1 **Supplemental Information**

Table S1. Preparation of Different EDS Devices

Experiment	PDMS amount and format	Amount of compound added (μL)[a]					
		C1	C2	C3	C4	C5	C6
Effect of PDMS size	2.0 g, 3 mm blocks	1.0	2.0	2.8	5.5	19.5	21.1
	2.0 g, 10 mm blocks						
	2.0 g, solid block, 14.53 mm o.d.						
Comparison of EDS system with conventional liquid standard mixture	No PDMS	4 μL of stock solution, prepared by mixing 0.4 mL methylene chloride (14.3%, v/v), 0.1 mL toluene (3.6%, v/v), 0.1 mL bromoform (3.6%, v/v), 0.2 mL *n*-undecane (7.1%, v/v), 1.0 mL methyl salicylate (35.7%, v/v) and 1 mL *n*-tetradecane (35.7%, v/v).					
	2.0 g, 200 μm particles	4.0	20.2	28.0	55.0	195.0	211.0
Relationship between analytes added and amount extracted	2.0 g, 200 μm particles	0.4	2.0	2.8	5.5	19.5	21.1
		0.8	4.0	5.6	11.0	40.0	42.2
		0.1	0.5	0.7	1.4	5.0	5.0
Stability	2.0 g, 200 μm particles	0.4	2.0	2.8	5.5	19.5	21.1

2 [a]C1 to C6 represents: (C1) methylene chloride, (C2) toluene, (C3) bromoform, (C4) *n*-undecane,
3 (C5) methyl salicylate, (C6) *n*-tetradecane.

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Table S2. Repetitive Sampling of EDS Vial Headspace Containing Different Forms of PDMS.

Form	Methylene chloride		Toluene		Bromoform		*n*-Undecane		Methyl salicylate		*n*-Tetradecane	
	%RSD	Slope[a]	%RSD	Slope[a]	%RSD	Slope[a]	%RSD	Slope[a]	%RSD	Slope[a]	%RSD	Slope[a]
Solid	2.17	ns	0.58	ns	0.31[b]	-8.09[b]	0.92[b]	-3.46[b]	1.03[b]	-2.36[b]	3.16	ns
10 mm blocks	4.92	ns	0.34	ns	0.35	ns	0.66	ns	0.89	ns	3.73	ns
3 mm blocks	0.43	ns	0.14	ns	5.40[c]	ns	0.32[b]	0.16[b]	1.77	ns	3.35	ns

[a]Slope refers to the change in measured amount of compound per repeated measurement (5 measurements total). Units are in ng/run, negative sign indicates a decrease, and "ns" means not statistically significant at $\alpha = 0.05$.

[b]In cases where the data show variation about a line that is decreasing, the total variation would include contributions from both the random noise (measurement error) and the slope of the regression line. In these cases, the approximate %RSD value is the standard error adjusted for the regression line divided by the average peak area over the range of the experiment. This ratio is used here under the heading %RSD only when the regression slope is statistically significant. It is a measurement of the repeatability, adjusting for the effects of the temporal sequence.

[c]This data point is suspected to be inaccurate, causing an apparent increase; omitting this data point gave an %RSD of 0.77% and a slope of -0.07 ng/run.

Table S3. Least-squares Fit of Fig. 2 Data.

	Equation	R^2 Value	t-Ratio for quadratic term
Methylene chloride	$y = -0.035\ x^2 + 1.54\ x + 136$	0.937	– 3.98
Toluene	$y = 1.84\ x + 28.5$	0.997	– 1.25
Bromoform	$y = 21.8\ x + 29.9$	0.999	1.46
n-Undecane	$y = 0.131\ x^2 + 4.51\ x - 60.9$	0.919	12.24
Methyl salicylate	$y = 0.316\ x^2 + 10\ x - 129.2$	0.906	10.53
n-Tetradecane	$y = -0.088\ x^2 + 1.92\ x - 37.2$	0.854	7.45

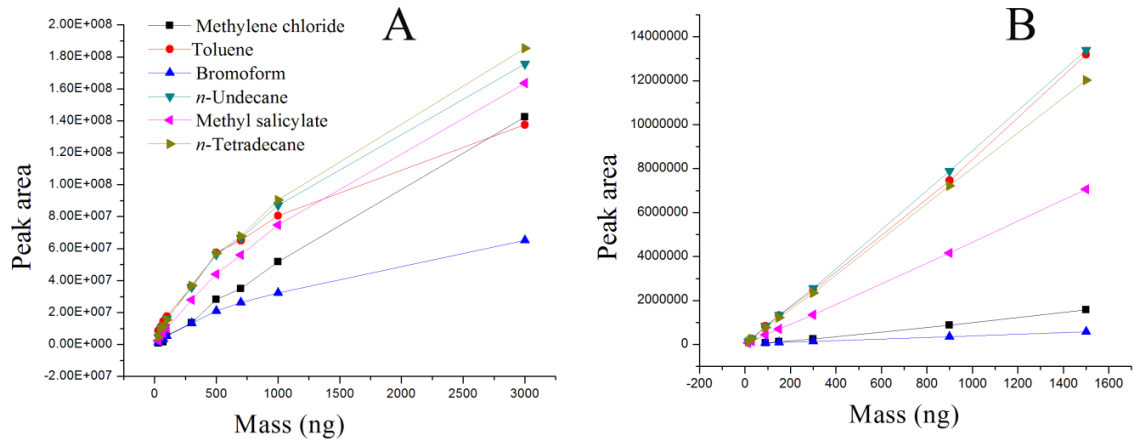
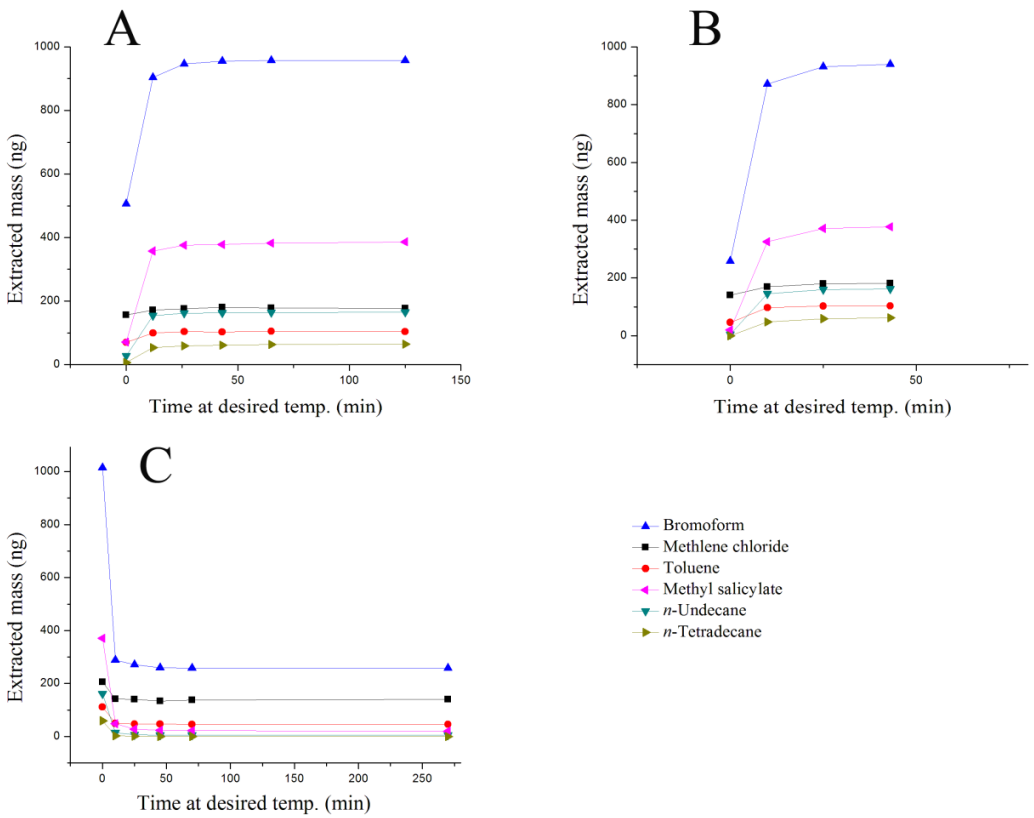


Fig. S1. Calibration curves obtained using conventional syringe liquid injection of a standard solution and analysis using (A) GC-MSD and (B) GC-FID.



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22 Fig. S2. Time required for re-equilibrium of test analytes in an EDS vial (A) from room

23 temperature (22-23°C) to 45°C, (B) from 10°C to 45°C, and (C) from 45°C to 10°C.

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Measurement of the headspace concentration of toluene in an EDS vial

Three identical sets of model EDS devices were prepared at different times, each containing duplicate devices. All PDMS particles used were fabricated in one batch to reduce variation. Each device was sampled with a gas-tight syringe and analyzed using GC-FID. The peak areas were then be quantified using two approaches: comparison to an injection of 1.0 ppm commercial standard toluene sample, and a liquid injection calibration curve.

Measurements were first conducted using a 500 µL gas-tight syringe. The tip of the syringe was heated to 200 °C before each sampling to reduce sample carry-over. An Agilent 7820A GC-FID system was used for detection. Three duplicate sets of devices (6 devices total) were prepared by adding 2 µL toluene into 2-dram vials with 2 g PDMS at different times. After approximately 3 days equilibrium at room temperature, each device was sampled and analyzed using a 500 µL gas-tight syringe multiple times during a 30-day test period. Two 1.0 ppm standard toluene air bags were sampled and analyzed at the same time to provide a quantitative reference. Using a 1.0 ppm toluene gas standard, the concentration in the headspace was found to be 20.3 ppm (see Table S4).

We also constructed two liquid calibration curves by injecting 1.0 µL standard solutions of toluene in methanol. The first included six data points (1.6 ng, 4.0 ng, 10 ng, 20 ng, 40 ng and 100 ng, each with at least duplicate measurements) and gave a calibration curve of $y = 4369.2 x + 4793.5$, with $R^2 = 0.9935$. Another calibration with nine data points (0.25 ng, 0.5 ng, 1.0 ng, 3.0 ng, 5.0 ng, 7.0 ng, 10 ng, 30 ng, and 50 ng) gave a calibration curve of $y = 2997 + 4733.6 x$, with $R^2 = 0.9987$. With an average peak area of 1.36×10^5, the liquid calibration curve 1 gave a result of 16.6 ppm, while curve 2 gave 15.5 ppm. The average is 16.0 ppm (see Table S4).

Table S4. Headspace Concentration Determined Using a Standard Gas Sample and Gas-Tight Syringe.

Vial designation (set / number)	Average peak area	RDS (%)[a]
1 / 1	1.46×10^5	16.2
1 / 2	1.76×10^5	22.9
2 / 1	1.46×10^5	16.4
2 / 2	1.34×10^5	17.9
3 / 1	1.18×10^5	23.9
3 / 2	1.21×10^5	23.7
1.0 ppm standard	6.72×10^3	15.7
Average of all vials	1.36×10^5 (20.3 ppm[b])	22.6

[a] Percentage RSD was calculated for each set and device using repeat observations.
[b] Calibrated concentration using the 1.0 ppm standard.

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Table S5. Data Measured by Liquid Injection for Construction of Calibration Curves.

Calibration curve 1		Calibration curve 2	
Amount injected (ng)	Peak area (%RSD)[a]	Amount injected (ng)	Peak area (%RSD)[a]
1.6	0.60×10^4 (3.2)	0.25	0.268×10^4 (17)
4	0.10×10^4 (8.0)	0.5	0.401×10^4 (1.4)
10	4.43×10^4 (13)	1.0	0.606×10^4 (15)
20	1.02×10^5 (8.7)	3.0	1.91×10^4 (5.0)
40	2.01×10^5 (10)	5.0	2.44×10^4 (3.5)
100	4.32×10^5 (23)	7.0	3.07×10^4 (2.8)
		10	5.46×10^4 (5.6)
		30	1.50×10^5 (7.4)
		50	2.36×10^5 (3.8)
EDS average	1.36×10^5		
Calc. Conc. (ppm)	16.6[b]		15.5[c]
Ave. (ppm)	16.0		

52 [a]%RSD was calculated for 2-3 repeated measurements for each dilution.
53 [b]Concentration based on calibration curve 1.
54 [c]Concentration based on calibration curve 2.
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Calculation of partition coefficient using headspace concentration

According to simple partition theory, as an analyte enters a closed system, it is distributed between the vapor phase and solid/polymer phase. The ratio of concentration of analyte in the sorbent/polymer to concentration of analyte in the vapor phase is defined as the partition coefficient, K (or distribution coefficient if more than just simple partition is involved):

$$K = \frac{C_2}{C_1} \qquad (1)$$

where C_2 is the concentration in the polymer phase, and C_1 is the concentration in the gas phase.

In our EDS system, as the total volume, PDMS amount and analyte amount are known, and the headspace concentration can be measured, we can easily calculate the distribution coefficient.

$$m = C_1V_1 + C_2V_2 \qquad (2)$$

$$K = \frac{C_2}{C_1} = \frac{(m - C_1V_1)/V_2}{C_1} \qquad (3)$$

where m is the total amount of analyte added, m = 2.0 µL x 0.8669 mg/ µL = 1.73 mg, V_2 is the volume of the polymer, the PDMS density is 0.965 g/mL, V_2 = 2.0 g /(0.869 g/ mL) = 2.07 mL, V_1 is the headspace volume, the vial volume is 8.5 mL, V_1 = 8.5 - V_2 = 8.5-2.07 = 6.43 mL, and the headspace concentration, C_1, is 16.0 to 20.3 ppm.

At 25 ˚C and 1 atm, the toluene (concentration can be converted from ppm to mg/m^3 using the following equation:

X ppm = (Y mg/m^3)(24.45)/(molecular weight) (4)

$$For\ C_1 = 16.0\ ppm,\ \text{converted into}\ 16.0\ x\ \frac{92.14}{24.45}\frac{mg}{m^3} = 60.3\ \frac{mg}{m^3} \qquad m.w. = 92.14\ g/mol$$

$$K = \frac{(m - C_1V_1)/V_2}{C_1} = (1.73mg - 60.3mg * m^{-3} * 6.43\ mL * 10^{-6}\frac{m^3}{mL})/(2.07mL * 10^{-6}\frac{m^3}{mL})/$$

$$(60.3\ \frac{\text{mg}}{\text{m}^3}) = 1.38 \times 10^4$$

For $C_1 = 20.3\ ppm$, converted into $20.3x\frac{92.14}{24.45}\frac{\text{mg}}{\text{m}^3} = 76.5\ \frac{\text{mg}}{\text{m}^3}$

$K = \frac{(m - C_1V_1)/V_2}{C_1} = (1.73mg - 76.5mg * m^{-3} * 6.43\ mL * 10^{-6}\frac{m^3}{mL})/(2.07mL * 10^{-6}\frac{m^3}{mL})/$

$(76.5\ \frac{\text{mg}}{\text{m}^3}) = 1.09 \times 10^4$

Construction of calibration curve

For construction of a calibration curve, three duplicate sets, each set containing eight 2-dram devices with 2.0 g PDMS, were prepared. In each set, the eight devices were divided evenly into 4 groups, and then 0.1 μL, 0.5 μL, 1.0 μL, and 2.0 μL of toluene were added into vials of each group, respectively. Each device was sampled and analyzed using the gas-tight syringe and GC-FID for more than 6 times after equilibrium. The results are summarized in Table S6 and used to construct the calibration curve (Fig. S3).

Table S6. EDS Headspace Concentrations for Different Amounts of Toluene.

Device #	Toluene amount (μL)	Peak area[a]	ppm[b]	RSD
1	0.5	2.85×10^4	4.25	40.0%
2	0.5	3.51×10^4	5.22	70.2%
3	1.0	6.10×10^4	9.08	16.3%
4	1.0	5.94×10^4	8.84	18.6%
5	2.0	1.41×10^5	20.99	18.5%
6	2.0	1.37×10^5	20.37	27.0%
11	0.1	0.479×10^4	0.71	26.5%
12	0.1	0.482×10^4	0.72	21.7%

[a] Average of three sets.

[b] Determined using a 1.0 ppm toluene standard gas sample.

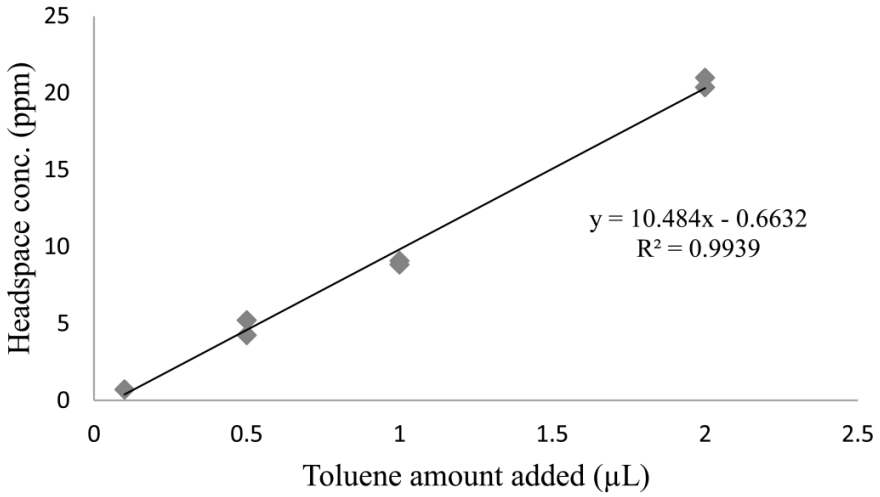

Fig. S3 Calibration curve constructed using eight EDS devices and different amounts of toluene.