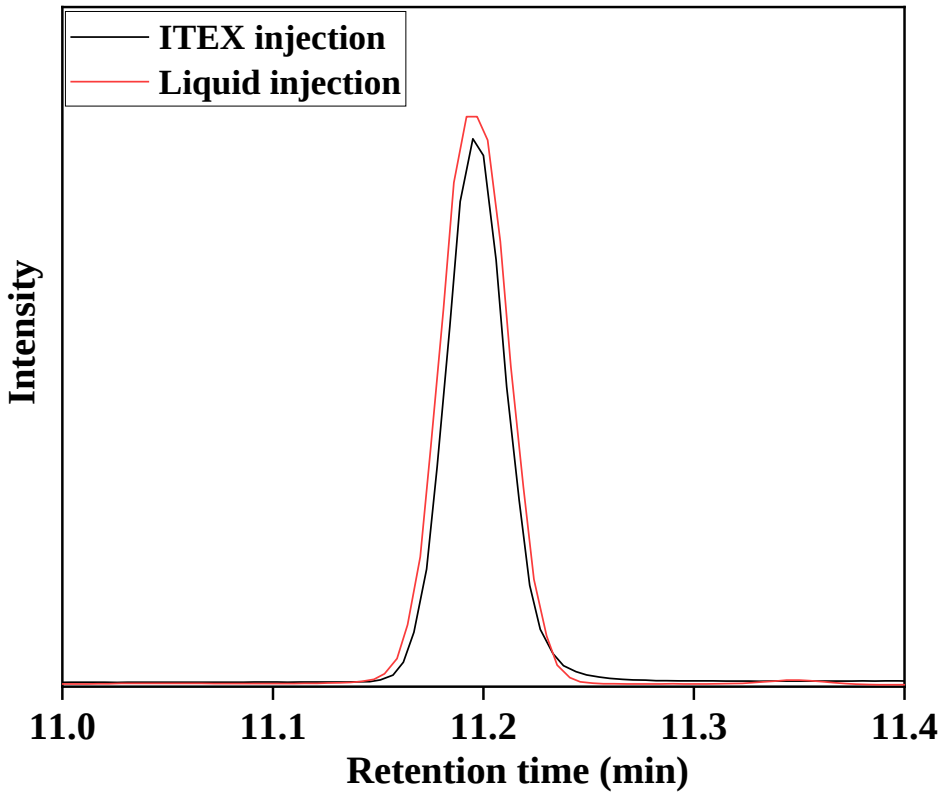


Figure S-7. Comparison of liquid syringe (liquid standard) and ITEX (collected gaseous sample from permeation system) injections of 120 ng of 2-ethyl-1-hexanol.

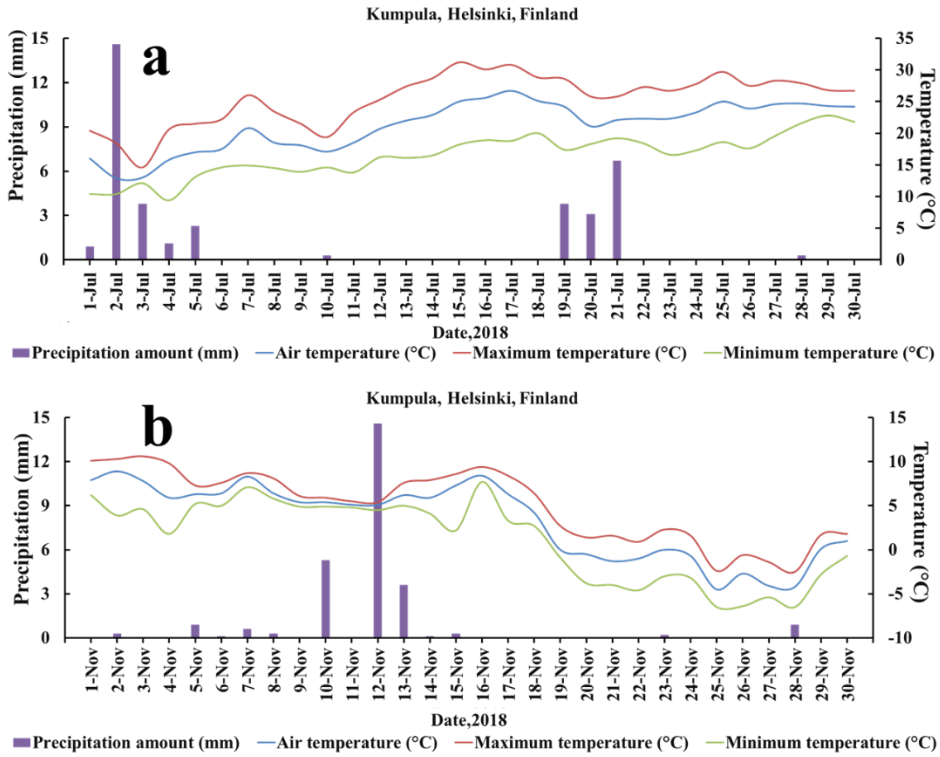


Figure S-8. Weather data during the campaigns in a) July and b) November, 2018, in Kumpula Campus, University of Helsinki, Helsinki, Finland.

Table S-1. List of compounds used to compare different ITEX materials.

Amines	
1	Methylamine
2	Dimethylamine
3	Trimethylamine
Acids	
4	Acetic acid
5	Butyric acid
Sulfides	
6	Dimethyl sulfide
7	Carbon disulfide
8	Allyl methyl sulfide
9	Methyl propyl sulfide
Nitrile	
10	Acetonitrile
Alcohols	
11	Methanol
12	Ethanol
13	1-Propanol
14	2-Methyl propanol
15	1-Butanol
16	2-Methyl butanol
17	2-Ethyl-1-hexanol
Aldehydes	
18	Hexanal
19	Furfural
20	Heptanal
21	Octanal
22	Nonanal
23	Decanal
24	Acetaldehyde
Ketones	
25	Acetone
26	2-Butanone
27	3-Pentanone
28	Methylisobutylketone
Acetate	
29	Ethyl acetate
Ether	
30	Tert-butyl-ethyl ether
Furans	
31	Tetrahydrofuran
32	2-Pentylfuran
Hydrocarbons	
33	Isoprene

34	4-Methyl-1-hexene
35	Cyclohexane
36	Toluene
37	1,4-Dimethylcyclohexane
38	Ethylbenzene
39	Delta-3-Carene
40	1-Undecene
41	Hexylcyclohexane
42	Tridecane
43	Tetradecane
44	Longifolene

Table S-2. List of compounds used for the testing of permeation system.

	Analytes
1	2-Butanone
2	Acetophenone
3	2-Ethyl-1-hexanol
4	Hexanal
5	Heptanal
6	Octanal
7	Nonanal
8	Toluene
9	Ethylbenzene
10	Benzaldehyde
11	Alpha-pinene
12	Delta-3-Carene
13	p-Cymene
14	p-Xylene

Table S-3. Detected VOCs from indoor air of Laboratory of Analytical Chemistry, Department of Chemistry, University of Helsinki, Helsinki, Finland.

	Detected VOCs
1	Acetic acid
2	Ethyl acetate
3	Trichloromethane
4	Carbonic acid, hexyl methyl ester
5	2-Propanone, 1-hydroxy-
6	Pentanal
7	Heptane
8	Isobutyl acetate
9	1,2-propanediol
10	Pyridine
11	Toluene
12	Hexanal
13	Octane
14	2-Butanone
15	1-methyl-2-propyl acetate
16	Methoxy-phenyl-oxime
17	Ethylbenzene
18	p-Xylene
19	Heptanal
20	2-butoxy-ethanol
21	o-Xylene
22	Methoxybenzene
23	Hexanoic acid
24	2-Undecanone
25	Phenol
26	Benzaldehyde
27	Octanal
28	Decane
29	1,2,4-Trimethylbenzene
30	1,2,3-Trimethylbenzene
31	1,3,5-Trimethylbenzene
32	2-Ethyl-1-hexanol
33	Benzyl alcohol
34	Phthalane
35	2-Hydroxy-benzaldehyde

36	Eucalyptol
37	Acetophenone
38	Nonanal
39	Undecane
40	Benzoic acid
41	1-(2-butoxyethoxy)-ethanol
42	5-Methyl-2-(1-methylethyl)-cyclohexanone
43	Levomenthol
44	Methyl salicylate
45	2-Coumaranone
46	2-Octyl-1-decanol
47	Tridecane
48	Tetradecane

Table S-4. Original optimization data of sampling flow rate of 10% PAN-ITEX.

Sampling time (min)		200 mL min^{-1} Average peak area (n=3)	SD	RSD (%)	56 mL min^{-1} Average peak area (n=3)	SD	RSD (%)	35 mL min^{-1} Average peak area (n=3)	SD	RSD (%)
	Toluene									
1		34483	485	1.41	15693	155	0.99	8653	86	1.00
2		58117	589	1.01	27902	326	1.17	14979	124	0.82
5		110532	1535	1.39	62278	779	1.25	33638	820	2.44
10		170561	2299	1.35	111250	753	0.68	73680	675	0.92
15		207156	3384	1.63	147977	889	0.60	91793	925	1.01
20		235846	3798	1.61	182214	573	0.31	116990	1009	0.86
30		263560	6600	2.50	229118	837	0.37	154389	1047	0.68
40		279984	3814	1.36	259773	1920	0.74	188137	9114	4.84
50		287782	2206	0.77	300998	1646	0.55	212088	383	0.18
60		290939	6809	2.34	321263	2789	0.87	242725	821	0.34
90		282516	2504	0.89	360132	3941	1.09	290634	841	0.29
	Delta-3-carene									
1		837298	2214	0.26	465825	4420	7057	208835	7057	3.38
2		1281105	2807	0.22	881392	8237	16271	374734	16271	4.34
5		2210877	10423	0.47	1916795	4703	43302	909418	43302	4.76
10		3022521	35212	1.16	3119859	39290	31936	1769221	31936	1.81
15		3525406	55318	1.57	3958551	60940	138247	2345238	138247	5.89
20		3619212	12404	0.34	4593234	115288	29407	2886072	29407	1.02
30		4580159	77238	1.69	5526603	105452	33103	3726183	33103	0.89
40		5171434	32326	0.63	6136077	21599	63110	4419671	63110	1.43
50		5732697	7747	0.14	6792053	21653	38335	4987241	38335	0.77
60		6228031	61219	0.98	7259375	12519	35470	5613292	35470	0.63
90		7758263	80268	1.03	8265293	51685	101013	6747808	101013	1.50
	Nonanal									
1		1094562	22388	2.05	301220	1113	0.37	168324	5313	3.16
2		1579685	32324	2.05	601220	3372	0.56	318324	7781	2.44
5		3570681	43097	1.21	1389721	2933	0.21	669135	10463	1.56
10		5594223	68068	1.22	2638218	19059	0.72	1334116	13874	1.04
15		6779036	19467	0.29	3645414	22562	0.62	1939737	24562	1.27
20		7331139	9386	0.13	4422364	27863	0.63	2505210	24101	0.96
30		7503097	216556	2.89	5515120	37152	0.67	3453676	40112	1.16
40		7442344	104371	1.40	6246374	63985	1.02	4209583	64255	1.53
50		7494371	104325	1.39	6612924	30201	0.46	4853288	111767	2.30
60		7556237	11480	0.15	6982756	24218	0.35	5444358	140204	2.58
90		7519771	3057	0.04	7179961	67073	0.93	6494355	37161	0.57
	ISTD									
1		45602	161	0.35	24453	432	1.76	31432	329	1.05

2	39507	126	0.32	25467	1384	5.43	29280	1078	3.68
5	34608	60	0.17	25993	332	1.28	28514	75	0.26
10	27170	170	0.63	26241	116	0.44	28520	224	0.79
15	19917	45	0.23	26508	106	0.40	28739	520	1.81
20	14179	20	0.14	26936	121	0.45	28855	1514	5.25
30	10984	75	0.68	25325	95	0.37	29868	841	2.82
40	9358	118	1.26	22724	105	0.46	29751	264	0.89
50	7832	64	0.82	20500	191	0.93	32617	186	0.57
60	7406	226	3.05	19430	113	0.58	32458	202	0.62
90	2789	6	0.22	15535	123	0.79	28302	126	0.45

Table S-5. Comparison with other sorbent trap-based methods for the determination of VOCs.

Method	Sorbent mass	Sample	LOQ (ng L^{-1})	Repeatability (RSD %)	Reference
Dynamic headspace ITEX-GC-MS	Not mentioned	Water	35 (Toluene)[a] 29 (*p*-Xylene)[a] 68 (1,2,3-Trimethylbenzene)[a]	3.2-7.4	1
Dynamic headspace ITEX-GC-MS	Not mentioned	Water	4 (Toluene) 11 (*p*-Xylene)	4.0-6.8	2
Thermal desorption unit-GC-MS	Not mentioned	Atmospheric air	0.089 (Toluene)[b] 0.022 (*m/p*-Xylene)[b] 0.013 (1,2,3-Trimethylbenzene)[b]	Not mentioned	3
Thermal desorption tube-GC-MS	200 mg	Atmospheric air	0.146 (Toluene)[b] 0.114 (*m/p*-Xylene)[b] 0.008 (1,2,3-Trimethylbenzene)[b]	4.6-30.8	4
Dynamic NT-GC-flame ionization detector	Not mentioned	Water	<1000 (Toluene and *p*-Xylene)[b]	<4%	5
This article	50 mg	Atmospheric air	0.025 (Toluene)[c] 0.025 (*p*-Xylene)[c] 0.12 (Benzaldehyde)[c] 0.12 (Acetophenone)[c] 0.08 (1,2,3-Trimethylbenzene)[c]	<7.6%	

[a] Signal-to-noise ratio=5

[b] Limit of detection

[c] Signal-to-noise ratio=10

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