A New Method for Decreasing Mass Limit of Detection and Increasing Number of Theoretical Plates in Capillary Electrophoresis with Amperometric Detection
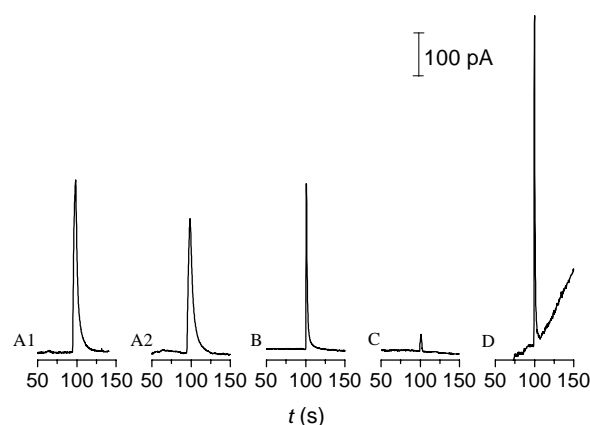
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Abstract: A new method was developed to decrease the mass limit of detection (LOD) and increase the number of theoretical plates (N) in capillary electrophoresis with amperometric detection. When the single microcylinder electrode, the 10 μm ID capillary with the etched detection end and the in-capillary alignment were used, the mass LOD for phenol was reduced 124 times and N was increased 36 times in comparison with the normal situation.

Keywords: Capillary electrophoresis, electrochemical detection, microelectrode, phenol.

Much attention has been focused recently on pushing down the limit of detection (LOD)[1-3]. LOD in terms of amount is a combination of concentration LOD and the volume of sample required. The detection of small amount of sample can be achieved by reducing the sample volume, lowering the sample concentration LOD or a combination. Sampling with capillary can reduce sample volume to nL-pL level. To lower the concentration LOD is related to improve the signal-to-noise ratio. In the present work, we used phenol as a model to investigate the method of decreasing the mass LOD. In this method, capillary electrophoresis (CE) system used was similar to our previous description[4]. The working electrodes were made of carbon fiber. The shape and size of electrode, the shape of capillary detection end and the alignment methods are shown in **Figure 1**, where A is a microdisk bundle electrode (MDBE) with a normal capillary, B is the MDBE with an etched capillary, C is a single microdisk electrode (SMDE) with a normal capillary and D is a single microcylinder electrode (SMCE) with an etched capillary. The electropherograms of phenol for different cases (in **Figure 1)** are shown in **Figure 2**, respectively. Curve A1 and A2 correspond to the case shown in **Figure 1A**. The difference is only the capillary inner diameter (20 μm ID for curve A1 and 10 μm ID for curve A2). Curve B, C and D correspond to the cases shown in **Figure 1B, C and D**, respectively. In these cases, the peak current, i_p, the sample volume V, the number of theoretical plates bN, the mass LOD of phenol obtained are listed in **Table 1.** Since the injected sample volumes in each case were not the same, the ratios of peak current i_p, to sample volume V, are used to evaluate the

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Figure 1 Shape and size of electrodes, shape of capillary end and their alignment methods

Electrode   Capillary

A

B

C

D
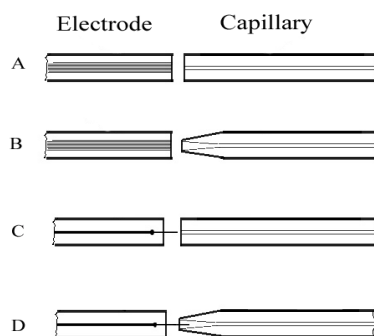
Figure 2 Electropherograms of phenol in different cases shown in **Figure 1**

100 pA

A1   A2   B   C   D

50 100 150 50 100 150 50 100 150 50 100 150 50 100 150

t (s)

2.60×10^{-5} mol/L phenol; 1.0×10^{-2} mol/L $Na_2B_4O_7$-3.0×10^{-2} mol/L NaOH (pH 9.8); separation voltage, 20.0 kV; injection, A1 and A2, 5.0 kV for 10 s; B and C, 2.5 kV for 5 s; D, 2.5 kV for 2 s; capillary ID: A1, 20 μm; A2, B, C and D, 10 μm; capillary length, 30 cm; detection potential, 1.05 V (*vs.* saturated calomel electrode).

effect on the LOD of phenol. i_p/V values were also listed in **Table 1.** i_p/V obtained in D was the highest among all cases, 76 times higher than that for A1. When D was used, a mass LOD of phenol as low as 4.9×10^{-18} mol could be obtained, 126 times lower than that in A1. It was found that N values obtained by using the etched capillary (cases B and D) were higher than that by using the normal capillary (situations A1, A2 and C). This is because when the analyte flows from the inside of the capillary to the etched and extended detection end of the capillary, the zone becomes narrower. N value for D can be achieved to 6.6×10^4, *ca.* 36 times higher than that for A1.

Table 1 i_p, V, i_p/V, N, and mass LOD of phenol at different situations shown in **Figure 1**

Case	i_p (pA)	V (nL)	i_p/V (nA/nL)	$10^{-3}N$	Mass LOD (mol)
A1	401	2.4	0.17	1.8	6.1×10^{-16}
A2	319	0.57	0.56	2.0	1.4×10^{-16}
B	396	0.14	2.9	29	2.5×10^{-17}
C	37.8	0.14	0.27	6.1	5.2×10^{-16}
D	705	0.056	13	66	4.9×10^{-18}

Conditions as in **Figure 2.**

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