Supplementary Information to

Low-Power Miniaturized Helium Dielectric Barrier Discharge Photoionization Detectors for Highly Sensitive Vapor Detection

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Table S1: A detailed comparison of our µHDBD-PID with other HD-PIDs

	Mesoscale Pulsed HDBD-PID[1]	**VICI PD-D2-IM**	**Shimadzu BID**	**Integrated µDPID[2-4]**	**µHDBD-PID (our work)**
Discharge mechanism	Pulsed discharge	Pulsed discharge	Dielectric barrier discharge	DC discharge	Dielectric barrier discharge
Minimum or typical auxiliary helium flow rate (mL/min)	35	10	50 - 100	1	5.8
Detection limit	A few pg	Low to sub-pg	Low to sub-pg	10 pg	A few pg
Dimensions	10 mL	~400 mL	As big as a commercial FID	On-chip scale	On-chip scale (0.1 mL)
Power consumption	Unknown	Unknown	Unknown	1.4 mW (without including power consumption of power supply)	385 mW (all-inclusive) ~3 mW on HDBD-PID itself. Heating needs extra power
Type of chemicals	Universal	Universal	Universal	Universal	Universal
Electrodes destruction	Yes	Yes	No	Yes	No
Warm-up time	Unknown	A few minutes	A few hours	Unknown	<5 min
Comments	**Pros:** Sensitive and small in footprint **Cons:** High helium consumption and electrode maintenance	**Pros:** Very sensitive, quick warm up, and affordable helium consumption, **Cons:** Bulky, electrode maintenance	**Pros:** Very sensitive and maintenance free **Cons:** High helium consumption, lengthy warm up time and bulky in size	**Pros:** Sensitive, tiny footprint, and very low helium consumption **Cons:** Electrode maintenance and unexpected negative signal, external high voltage generator needed	**Pros:** Sensitive, tiny footprint, quick warm up time, complete miniaturized system **Cons:** Relatively high helium consumption compared to Integrated µDPID

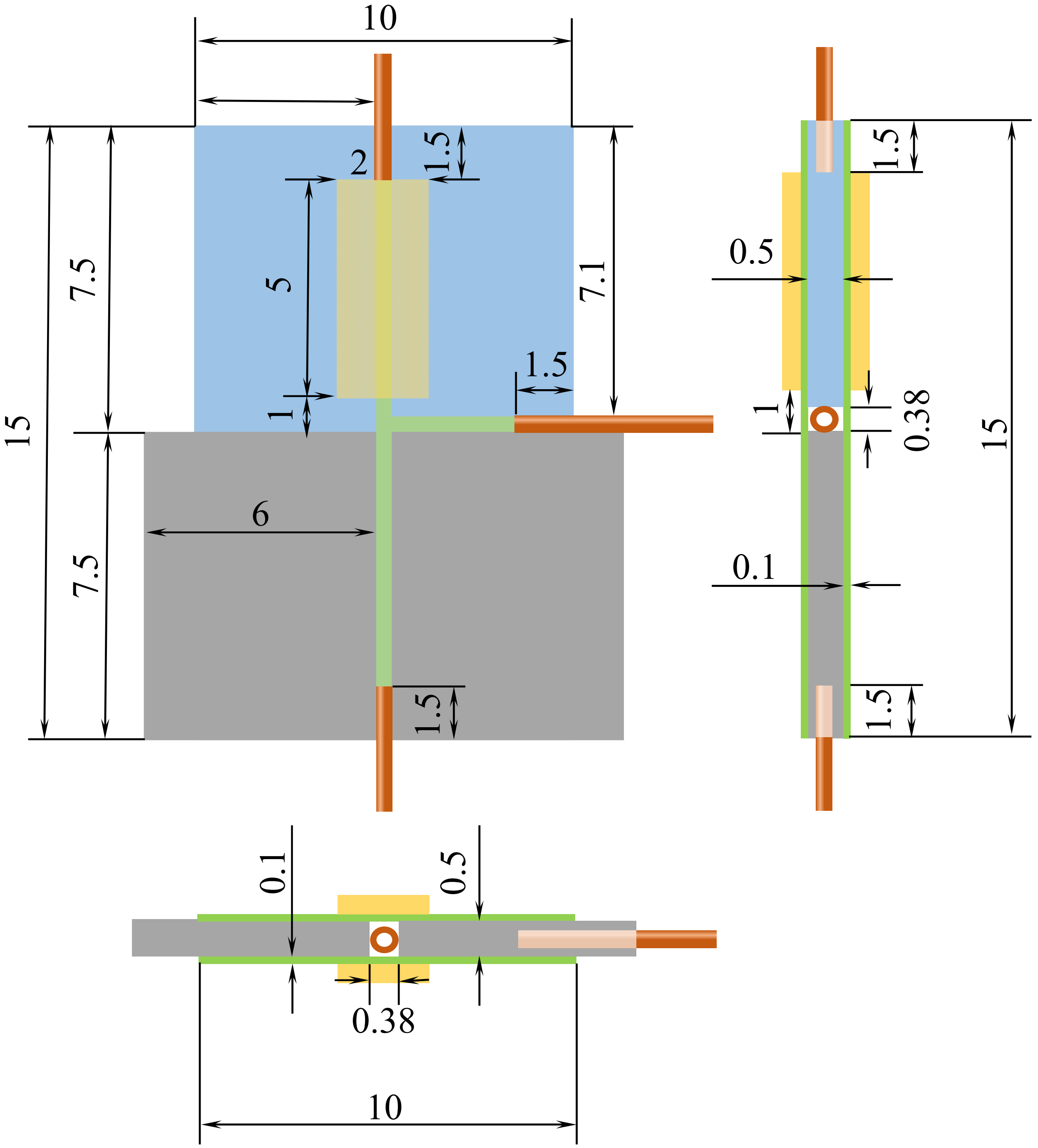

Figure S1 3-view diagram of the μHDBD-PID. Units: mm.

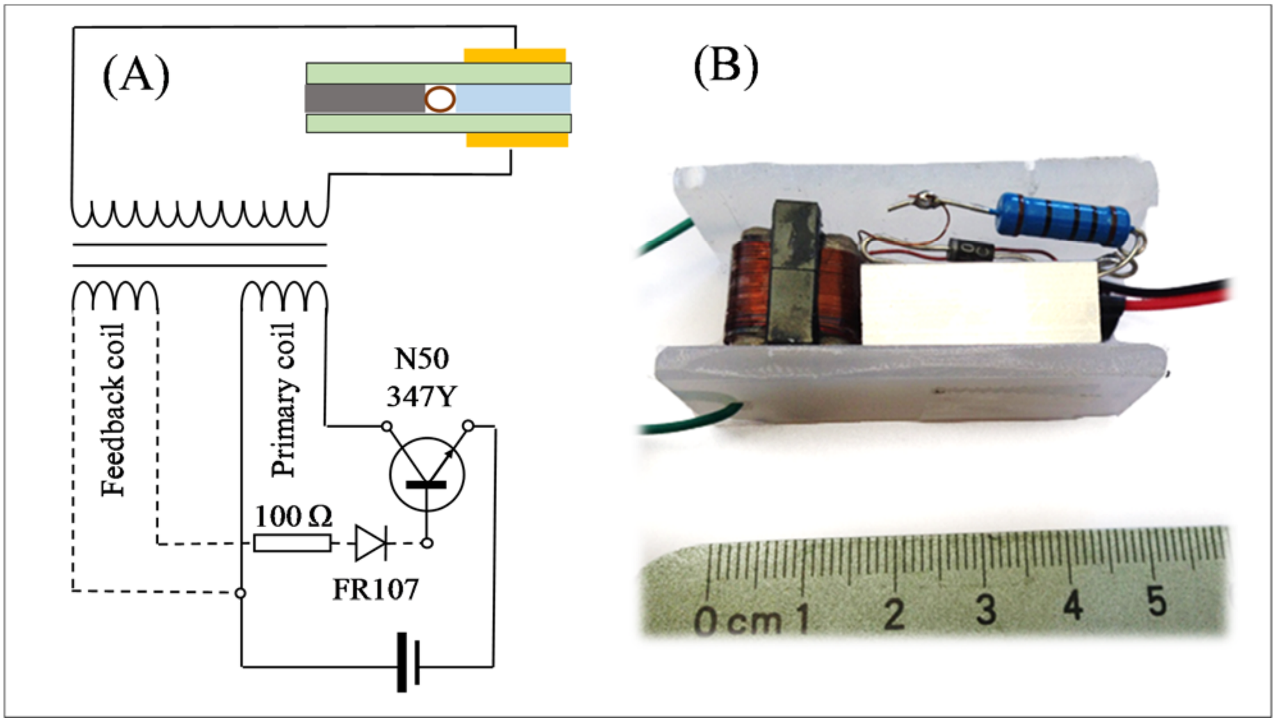

Figure S2 (A) Circuitry for helium discharge plasma excitation. DC input: 1.5 V and 257 mA. AC output: 7.7 kHz, 4 kV. (B) Picture of the power supply.

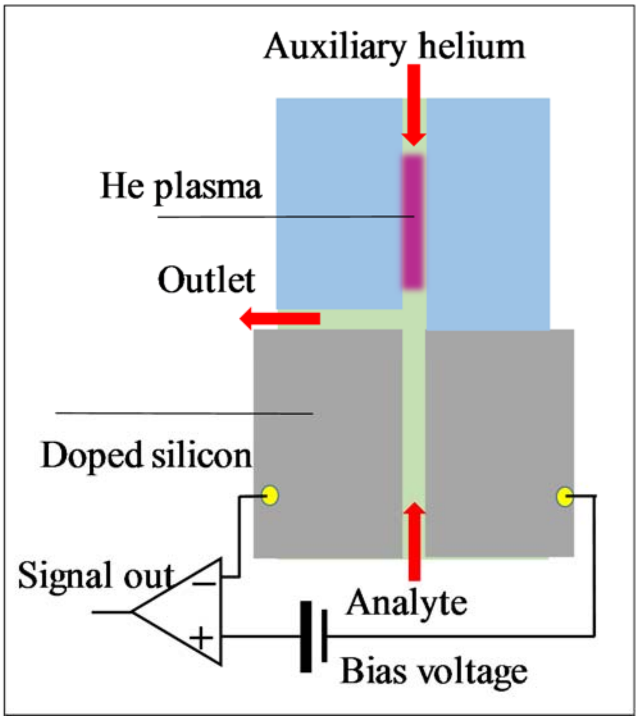

Figure S3 Circuitry for signal read-out.

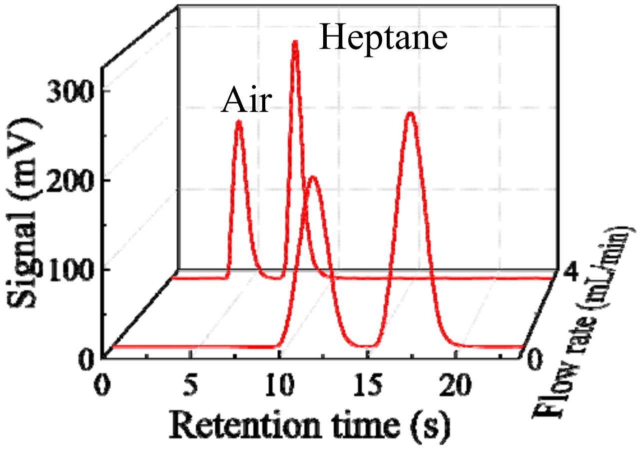

Figure S4 Eluent peaks become sharper and elution time becomes shorter at a higher carrier gas flow rate.

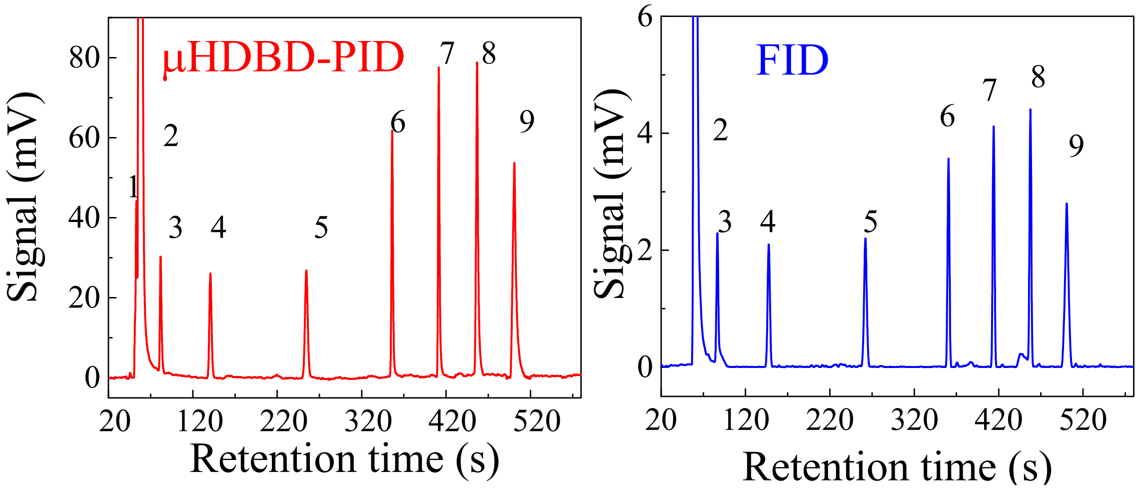

Figure S5 0.1 μL (100 split ratio) aliphatics mixture (C_5-C_{12}) was detected by μHDBD-PID and FID, respectively. The mixture was separated via a 7-m long Rtx®-VMS column at a flow rate of 1.5 mL/min with temperature ramping from T=40 ºC for 2 min and then to 200 ºC at a rate of 30 ºC/min. 1. Water, 2. Methanol and Pentane, 3. Hexane, 4. Heptane, 5. Octane, 6. Nonane, 7. Decane, 8. Undecane, 9. Dodecane. FWHM (in units of second) of μHDBD-PID and FID were: Hexane (2.00, 2.14); Heptane (2.84, 2.98); Octane (3.59, 3.29); Nonane (1.95, 2.12); Decane (1.86, 2.40); Undecane (2.31, 2.32); Dodecane (4.06, 4.14).

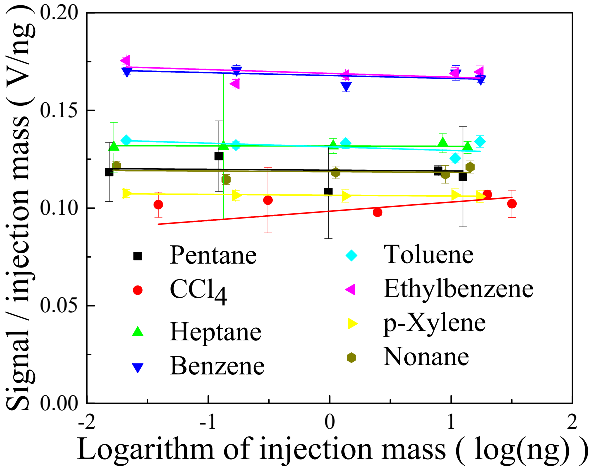

Figure S6 Plot of peak height divided by injection mass as a function of logarithm of injection mass for eight VOCs in Fig. 8. The slope of each curve is: Pentane (-4.27×10^{-4}), CCl_4 (4.7×10^{-3}), Heptane (-1.06×10^{-4}), Benzene (-1.48×10^{-3}), Toluene (1.87×10^{-3}), Ethylbenzene (-1.94×10^{-3}), p-Xylene (-4.21×10^{-4}), and Nonane (-3.35×10^{-4}).

Table S2: Linear regression parameters of 8 VOCs for signal vs mass curve with intercept set to zero

	Slope	Adjusted R	P-value
Pentane	0.1191	0.9998	7.81E-04
Carbon tetrachloride	0.1017	0.9978	2.15E-03
Heptane	0.1317	0.9999	3.96E-04
Benzene	0.1681	0.9997	1.31E-03
Toluene	0.1321	0.9992	1.64E-03
Ethylbenzene	0.1698	0.9992	2.21E-03
p-Xylene	0.1068	0.9999	3.35E-04
Nonane	0.1189	0.9993	1.45E-03

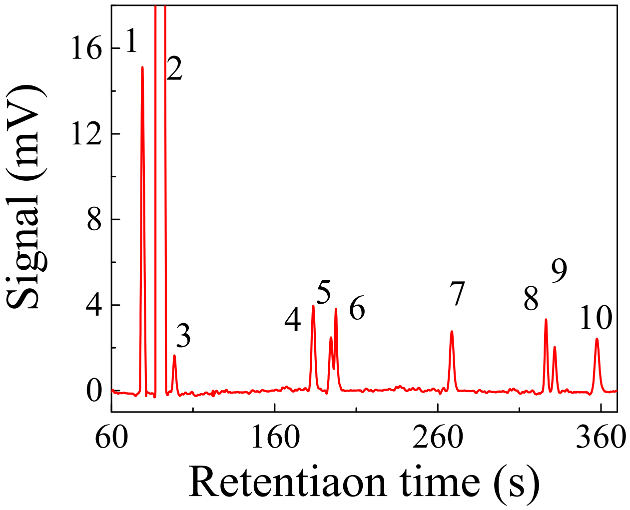

Figure S7 μHDBD-PID detection of VOCs mixture prepared in methanol with 195 ppm (V/V) concentration for all 8 VOCs. The mixture was separated by GC using a 7-m long Rtx®-VMS column. The injected mass and FWHM were: 1. Water (trace, 2.00 s); 2. Methanol (N/A, 2.01 s); 3. Pentane (15.28 pg, 1.84 s); 4. Carbon tetrachloride (38.83 pg, 2.33 s); 5. Heptane (16.7 pg, 2.34 s); 6. Benzene (21.39 g, 1.52 s); 7. Toluene (21.17 pg, 2.58 s); 8. Ethylbenzene (21.14 pg, 1.79 s); 9. p-Xylene (21.02 pg, 1.98 s); 10. Nonane (17.53 pg, 2.91 s). Temperature ramping: T=25 ºC for 0.6 min and then to 200 ºC at a rate of 30 ºC/min. Helium was used as the carrier gas at a flow rate of 1.5 mL/min.

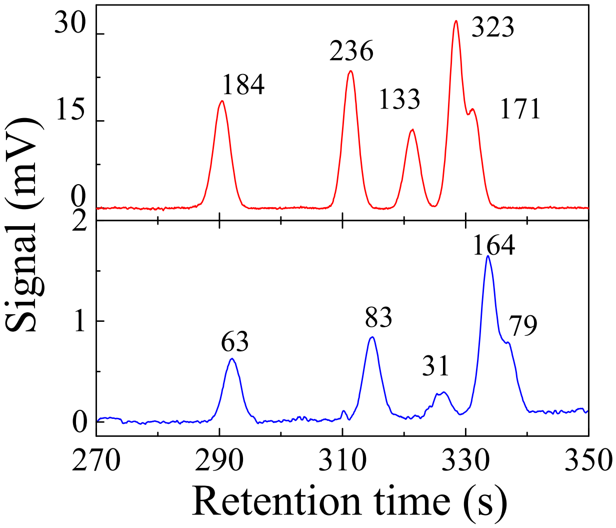

Figure S8 Enlarged part of Fig. 10 with the SNR labeled on the corresponding peak. Slight offset in the peak elution times between μHDBD-PID and FID results is due to a slight difference in temperature ramping during two separations.

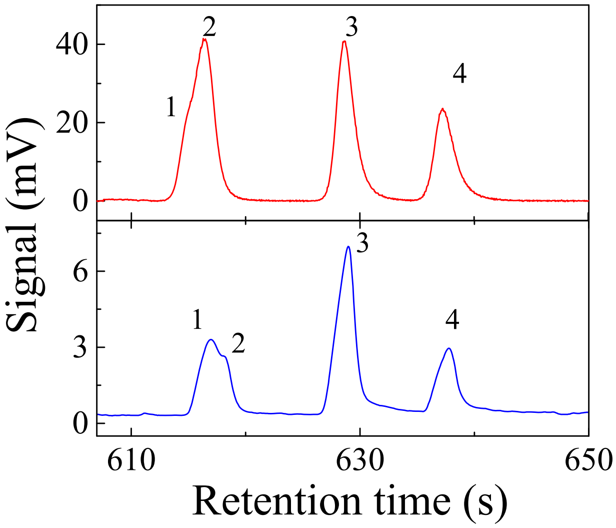

Figure S9 Enlarged part of Fig. 10. Identified peaks and the corresponding FWHM values of μHDBD-PID and FID are: 1. hexachloro-1,3-butadiene (not available due to co-elution), 2. 1,2,4-trichlorobenzene (not available due to co-elution), 3. Naphthalene (1.95 s / 1.78 s), 4 1,2,3-trichorobenzene (2.14 s / 1.93 s). Slight offset in the peak elution times between the μHDBD-PID and FID results is due to a slight difference in temperature ramping during two separations.

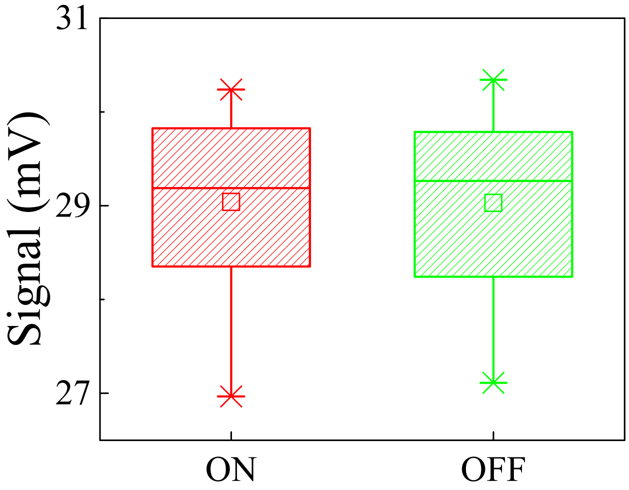

Figure S10 Testing of non-destructive nature of the μHDBD-PID. Boxplot of 15 times of 2.356 ng heptane injection under the plasma "ON" and "OFF" condition. A p-value of 0.9779 was calculated using an unpaired two sample t-test for equal population means with same sample size.

Table S3: Names of the 51 VOCs used in Fig. 10 provided by Sigma-Aldrich

1. 1,1-Dichloroethylene
2. Dichloromethane
3. trans-1,2-Dichloroethylene
4. 1,1-Dichloroethane
5. cis-1,2-Dichloroethylene
6. 2,2-Dichloropropane
7. Bromochloromethane
8. Chloroform
9. Carbon tetrachloride
10. 1,1,1-Trichloroethane
11. 1,1-Dichloro-1-propene
12. Benzene
13. 1,2-Dichloroethane
14. Trichloroethylene
15. Dibromomethane
16. 1,2-Dichloropropane
17. Bromodichloromethane
18. Toluene
19. Tetrachloroethylene
20. 1,1,2-Trichloroethane
21. Dibromochloromethane
22. 1,3-Dichloropropane
23. 1,2-Dibromoethane
24. Chlorobenzene
25. Ethylbenzene
26. 1,1,1,2-Tetrachloroethane
27. m-Xylene
28. p-Xylene
29. o-Xylene
30. Styrene
31. Bromoform
32. Bromobenzene
33. Propylbenzene
34. 1,1,2,2-Tetrachloroethane
35. 2-Chlorotoluene
36. Mesitylene
37. 1,2,3-Trichloropropane
38. 4-Chlorotoluene
39. tert-Butylbenzene
40. 1,2,4-Trimethylbenzene
41. sec-Butylbenzene
42. Isopropyl toluene
43. 1,3-Dichlorobenzene
44. 1,4-Dichlorobenzene
45. Butylbenzene
46. 1,2-Dichlorobenzene
47. 1,2-Dibromo-3-chloropropane
48. Hexachloro-1,3-butadiene
49. 1,2,4-Trichlorobenzene
50. Naphthalene
51. 1,2,3-Trichlorobenzene

REFERENCES

(1) Manginell, R. P.; Mowry, C. D.; Pimentel, A. S.; Mangan, M. A.; Moorman, M. W.; Sparks, E. S.; Allen, A.; Achyuthan, K. E. *Anal. Sci.* **2015**, *31*, 1183-1188.

(2) Narayanan, S.; Rice, G.; Agah, M. *Electrochim. Acta* **2014**, *181*, 493-499.

(3) Akbar, M.; Shakeel, H.; Agah, M. *Lab Chip* **2015**, *15*, 1748-1758.

(4) Narayanan, S.; Rice, G.; Agah, M. *Sens. Actuator B-Chem.* **2015**, *206*, 190-197.