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Carbon Fiber-gold/mercury Dual-electrode Detection for Capillary Electrophoresis

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Abstract: A carbon fiber-gold/mercury dual-electrode for capillary electrophoresis is constructed. Cysteine, glutathione, ascorbic acid and uric acid can be detected simultaneously and selectively at the dual-electrode, respectively. The capillary electrophoresis / dual-electrode detection system has been used to determine these compounds in human blood samples.

Keywords: Ascorbic acid, capillary electrophoresis, cysteine, electrochemical detection, electrode, glutathione, uric acid.

Capillary electrophoresis (CE) has become a useful and powerful separation technique and has many applications. Electrochemical detection (ED) has been shown to be one of the most sensitive detection techniques available for use in CE. Dual-electrode detection can expand the applicability of CE-ED[1-5], the materials such as gold/mercury[1,3], carbon fiber[2], Pt[4] and Au[3,5] have been used for the two electrodes in dual-electrodes.

As is well known, the electrochemical response of different compounds is different for different types of electrode material. For example, glutathione (GSH) is sensitive for mercury electrode, but not for the carbon electrode. Ascorbic acid (AA) and uric acid (UA) can be oxidized at the carbon electrode, but not at the mercury electrode. Therefore, they can not be detected in one run in CE. In order to determine these compounds simultaneously in CE, we developed a CE method using a carbon fiber-gold/mecury dual-electrode (CGMDE) with a parallel mode. In this method, GSH and cysteine (Cys) were measured at the carbon fiber electrode (CFE), and AA and UA were measured at the gold/mercury electrode (GME) simultaneously.

CZE system used in this work was similar to our previous description[6]. A high-voltage power supply provided a voltage of 0-30 kV. Fused-silica capillaries (25 μm×50 cm) were used. The reservoir containing the electrochemical detection cell was held at ground potential. The electrochemical detection (ED) at two different constant potentials was performed with two electrochemical analyzers. ED was carried out with two three-electrode system consisted of a CFE (0.0078 μm^2) and a GME (0.0014 μm^2) of the CGMDE as the working electrodes, a saturated calomel electrode as the reference electrode, and two coiled Pt wires as the auxiliary electrodes. **Figure 1** shows the

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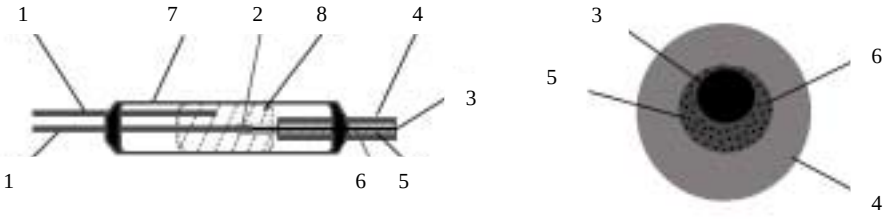
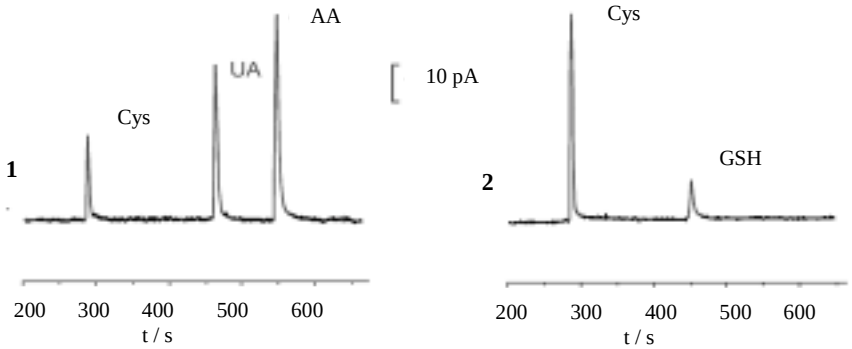
construction of the CGMDE. The experimental conditions were: 3.7×10^{-2} mol/L NaH_2PO_4-3.2×10^{-3} mol/L Na_2HPO_4 (pH 5.8) for the buffer, 20 kV for the separation voltage, 5 kV and 10 s for the injection voltage and the injection time, 0.1 V and 0.8 V for the detection potential of the GME and the CFE of the CGMDE, respectively. **Figure 2** showed the electropherograms of the standard solution containing 5.00×10^{-5} mol/L Cys, GSH, UA and AA at the CGMDE. Three peaks with the migration time (t_m) of 285, 470 and 550 s appeared in the electropherogram detected by the CFE (curve 1), which corresponded to Cys, UA and AA, respectively. Two peaks with t_m of 285 and 453 s appeared in the electropherogram detected by the GME (curve 2), which corresponded to Cys and GSH, respectively. It was noted that the peak current of Cys detected by the CFE was lower than that detected by the GME.

Figure 1 Manufacturing process of the CGMDE. 1, copper lead; 2, epoxy resin; 3, GME; 4, fused-silica capillary; 5, CFE; 6, ethyl α-cyanoacrylate adhesive; 7, glass capillary; 8, mercury.



The linear ranges, limits of detection (LOD) and correlation coefficients of Cys and GSH at GME, and Cys, UA and AA at CFE are listed in **Table 1**. The relative standard deviations of the method for Cys (using CFE), Cys (using GME), GSH, UA and AA were between 2.4 (CFE) , 2.4 (GME), 3.1, 2.0 and 2.3 % for t_m and 5.0 (CFE), 4.5 (GME), 3.8, 2.6 and 3.0% for the peak current, respectively, for a series of six injections of 2.5×10^{-5} mol/L each compound. The method has been used to determine Cys, GSH, UA in human blood. However, the electrophoretic peak of AA could not be found, because AA has been oxidized during the sample treatment due to its strong

Figure 2 Electropherograms of the standard solution containing 5.00×10^{-5} mol/L Cys, GSH, UA and AA at the CGMDE 1, using CFE; 2, using GME.



reduction ability. The concentrations of Cys, GSH and UA in the human blood obtained by the standard calibration method were 3.78×10^{-5} mol/L for Cys, 3.08×10^{-4} mol/L for GSH and 7.67×10^{-4} mol/L for UA, which were very close to the values (3.70×10^{-5} mol/L for Cys, 4.24×10^{-4} mol/L for GSH and 4.17×10^{-4} mol/L for UA) reported in literature[7]. The recoveries of the method for Cys, GSH and UA were between 99, 102 and 95%, respectively.

Table 1 Analysis data of Cys, GSH, UA and AA

Compound	Linear range (mol/L)	LOD (mol/L)	Correlation coefficient
Cys[a]	5.00×10^{-6}-5.00×10^{-4}	4.50×10^{-6}	0.9998
Cys[b]	1.00×10^{-6}-5.00×10^{-4}	8.76×10^{-7}	0.9999
GSH[b]	5.00×10^{-6}-5.00×10^{-4}	5.00×10^{-6}	0.9998
UA[a]	5.00×10^{-6}-5.00×10^{-4}	2.35×10^{-6}	0.9993
AA[a]	2.50×10^{-6}-5.00×10^{-4}	1.10×10^{-6}	0.9997

[a] using carbon fiber electrode; [b] using Au/Hg electrode. Conditions as in **Figure 2**.

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References

1. Lin, B. L., Colon, L. A., Zare, R. N., *J. Chromatogr. A*, **1994**, *680*, 263.
2. Zhong, M., Zhou, J., Lunte, S. M., *Anal. Chem.*, **1996**, *68*, 203.
3. Zhong, M., Lunte, S. M., *Anal. Chem.*, **1999**, *71*, 251.
4. Holland, L. A., Lunte, S. M., *Anal. Chem.*, **1999**, *71*, 407.
5. Chen., D., Chang, S., Chen, C., *Anal. Chem.*, **1999**, *71*, 3200.
6. Jin, W., Weng, Q., Wu, J., *Anal. Chim. Acta.*, **1997,** *342*, 67.
7. Zhang, S., Sun, W., Xia, Y., Zhang, W., Jin, L., Yamamoto, K., Tao, S., Jin, J., *Anal. Chim. Acta.*, **1999**, *399*, 213.

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