Supporting information for

Cavitands as superior sorbents for BTX detection at trace level

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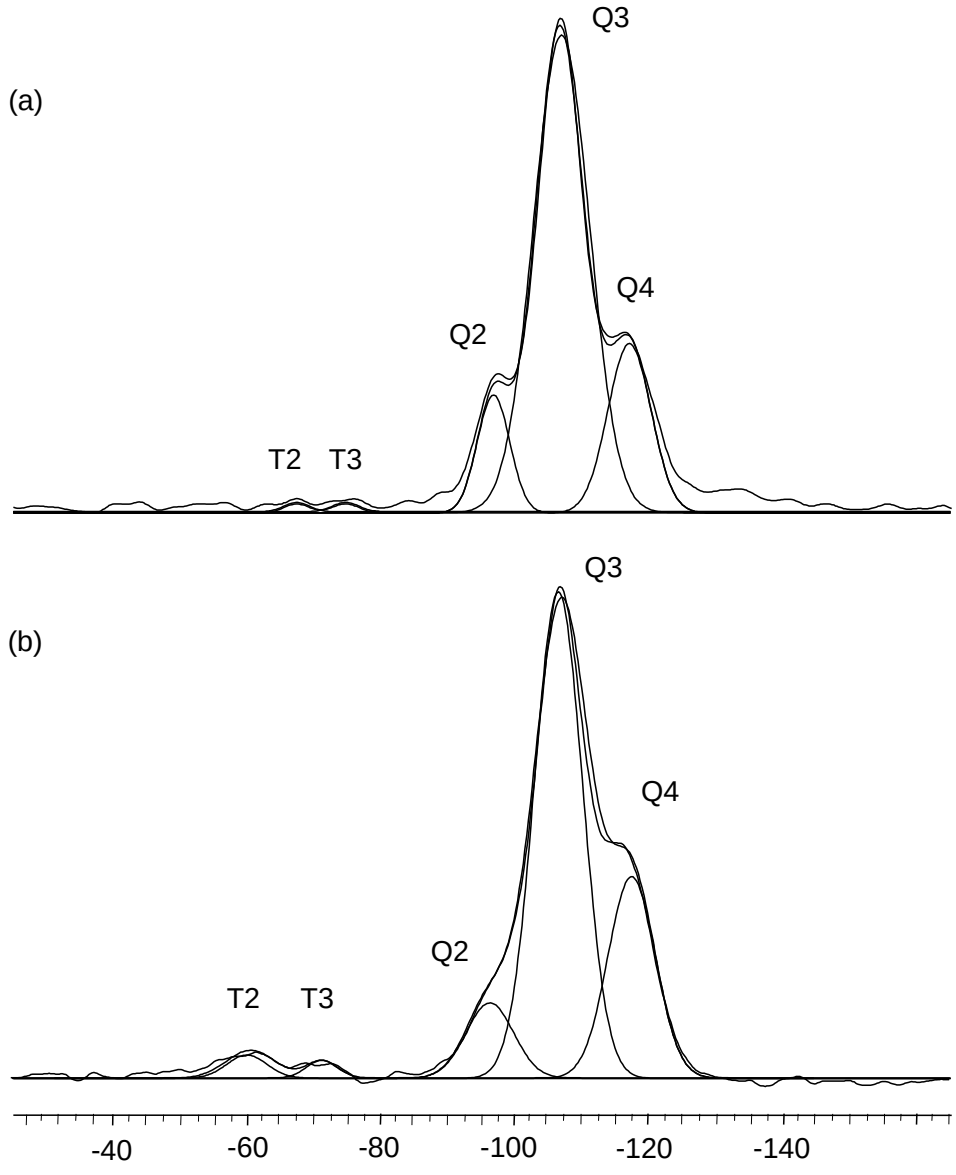
Cavitand 2. Bromochloromethane (16.95 g, 131 mmol) and K_2CO_3 (3.62 g, 26.20 mmol) were added, under argon, to a solution of resorcinarene **1** (2.73 g, 2.62 mmol) in dry DMA (100 mL) in a Schlenk reactor. The suspension was stirred at 88°C for 3 hours. The reaction was quenched in acid water, and the product was extracted with CH_2Cl_2 and dried on Mg_2SO_4. After filtration the solvent was removed under pressure, and the yellow oil obtained **2** in 97% yield (2.77 g) was used without any other purification. M.p. 106-108°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (s, 4H; Ar*H*), 6.47 (s, 4H; Ar*H*), 5.85-5.76 (m, 4H, RC*H*=CH_2), 5.72 (d, J=7.2 Hz; 4H; CH_{2out}), 4.93 (m, 8H, RC=CH_2), 4.72 (t, J=8.0 Hz, 4H; RC*H*Ar_2), 4.41 (d, J=7.2 Hz, 4H; CH_{2in}), 2.20 (m, 8H; RCH_2CHAr_2), 2.03 (m, 8H; RCH_2CH=CH_2), 1.29 (m, 48H; CH_2); ^{13}C NMR (300 MHz, $CDCl_3$): δ = 154.8 (*C*, resorcinarene), 139.2 (*CH*=CH_2), 138.4 (*C*, resorcinarene), 120.6 (*C*, resorcinarene), 116.5 (*C*, resorcinarene), 114.2 (CH=*CH*$_2$) 99.5 (O*CH*$_2$O), 36.3 (*CH*Ar_2), 33.8-27.8 (*CH*$_2$, chain); FT-IR (KBr): 1641, 968 (OCH_2O), 908 (C=C) cm^{-1}; MS (CI): *m/z* (%): 1090 (90) $[MH]^+$. Anal. Calcd for $C_{72}H_{96}O_8$: C, 79.37; H, 8.88. Found: C, 79.01; H, 9.07.

Cavitand 3. 2,3-dichloroquinoxaline (1.10 g, 7.97 mmol) and K_2CO_3 (6.37 g, 46.09 mmol) were added, under argon, to a solution of resorcinarene **1** (2.0 g, 1.92 mmol) in dry DMA (40 mL). The suspension was stirred at 40°-50°C for about 16 hours. The reaction was quenched in water (200 mL); the resulting suspension was acidified to pH 7 and filtered. The residue was dissolved in CH_2Cl_2 and the organic layer was washed with water to neutrality and evaporated under vacuum. The residue was then purified by column chromatography (SiO_2, CH_2Cl_2/Et_2O 99:1) to give cavitand **3** in 44% yield (1.32 g) as a white powder. M.p. 275-276°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (s, 4H; Ar*H*), 7.79 (m, 8H; Ar*H*, part AA′ of a AA′BB′ system), 7.47 (m, 8H; Ar*H*, part BB′ of a AA′BB′ system), 7.21 (s, 4H; Ar*H*), 5.84 (m, 4H; RC*H*=CH_2), 5.58 (t, J=7.3 Hz, 4H; RC*H*Ar_2), 4.98 (m, 8H; RCH=CH_2), 2.23 (m, 8H; RCH_2CHAr_2), 2.05 (m, 8H; RCH_2CH=CH_2), 1.35 (m, 48H; CH_2); FT-IR (KBr): 3072, 1640, 911 (C=C) cm^{-1}; MS (CI): *m/z* (%): 1546 (100) $[MH]^+$. Anal. Calcd for $C_{100}H_{104}N_8O_8$: C, 77.69; H, 6.78; N, 7.25. Found: C, 77.41; H, 6.97; N, 7.01.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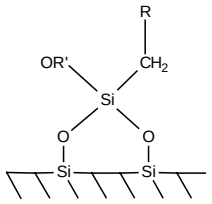
Q3
Q4
Q2
T2
T3
(b)
Q3
Q4
Q2
T2
T3
-40
-60
-80
-100
-120
-140
(ppm)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OR'
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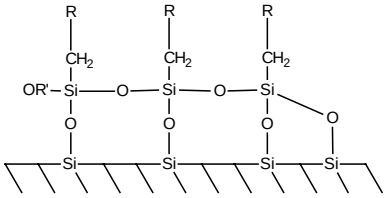
Si
O
O
Si
Si

T2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R
R
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CH2
OR'
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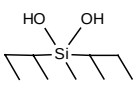
O
Si
O
Si
O
O
O
O
Si
Si
Si
Si

T3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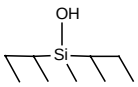
OH
Si

Q2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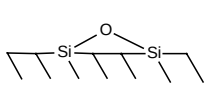
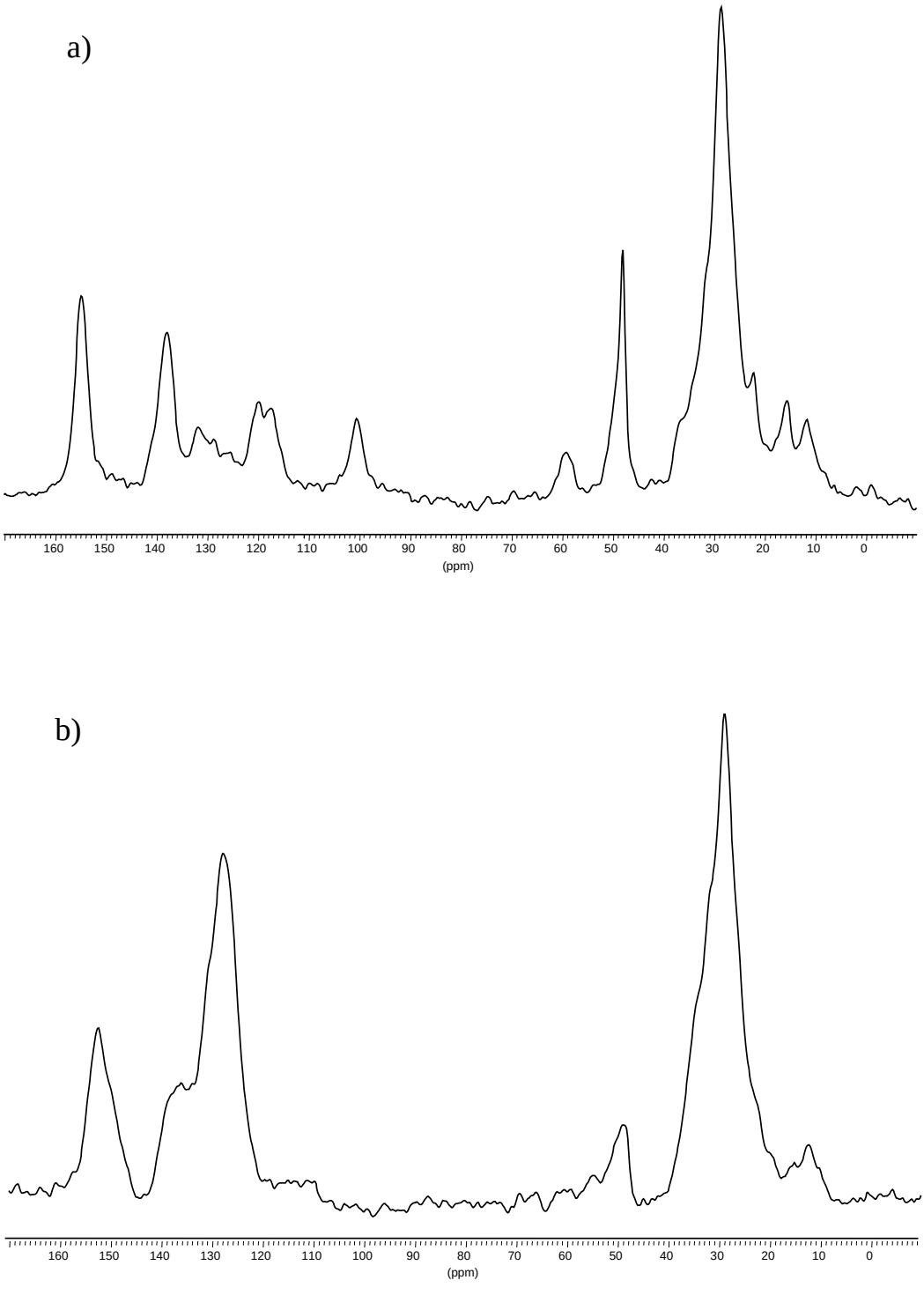
Si

Q3

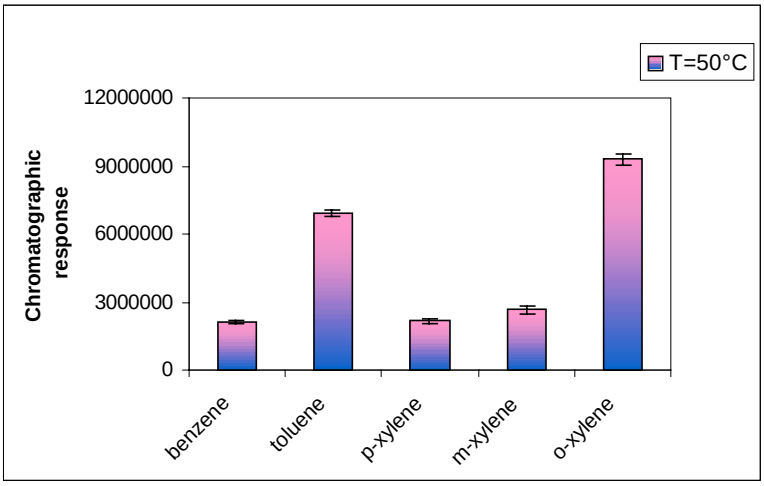

O
Si
Si

Q4

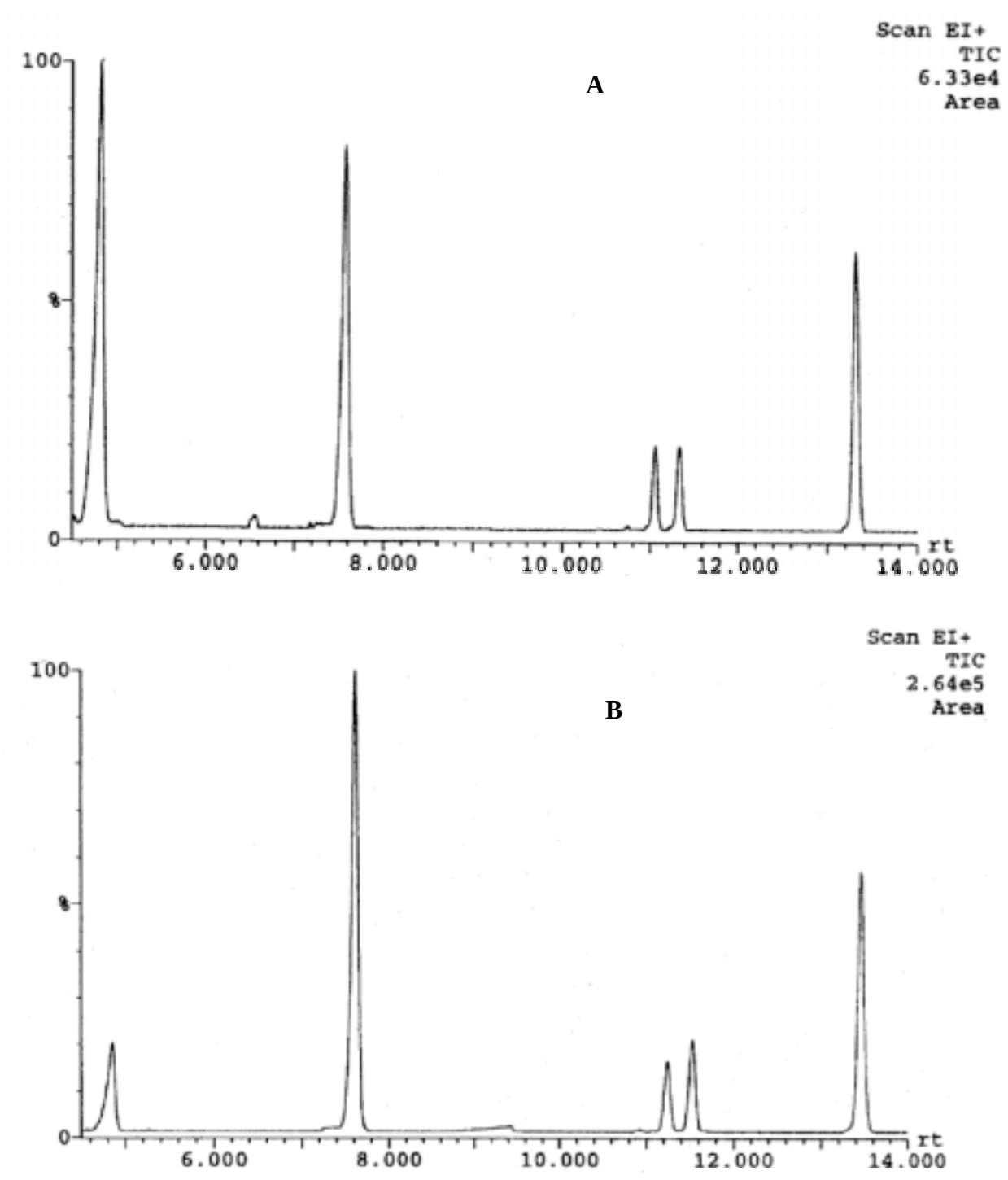
^{29}Si CP/MAS NMR spectra of: (a) MeCav coated silica; (b) QxCav coated silica



^{13}C CP/MAS NMR spectra of: (a) MeCav grafted on silica; (b) QxCav grafted on silica



Desorption pattern of BTX observed for Tenax TA® at 50°C.



Gas chromatographic traces obtained from the desorption at 75°C of the BTX mixture trapped on: **A**) QxCav trap and **B**) Carbotrap 100®.