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A New Dual-electrode and Multi-channel Electrochemical Detection System for Capillary Electrophoresis

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Abstract: A new type of dual-electrode and multi-channel electrochemical detection technology for capillary electrophoresis is described in this paper. Two detectors(the amperometric detector and the conductometric detector) or two conductometric detectors are connected to the same capillary electrophoresis system. The whole system possesses the advantages of the two electrochemical detectors including sparing time, improving the analytical speed and expanding the sample range. The working electrode and detector cell are handled easily. The system was applied to sample detection with satisfactory results.

Keywords: Capillary electrophoresis, dual-electrode, multi-channel electrochemical detection.

Capillary electrophoresis (CE) has become a powerful separation technique since it was introduced last decade. One of the most important factors in CE is the development of detectors. Optical detectors based on UV absorbance have been widely used.

Among non-optical modes in CE, electrochemical detection (EC) has been proved to be the tailor-made technique because of its many features superior to optical detection. The amperometric electrochemical detector (AEC), which is one of the two modes in EC, shows a number of advantages. The high sensitivity can be attained with AEC to such a degree that the limit of detection (LOD) is in the nanomolar range for many compounds. It is extremely selective because there are very few compounds, which can be oxidized or reduced, and the selectivity can be tuned through the proper control of the detection potential and/or the careful selection of the working electrode. Another mode --conductivity electrochemical detection (CEC) is one of the most popular method of detection, it is easy to operate and responds to a wide range of compounds.

In reality, there is no single detector possessing all these properties. Moreover, the diversity of the analytes often requires a combination of various detection techniques in order to determine all the sample of interest. A better way to increase the applicability of CEEC is through coupling two different kinds of detectors or dual-electrode. Therefore, the combination of AEC with CEC is tested for complement of the nature of these two techniques.

However, it is necessary to optimize two experimental conditions before using in

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practice. First, the placement of the working electrodes and the alignment of the working electrodes related to the outlet of the separation capillary significantly affected the sensitivity and reproducibility of the EC detection. Second, the peak currents generated from the different detectors will superimpose each other in the same detection cell, in the result of interaction of the currents may induce incorrect output signals.

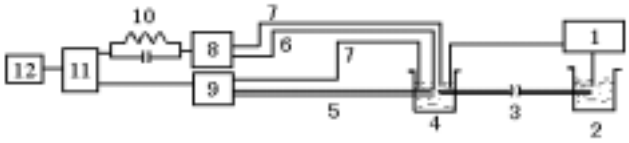
Up to now there are a few reports about the technique of coupling CE with dual-detector and dual-electrode detection[1-6]. However, the fabrication of working electrodes and the alignment of the working electrodes to the outlet of the separation capillary are hard to handle.

In this study a dual-electrode CE-EC system was described. A new electrochemical cell was designed for combination of AEC and CEC or another AEC. The advantages of dual-electrode and multi-channel electrochemical detection system are as follows: First, the fabrication of the detection cell and the working electrode are easy to assemble, disassemble the working electrode and the separation capillary. The alignment of the working electrodes to the outlet of the separation capillary can be easily done without the aid of three-dimensional adjustor. Second, the electroactive and inert components can be detected simultaneously by properly choosing the working electrode and detection potential. The identity and purity of sample can be verified. Third, through the design of software the output signal in different channel are magnified separately and processed by Spline wavelet method, which can extract the useful information from high noise signals. Fourth, the use of the filt circuit can effectively eliminate the disturbance between the two detectors. The system was applied to determine real sample with satisfactory results.

Experimental

The main part for this dual-electrode and multi-channel system was showed in **Figure 1**.

Figure 1 The structure of dual-electrode and multi-channel CEEC system

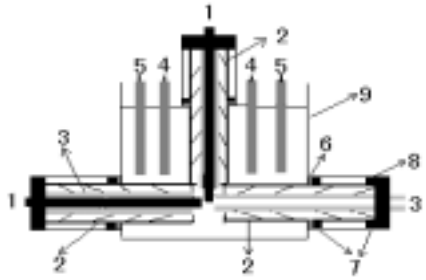


1.high voltage; 2.buffer cell;3. separation capillary; 4. detection cell; 5.the first working electrode; 6. the second working electrode; 7.reference electrode and auxiliary electrode; 8,9. detector; 10.filt circuit; 11.signal collecting card; 12.personal computer

A transparent cuboid plexglass container was used as a detection cell on the left and the right two parallel holes(Φ2mm) drilled 1 cm away from the bottom. First, two stainless steel syringe needles with the i.d. almost the same as o.d. of the capillary were used. The front of the syringe needles were ground flat. The syringe needles were inserted into the drilled holes from the two sides of the container. The distance between the needles was about 2 mm. Second, the another needle of the same kind was inserted vertically into the plexglass container, whose flat end was attached closely to the two parallel needles. The junctions were immobilized with epoxy resin so that the positions of three needles were fixed. The three needles were used as the guiding tubes of the

separation capillary and the working electrode. As the inner diameter of needle was similar to the outer diameter of the capillaries, at the same time the capillaries were used as the guiding tube for the working electrodes, therefore the alignment of the working electrode with the separation capillary outlet could be achieved precisely and easily without the aid of the micropositioner or microscope. Silica gel gaskets were used as the sheaths of the needles and plexglass screws helped to fix the cell. When the working electrodes and the separation capillary were installed correctly, the solution in the cell would not leak during the run. It was also easy to assemble, dissemble the working electrode and separation capillary. **Figure 2** showed the diagram of the electrochemical cell.

Figure 2 The diagram of detector cell for dual-electrode and multi-channel CEEC system



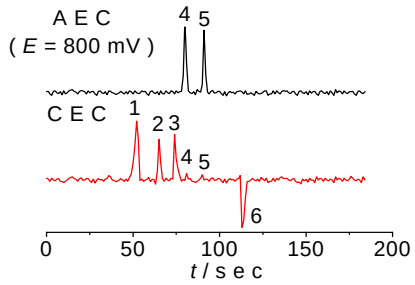
1. working electrode 2. stainless steel syringe needle 3. capillary;
4. reference electrode 5. auxiliary electrode 6. epoxy resin
7. silica gel gasket 8. plexglass screw 9. cuboid plexglass container

Results and Discussion

In order to evaluate the properties of this detection cell, two modes of dual-electrode and multi-channel detection were carried out. **Figure 3** were typical electropherograms of the sample of neurotransmitters and alkali metal ions detecting simultaneously by AEC and CEC.

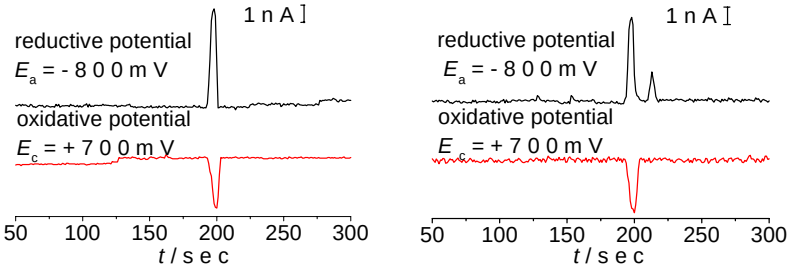
One of the applications in dual-electrode detection in HPLC and in CE is to identify analyte[1,2]. If the two working electrodes are set at different potentials, the ratio of reductive and oxidative current response ($N_c=i_r/i_o$) obtained at each electrode can be used to verify peak identity and purity. When the values of N_c of standard solution and sample is equal, the sample is pure, otherwise, it is impure. In this study, the oxidative and reductive potentials of the antihypertension agent-nitrendipine (NT) were determined by the combination of two AEC. The typical electropherograms were showed in **Figure 4**. The results indicated that N_c value of standard solution in NT was 1.974 while that of the tested sample was 1.508, indicating the sample to be impure. The electropherograms showed the peak of impurity.

Figure 3 Electrophorogram of sample detecting by AEC and CEC



1.K^+,2.Na^+,3.Li^+,4.Dopamine,5.Norepinephrine,6.solvent peak; capillary:50 μm×36cm; working electrodes: Pt electrode and carbon paste electrode; buffer: 10mmol/L Tris-1mmol/Lcitric acid

Figure 4 Electrophorogram of nitrendipine(NT) by dual-AEC



a. standard solution b.tested sample

capillary:50 μm×36 cm; separation voltage:15kV; buffer:8 mmol/L NH_3-NH_4Cl-10% methanol(V/V)-6mmol/L SDS; working electrodes: carbon past electrode

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