Supplementary Information for

Metal-Organic Framework-based High-Performance Column Chip for Micro Gas Chromatography: Hybrid Function for Simultaneous Preconcentration and Separation of Volatile Organic Compounds

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Developer	NTNU	University of Michigan	Virginia Tech	University of Michigan	University of Michigan	CNR-IMM
System	Prototype μ GC	INTREPID	Zebra GC system	2-D GC × GC device	PEMM-2	Compact GC
PC	1 μ-PC	1 μ-PC	1 μ-PC	1 μ-PC	1 μ-PC	1 μ-PC
column	1 capillary GC	1 μ-GC	1 μ-GC	4 μ-GC	3 μ-GC	1 μ-GC
System size (cm^3)	30 × 17 × 8 [4.08 L]	33 × 29 × 13 [12.44 L]	30 × 15 × 10 [4.5 L]	60 × 50 × 10 [30 L]	20 × 15 × 9 [2.7 L]	12 × 8 × 7.5 [0.72 L]
Weight	3 kg	5.4 kg	N/A	5 kg	2.1 kg	N/A
Year	2013[1]	2014[2]	2015[3]	2016[4]	2019[5]	2020[6]

Table S1 Details of the recently developed compact GC systems, including μ-PC and μ-GC.

MOF-5 coating concentration optimization

Control of the mass and volume of MOF and solvent in the suspension is essential for MOF coating. If the concentration of MOF relative to solvent is too low, the flow rate of the suspension may be too high and cause coating failure, and if the concentration is too high, the suspension may not pass through the column channel due to excessive friction between suspension and column channel wall. In this study, three different concentrations of MOF were tested to find the optimal MOF concentration: 10 mg·mL^{-1}, 15 mg·mL^{-1}, and 20 mg·mL^{-1}. The performance indices evaluated to find the optimum across the three concentrations were PF and R_S values.

Fig. S1a-c are chromatograms obtained by injecting 0.25 mL of 10 ppm BTEX through a hybrid GC chip coated with MOF-5 at concentrations of 10, 15, and 20 mg·mL^{-1}. And, Fig. S1d-f are chromatograms obtained after preconcentration of 10 ppm BTEX with 5 mL·min^{-1} for 10 min. PF values were obtained by comparing the peak areas between 10 ppm BTEX without preconcentration and 10 ppm BTEX with preconcentration. The hybrid GC chips coated with concentrations of 10, 15, and 20 mg·mL^{-1} showed average PF values of 77, 248, and 282 for 10 ppm of BTEX, respectively (Fig. S1g). The R_s values were calculated from the chromatograms obtained after preconcentration (Fig. S1h). While hybrid GC chips coated with 10 and 15 mg·mL^{-1} concentrations showed no problems in terms of separation performance, with R_s values between all chemicals exceeding 1.5, the GC column coated with a concentration of 20 mg·mL^{-1} showed bad separation performance in quantitative analysis as the R_s value between ethylbenzene and xylene was lower than the recommended value of 1.5. And, while concentration of 15 mg·mL^{-1} showed a PF value of 248, concentration of 10 mg·mL^{-1} showed a PF value of 77, confirming that it was 3.2 times better in terms of PF. Therefore, a MOF-5 suspension with concentration of 15 mg·mL^{-1} was selected as the optimal concentration as it showed good performance in terms of both PF and R_s.

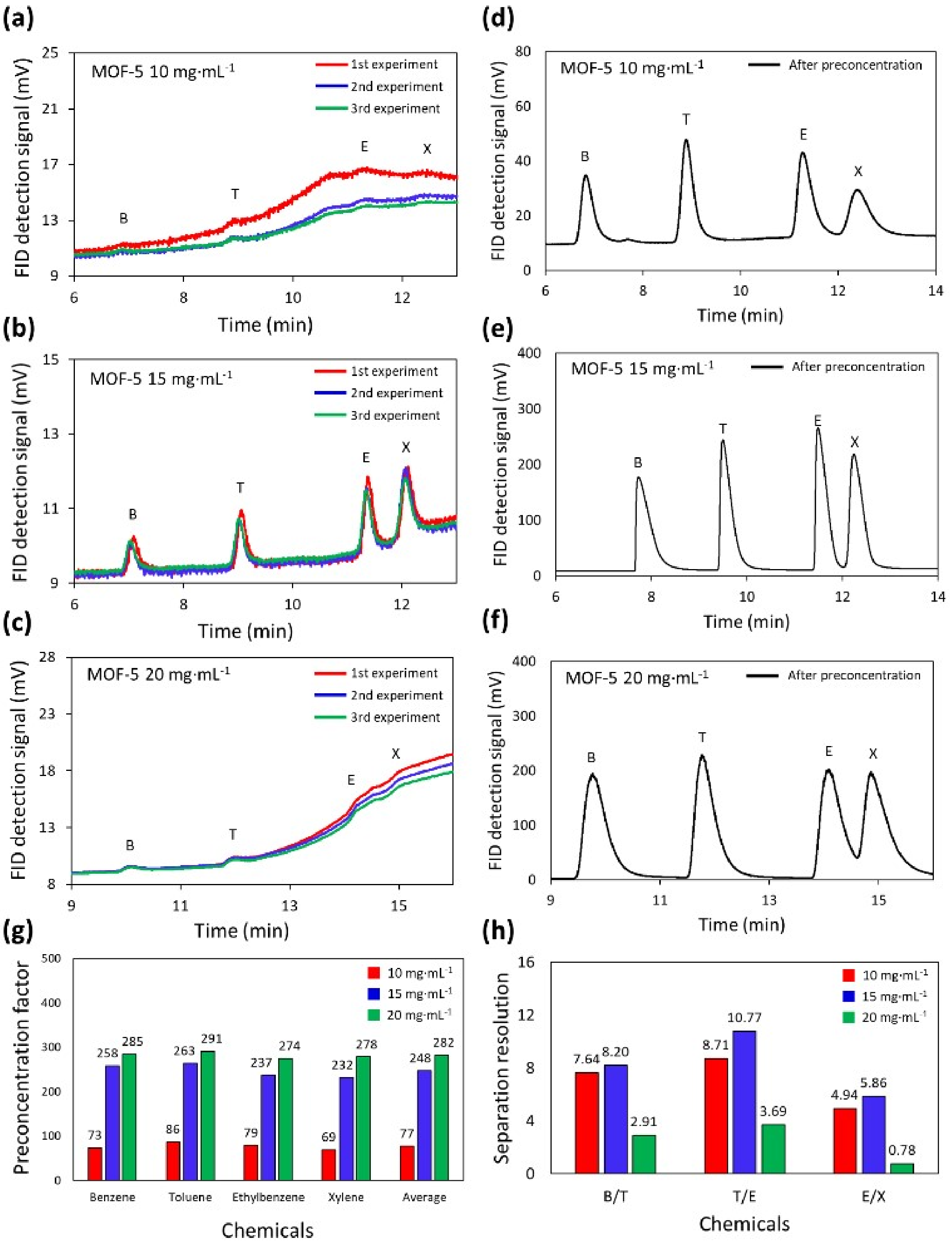

Fig. S1 Experimental results of hybrid GC chips coated with three different MOF-5 concentrations. (a-c) Chromatograms obtained by injecting 10 ppm BTEX onto the hybrid GC chips coated with concentrations of 10, 15, and 20 mg·mL⁻¹, respectively, (d-f) Chromatograms obtained after preconcentration using three types of hybrid GC chips, (g) PF values for each column, and (h) R_S values between chemicals using each column.

Concentration calibration curve

The initial concentration of the BTEX gas mixture is a controllable variable, but the BTEX concentration after preconcentration is unknown. The peak area from the FID signal of the target gas is proportional to its concentration under the same experimental conditions and target gas. The peak area obtained at various concentrations can be determined into a concentration calibration curve by linear regression. The initial concentration, final concentrations after preconcentration, and the PF value can be obtained by the concentration calibration curve. The injected BTEX mixtures at three different concentrations were separated, as shown in Fig. S2a. And, Fig. S2b shows the concentration calibration curves based on the BTEX concentrations and detected peak areas. In the hybrid GC chip, the R-squared values for benzene, toluene, ethylbenzene, and xylene were 0.9989, 0.9889, 0.9917, and 0.994, respectively, giving an average value of 0.9934.

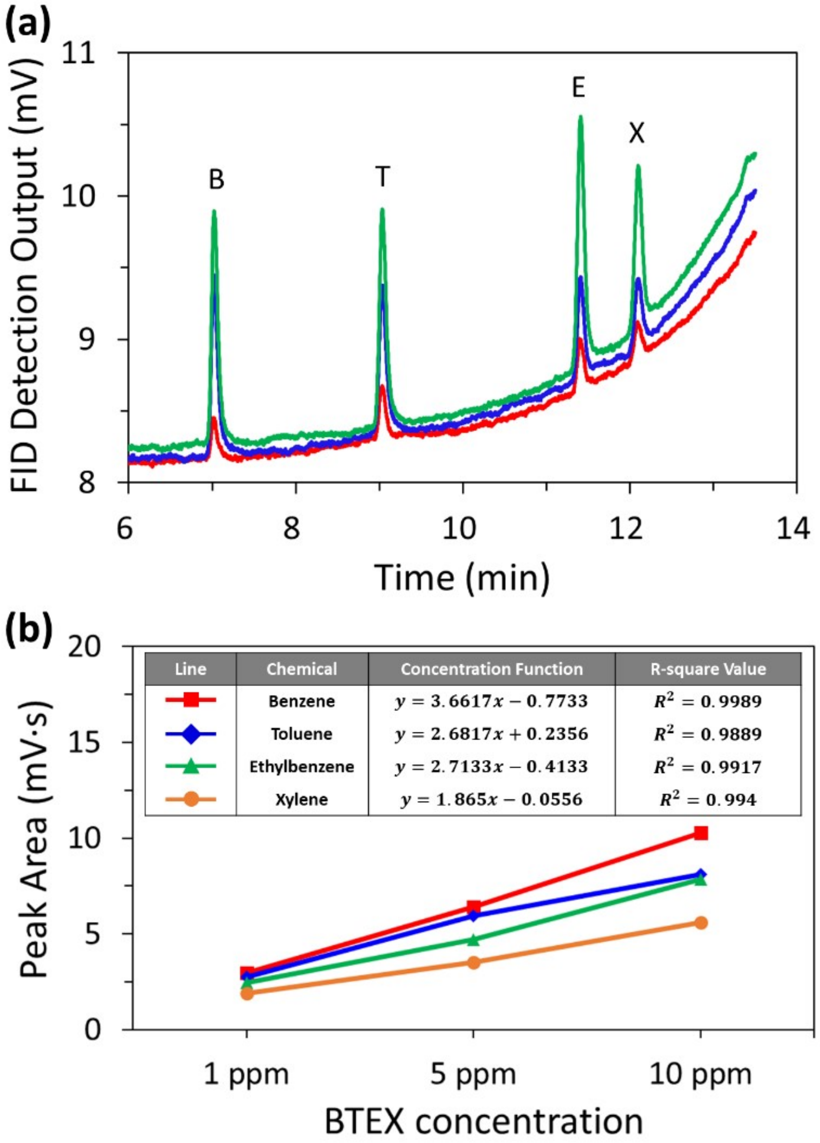

Fig. S2 Concentration calibration curve for the hybrid GC chip. (a) Chromatograms for 1, 5, and 10 ppm BTEX using hybrid GC chip installed in FID system, and (b) Concentration calibration curves for each BTEX gas.

Preconcentration result for 10 ppb BTEX

To conduct a preconcentration/separation test for 10 ppb BTEX, a specific concentration of BTEX was injected into a Tedlar bag (Polyester aluminum sampling bag, Dongbanghitech, Korea) and then diluted with additional pure nitrogen to obtain a sample analyte. Additionally, a mini pump (SP 500 EC-LC, Schwarzer Precision, Germany) was used for sampling, and the measured flow rate was 1.0-1.2 mL·min^{-1} with both the hybrid GC chip and Tedler bag connected. Since the sampling volume in this study was 50 mL, preconcentration was performed for 45 minutes to match the sampling volume as similar as possible. Through the chromatogram obtained after preconcentration, it was confirmed that the peak areas of each chemical were 42.82, 36.62, 30.90, and 23.50, respectively (Fig. S3). Based on the concentration calibration curve obtained from Fig. S2b, the peak area for 10 ppb BTEX is calculated as negative. Therefore, a modified concentration calibration curve was prepared to obtain a positive peak area for 10 ppb by removing the intercept past the origin: benzene, $y=3.3302x$, $R^2=0.9982$; toluene, $y=2.7826x$, $R^2=0.9983$; ethylbenzene, $y=2.5362x$, $R^2=0.9978$; xylene, $y=1.8412x$, $R^2=0.9991$. Since the peak areas of 10 ppb BTEX estimated through the above equation are 0.0333, 0.0278, 0.0256, and 0.0184, respectively, the PF values were calculated as 1,286, 1,316, 1,205, and 1,277, respectively. This was found to be slightly higher than the PF values found in Fig. 6b, which is speculated to be due to a reduction in quantity of unadsorbed and vented BTEX due to the lower concentration compared to 400 ppb, lack of reliability of the sample gas, or fluctuations in the sampling flow rate of the mini-pump.

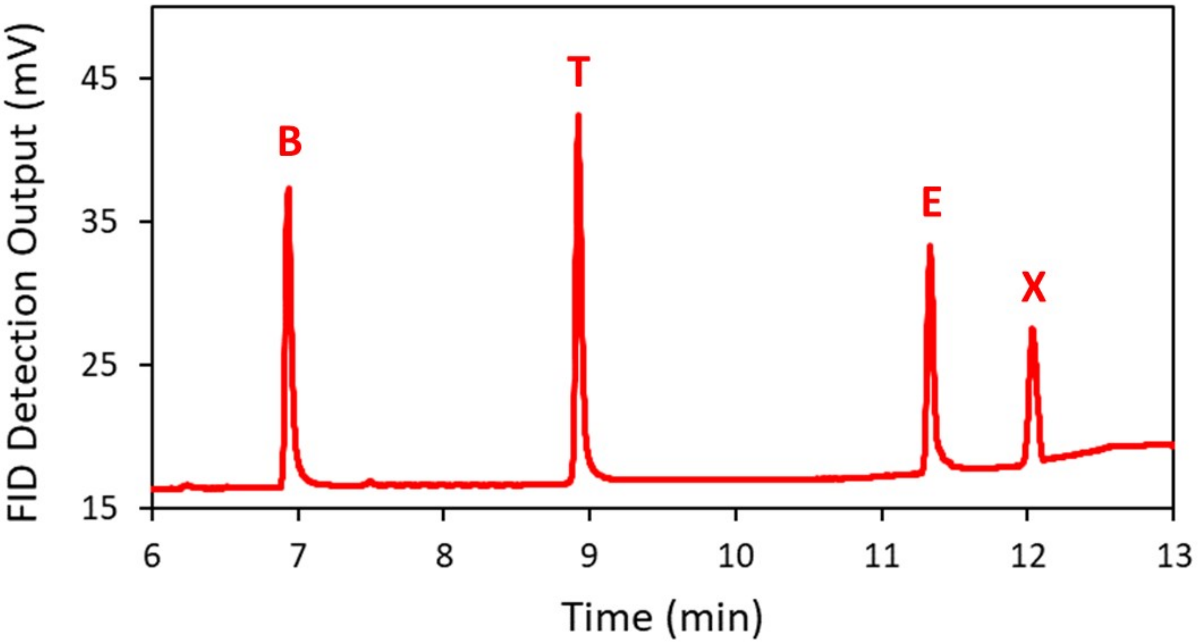

Fig. S3 Preconcentration test result for 10 ppb BTEX in Tedlar bag using the hybrid GC chip and mini-pump for 45 min at a flow rate of 1.1 mL·min^{-1}.

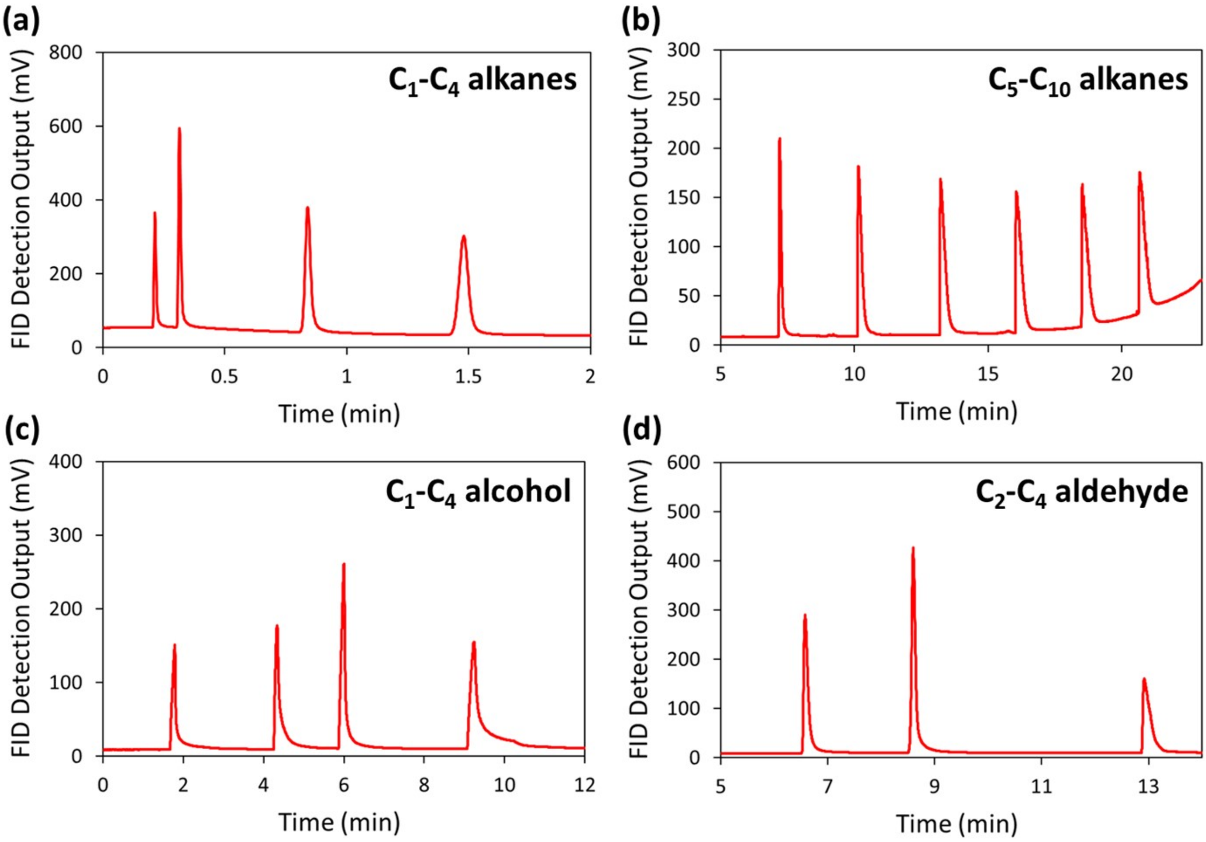

Fig. S4 Separation chromatograms using the hybrid GC chip for various analytes. (a) separation chromatogram for C_1-C_4 gaseous linear alkanes, (b) separation chromatogram for C_5-C_{10} liquid linear alkanes, (c) separation chromatogram for C_1-C_4 liquid alcohols, and (d) separation chromatogram for C_2-C_4 liquid aldehydes.

Table S2 Details on the repeatability obtained from 10 repeated test results using the hybrid GC chip.

1st experiment			**2nd experiment**			**3rd experiment**		
Chemical	RT [min]	PA [mV·s]	Chemical	RT [min]	PA [mV·s]	Chemical	RT [min]	PA [mV·s]
B	6.908	1009.720	B	6.899	768.831	B	6.897	790.654
T	8.923	1971.141	T	8.913	1522.536	T	8.915	1524.479
E	11.32	858.721	E	11.338	641.438	E	11.314	648.380
X	12.014	1039.834	X	12.015	739.383	X	12.008	757.200
4th experiment			**5th experiment**			**6th experiment**		
Chemical	RT [min]	PA [mV·s]	Chemical	RT [min]	PA [mV·s]	Chemical	RT [min]	PA [mV·s]
B	6.918	1008.042	B	6.921	781.421	B	6.931	738.615
T	8.935	1787.945	T	8.924	1506.677	T	8.921	1424.141
E	11.347	833.730	E	11.339	644.215	E	11.336	610.893
X	12.029	1013.109	X	12.021	741.003	X	12.020	712.658
7th experiment			**8th experiment**			**9th experiment**		
Chemical	RT [min]	PA [mV·s]	Chemical	RT [min]	PA [mV·s]	Chemical	RT [min]	PA [mV·s]
B	6.877	918.233	B	6.912	839.335	B	6.904	747.008
T	8.922	1840.055	T	8.904	1576.265	T	8.911	1492.112
E	11.338	779.583	E	11.319	694.197	E	11.320	606.728
X	12.026	885.964	X	12.014	762.059	X	12.008	689.173
10th experiment			**Average Value**		**Standard Deviation**		**Relative Standard Deviation**	
Chemical	RT [min]	PA [mV·s]	**RT [min]**	**PA [mV·s]**	**RT [min]**	**PA [mV·s]**	**RT [%]**	**PA [%]**
B	6.908	797.369	**6.908**	**839.923**	**0.014872**	**102.6532**	**0.2153**	**12.2217**
T	8.951	1537.425	**8.922**	**1618.278**	**0.013295**	**180.989**	**0.14902**	**11.184**
E	11.325	645.603	**11.330**	**696.349**	**0.011227**	**93.16353**	**0.09909**	**13.3789**
X	12.010	756.390	**12.017**	**809.677**	**0.007307**	**125.4451**	**0.06081**	**15.4932**

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