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CAPILLARY ELECTROPHORESIS - ELECTROSPRAY IONIZATION MASS SPECTROMETRY IN SMALL DIAMETER CAPILLARIES

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Capillary Electrophoresis - Electrospray Ionization Mass Spectrometry in Small Diameter Capillaries

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Currently, a major effort in our laboratory involves exploring methods to increase analyte sensitivity in capillary electrophoresis - electrospray ionization / mass spectrometry (CE-ESI/MS). The goal of this research involves the examination of small inner diameter capillaries for increased sensitivity in CE-ESI/MS.

Commonly in ESI/MS two detection regimes exist. First, at high analyte mass flow rates into the electrospray source an ESI limited detection regime exists; where, the electrospray source is saturated. Second, at low analyte mass flow rates an analyte limited regime is present. One effective means of reducing the mass flow rate and consequently work in the analyte limited regime incorporates the use of small inner diameter (i.d.) capillaries.

The experimental system used for these studies incorporates a modified triple-quadrupole mass spectrometer (Sciex TAGA 6000E), and an in-house built capillary electrophoresis system. In all studies, aminopropylsilane coated fused-silica capillaries of various i.d.'s are used. The buffer system used is a 10 mM acetic acid solution, pH = 3.4. All samples are electrokinetically injected

The solute mixture chosen for the initial study contains tryptophan (204 Da), leucine-enkephalin (555 Da) and melittin (2845 Da) with serial dilutions at ratios between 1:2 and 1:50. The separation for this mixture is performed with capillary i.d.'s of **100**, **50**, **20**, and **10** µm. The mass spectrometer is used in the selected ion monitoring mode. The results for melittin are summarized in Figure 1 where the solute peak area is shown as a function of amount injected. In general as the capillary i.d. is reduced from 100 to 10 µm, an increase in solute sensitivity occurs; where, for the 10 µm i.d. capillary, **~150 attomoles** of melittin is detected. Moreover, a four component protein mixture, which contains the solutes aprotinin (6.5 kDa), cytochrome c (12 kDa), myoglobin (17 kDa), and carbonic anhydrase (29 kDa) each at 30 µM, is separated using capillary i.d.'s of **50**, **20**, **10**, and **5** µm. The separations obtained for 50 and 5 µm i.d. capillaries and the extracted **full scan** mass spectra obtained from the **5** µm i.d. case are illustrated in Figure 2. In general from Figure 2, the relative signal intensity decreases only by approximately **half** in comparing the **50** and **5** µm i.d.'s; however, the relative amounts injected differ from **60 femtomoles** to **600 attomoles**.

Consequently, we have demonstrated that an increase in the solute sensitivity occurs when small i.d. capillaries (**<20** µm) are utilized in CE-ESI/MS for both a peptide and a protein mixture. Small i.d. capillaries provide an effective means of reducing mass flow rate to the ESI source without degradation of separation resolution or analysis time.

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Figure 1

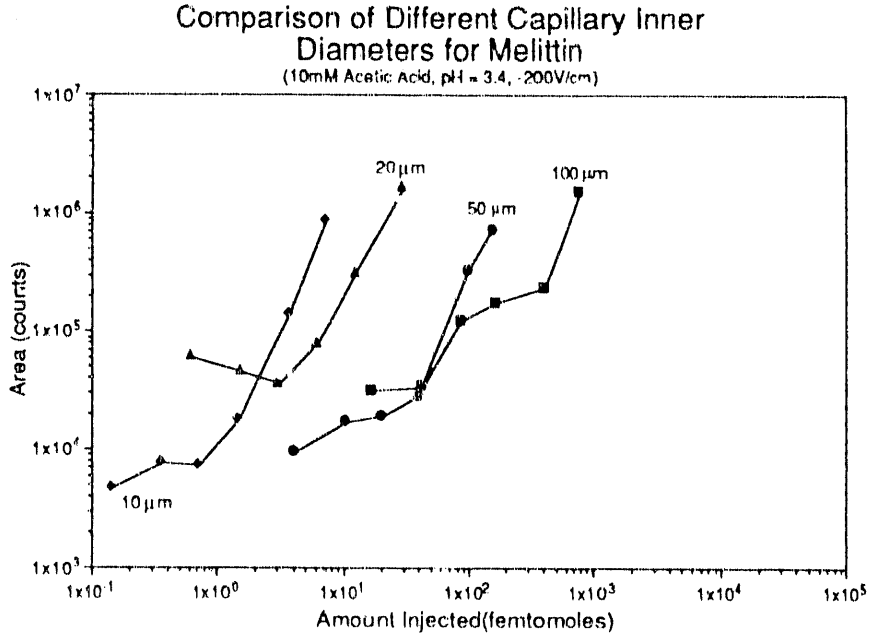
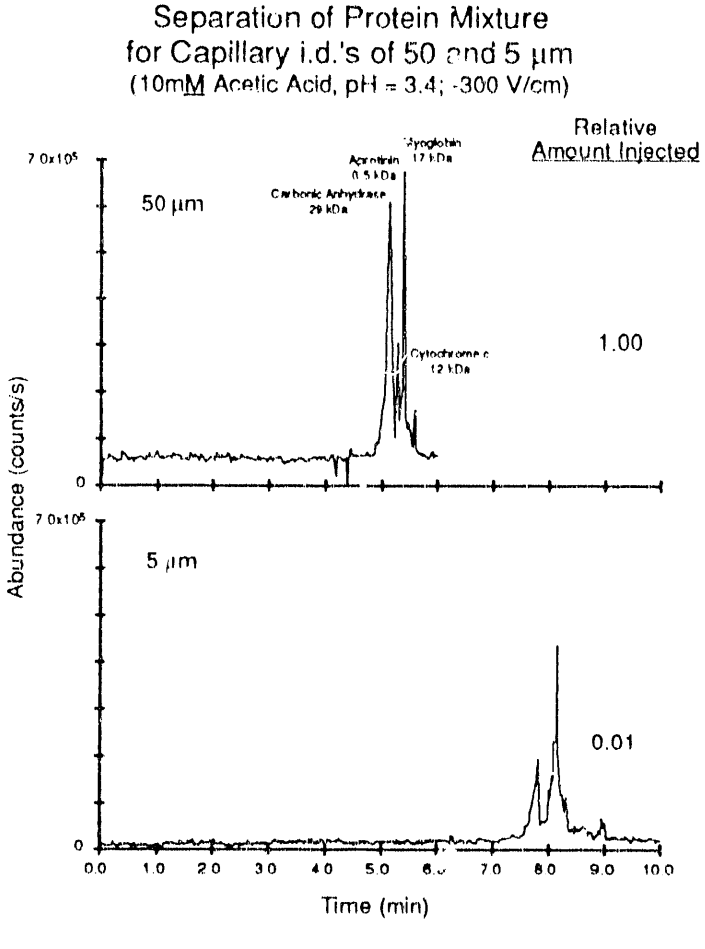
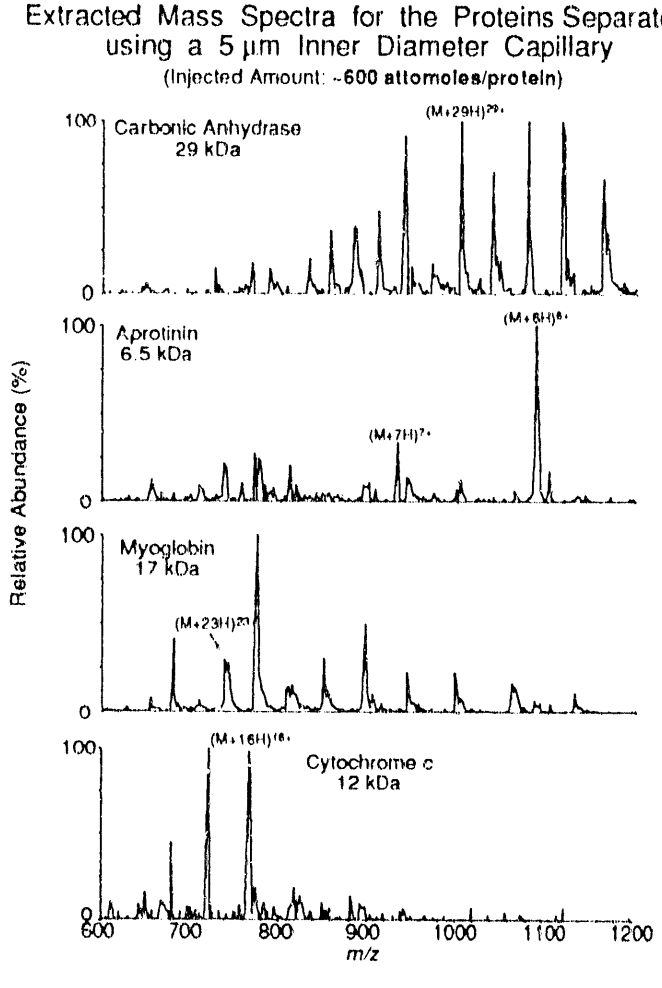


Figure 2





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