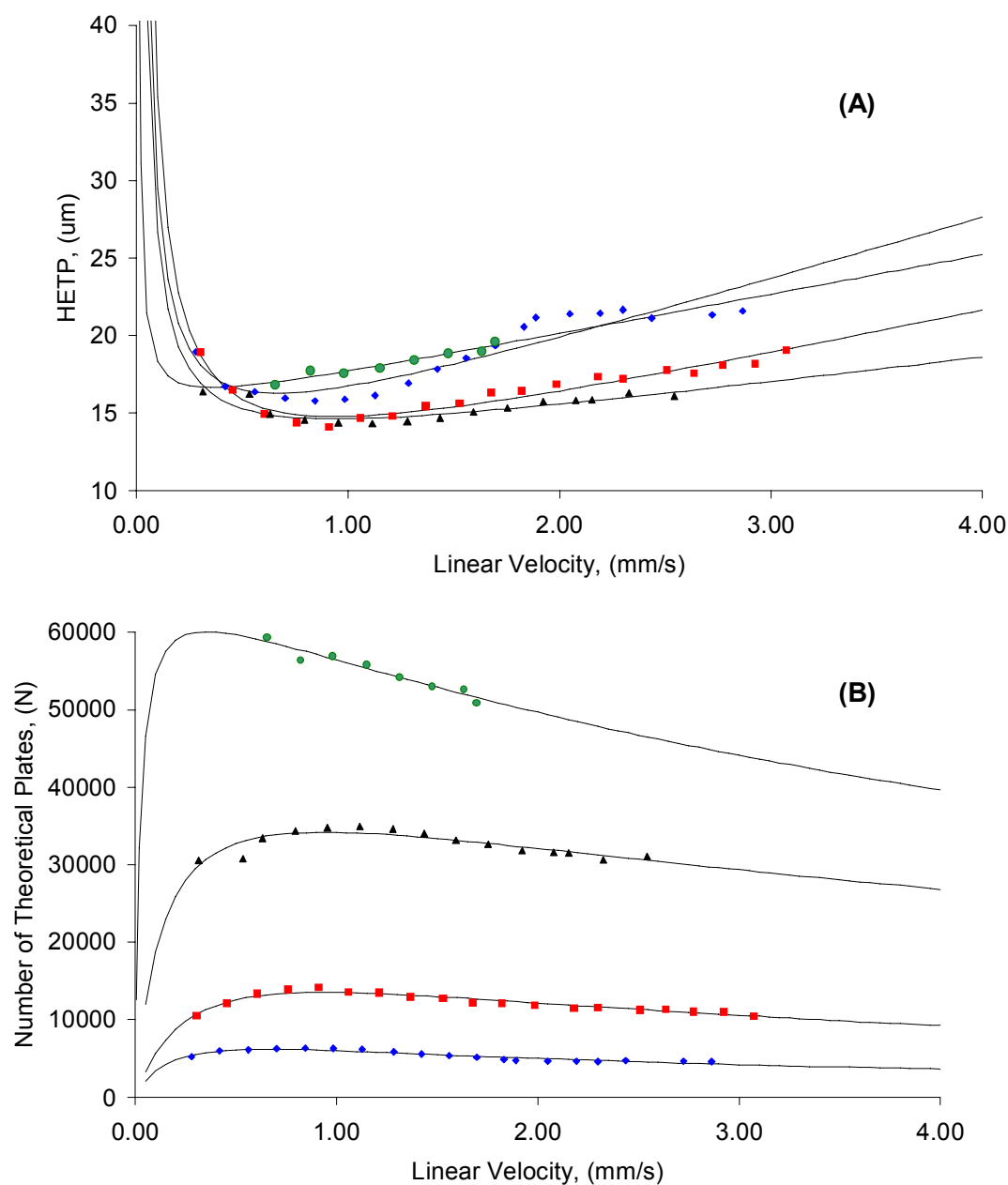
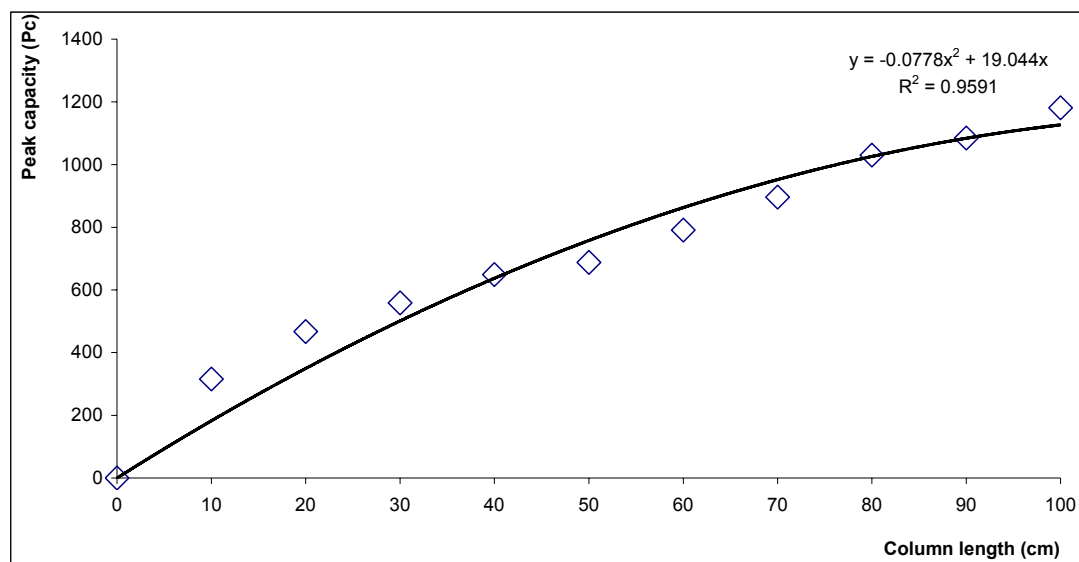




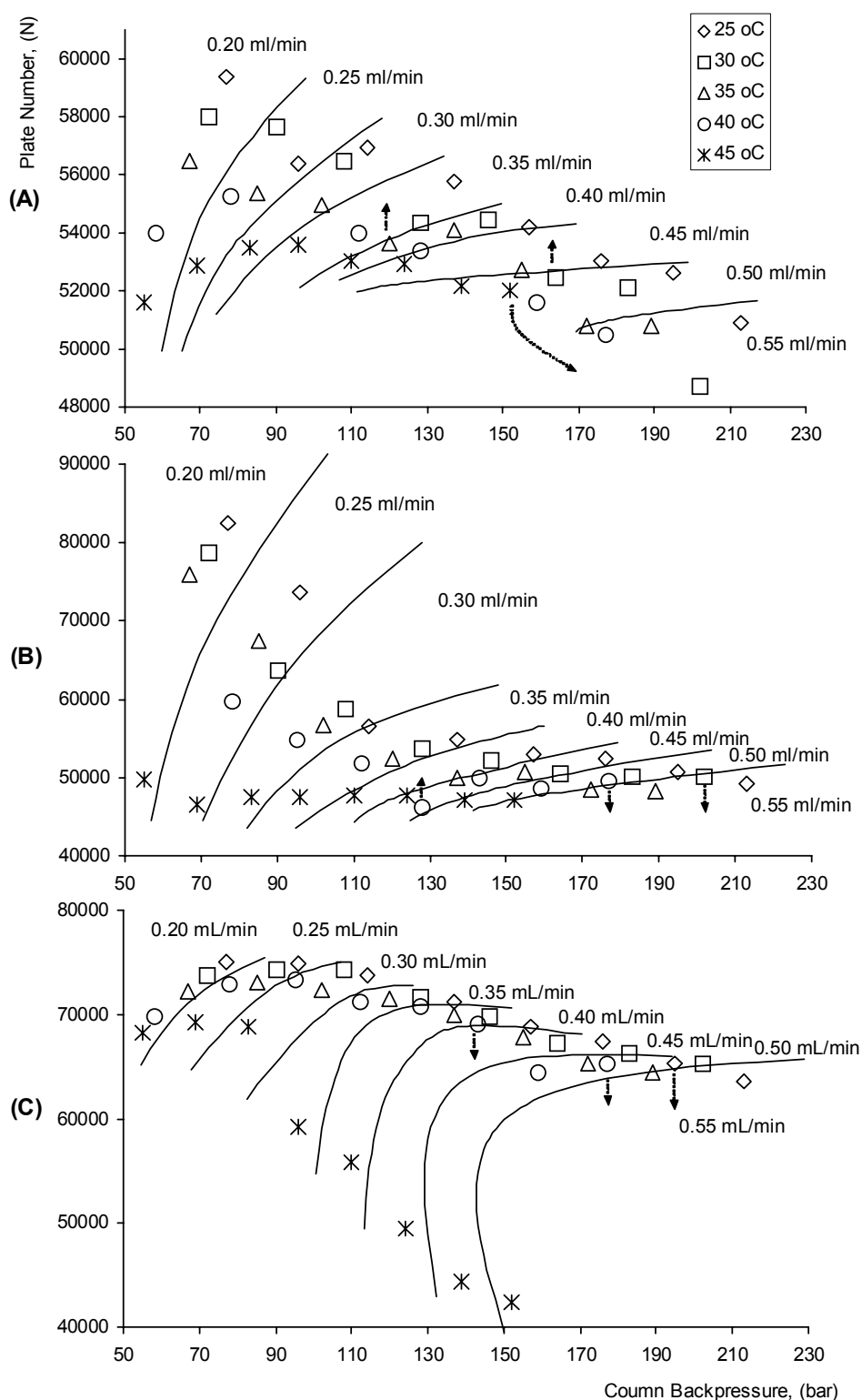
ESI Fig. S1. Plot of plate height (HETP) versus mobile phase linear velocity (μ_0) using acetophenone as the test analyte and (B) Plot of plate number (N) versus mobile phase linear velocity on the 10.0 cm monolithic column ($\blacklozenge$), the 20.0 cm monolithic column ($\blacksquare$), the 50.0 cm monolithic column ($\blacktriangle$) and the 100.0 cm monolithic column ($\bullet$). Mobile phase used was 60:40 acetonitrile water.

Column L	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W Average	Tg	Pc
0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0.1045	0.0887	0.0922	0.0935	0.0784	0.0821	0.0938	0.0998	0.0928	0.0946	0.09204	29	316
20	0.1281	0.1093	0.1249	0.1189	0.1217	0.1427	0.1118	0.1122	0.14	0.136	0.12456	58	467
30	0.1218	0.1377	0.1451	0.138	0.1653	0.1616	0.1809	0.1796	0.1714	0.1566	0.1558	87	559
40	0.143	0.1488	0.2004	0.1963	0.1759	0.1429	0.183	0.1928	0.2241	0.1824	0.17896	116	649
50	0.1571	0.1997	0.2332	0.2178	0.17	0.154	0.2164	0.2812	0.2467	0.2332	0.21093	145	688
60	0.1922	0.2307	0.2007	0.1644	0.1796	0.2274	0.2645	0.2514	0.2883	0.2027	0.22019	174	791
70	0.1834	0.2739	0.2224	0.185	0.1836	0.263	0.227	0.2376	0.2911	0.2018	0.22688	203	896
80	0.1979	0.1981	0.2163	0.2163	0.2027	0.1978	0.2481	0.2631	0.2936	0.2209	0.22548	232	1030
90	0.2104	0.2128	0.2381	0.1998	0.2347	0.2624	0.2933	0.2675	0.2615	0.2267	0.24072	261	1085
100	0.1952	0.2775	0.2522	0.2399	0.2106	0.2258	0.2739	0.2572	0.265	0.2605	0.24578	290	1181

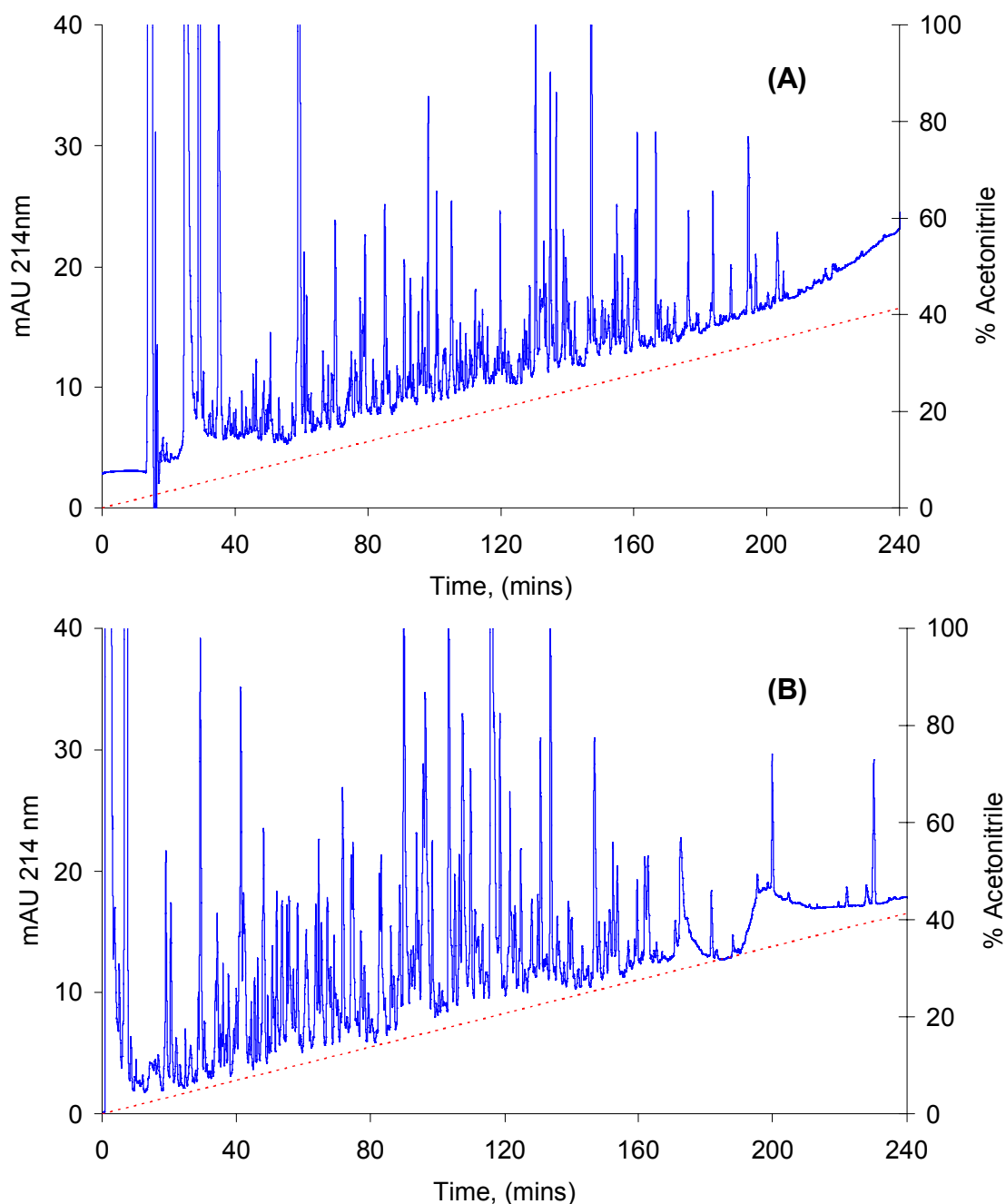


ESI Fig. S2. Effect of column length upon calculated peak capacity.

Constant flow rate, temp and gradient slope applied throughout, gradient time extended in accordance with column length.



ESI Fig S3. Graphs showing the relationship between column pressure drop and plate generation on the 100.0 cm monolithic coupled column at increasing column temperatures, for (A) acetophenone, (B) toluene, (C) butylbenzene. Corresponding flow rates for the pressure drops measured are also shown.



ESI Fig S4. The gradient separation of a mixed digest of BSA, carbonic anhydrase, cytochrome C, myoglobin, haemoglobin, enolase, alkaline phosphatase, insulin, phosphorylase B and alcohol dehydrogenase on the 100.0 cm monolithic column with UV detection at 214 nm. Injection volume = 100 μ L. (B) Gradient separation of the same ten protein digest mix on a Zorbax Eclipse XDB 50.0 x 2.1 mm I.D. 1.8 μ m particle packed reversed-phase column. Gradient separations using a mobile phase of 0.02% v/v trifluoroacetic acid (TFA) in water as solvent A and 0.02% TFA in acetonitrile as solvent B. Initial conditions of 100 % solvent A followed by a linear increase to 50 % solvent B over a period of 290 minutes. A flow rate of 0.4 mL min⁻¹ was used with 1 m monolith. A flow rate of 0.2 mL min⁻¹ was used with the 1.8 μ m particle packed reversed-phase column. When performing LC-MS analyses TFA in both mobile phase solvents was substituted by formic acid (FA).

ESI Table S1. Column efficiency and pressure drop data for each of the ten individual monolithic columns used to produce coupled 1m long monolithic phase.

Column No.	N/m ¹	Column pressure drop ¹
1	100967	348
2	115845	334
3	105221	377
4	95920	363
5	108926	363
6	106219	348
7	101311	363
8	98045	334
9	83074	334
10	94484	348
Average	101001	351
%RSD	8.89	4.25

¹ – Using 60% MeCN/H₂O mobile phase delivered at 0.85 mL/min, for 1 μ L injection of anthracene.

Columns used during this study - Phenomenex Onyx monolithic C₁₈ 100.0 x 3.0 mm I.D. columns, (Phenomenex, Macclesfield, Cheshire, UK).