Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

Selective determination of semi-volatile thiophene compounds in water by molecularly imprinted polymer thin-films with direct headspace gas chromatography sulfur chemiluminescence detection

Hassan. Y. Hijazi, Christina. S. Bottaro*

This supporting information gives a detailed description of the rebinding experiments, SEM images and photo of the polymer thin-film, and selectivity of MIP thin-film for thiophene compounds.

Selectivity experiments

In the rebinding experiments, each MIP slide was placed in a 100-mL beaker containing 40 mL of water spiked with a mixture of thiophene compounds at a concentration of 100 µg L^{-1} each for uploading and was stirred for 2 h at room temperature. Stock spiking solutions of thiophene compounds were prepared in acetonitrile and stored in the refrigerator at 4 °C when not in use. Working solutions were prepared daily by appropriate dilution of the spiking solutions with distilled water. The binding capacity of polymer Q_t (µg g^{-1}) for each analyte at time *t* was calculated using the following equation:

$$\mathrm{Qt} = \frac{m_{analyte}}{m_{film}} \qquad (S1.1)$$

where $m_{analyte}$ (µg) is the mass of adsorbed thiophene compound into the polymer film and m_{film} (g) is the mass of the polymer film. The imprinting factor (*IF*) values for all thiophene compounds were calculated as follow,

$$IF = \frac{\mathrm{Q_{MIP}}}{\mathrm{Q_{NIP}}} \qquad (S1.2)$$

Where Q_{MIP} (µg g^{-1}) is the binding capacity of MIP and Q_{NIP} (µg g^{-1}) is the binding capacity of NIP.

Table S1. Percent recovery values of thiophene compounds obtained from the analysis of small and large volumes of DI water and seawater spiked at the same concentration (50 µg L^{-1}) using MIP thin-film for two hours followed by HS-GC-SCD analysis.

Sample volume (mL)	Mass of analyte recovered (ng) (RSD%)									
	BT		3-MBT		DBT		4-MDBT		4,6-DMDBT	
	DI	SW	DI	SW	DI	SW	DI	SW	DI	SW
10	201 (1.5)	194 (2.8)	168 (0.7)	149 (1.9)	253 (1.0)	286 (3.2)	197 (0.6)	207 (2.6)	115 (1.0)	107 (2.9)
Matrix Effect (% of DI water recovery)	97		89		97		98		94	
800	1861 (2.0)	1758 (1.7)	1617 (6.0)	1467 (6.4)	1841 (5.0)	1622 (5.4)	1473 (2.9)	1263 (2.6)	989 (4.1)	673 (5.7)
Matrix Effect (% of DI water recovery)	94		93		89		86		68	

Characterization of polymer thin-films

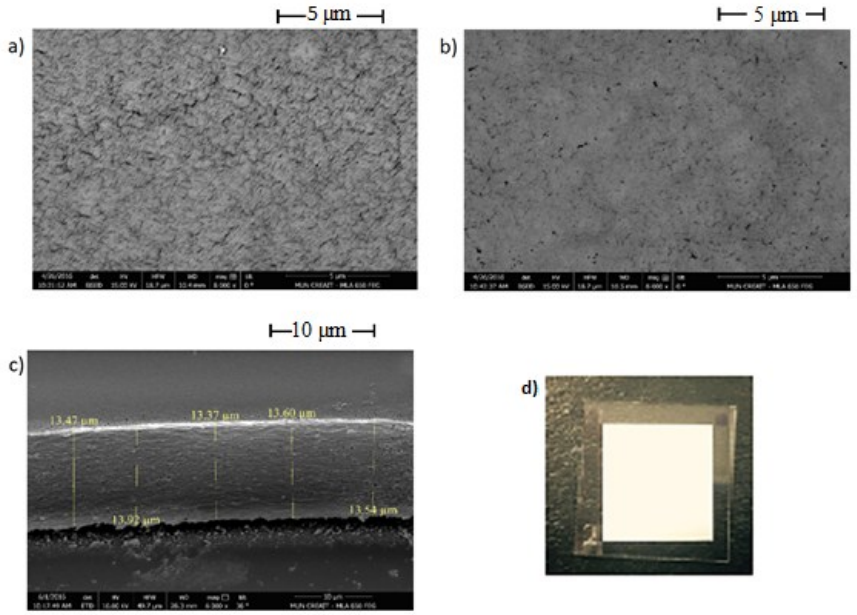

Figure S1. a) SEM image of the MIP film surface, b) SEM image of NIP films, c) SEM image of cross-section of MIP film, and d) MIP coated slide.

Selectivity of MIP thin-film for thiophene compounds

Table S2. Log K_{ow} of targeted thiophene compounds.

Compound	Log K_{ow}
Benzothiophene (BT)	3.12
3-Methylbenzothiophene (3-MBT)	3.71
Dibenzothiophene (DBT)	4.38
4,6-Dimethyl-dibenzothiophene (4,6-DMDBT)	5.50

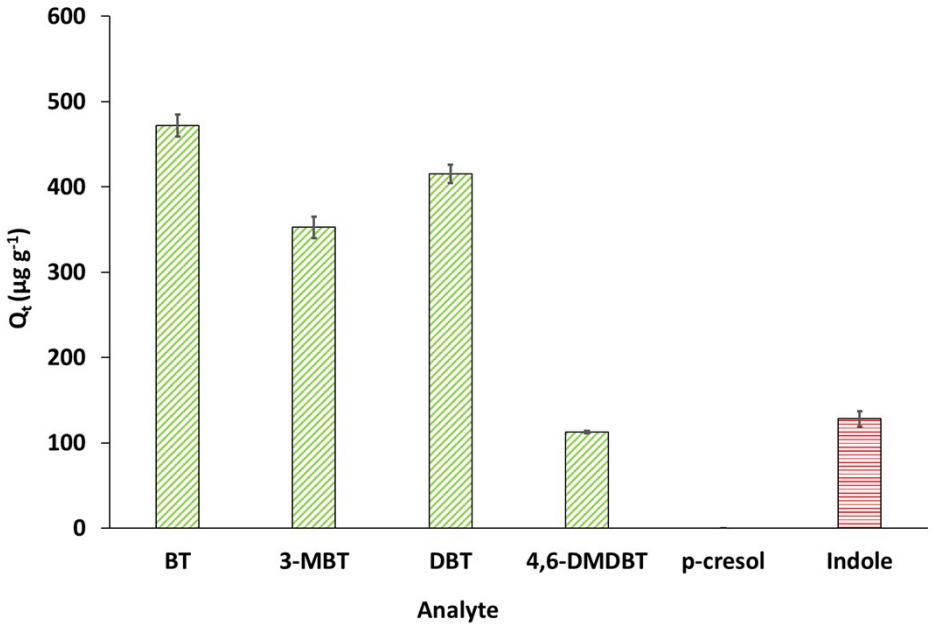

Figure S2. Selectivity of MIP thin-film for thiophene compounds versus p-cresol and indole (n=3). Error bars represent standard deviation.