

[*Bunseki Kagaku*, **46**, 95-100 (1997)]

[Lab. of Pharm. Analytical Chemistry]

**Development of a Rapid and Sensitive Determination Method of  
Carbohydrates and Their Related Compounds by Capillary Electrophoresis  
with Amperometric Detection at a Copper Microelectrode.**

Masashi GOTO,\* Kazuya TANAKA, Yukihiro ESAKA and Bunji UNO

Capillary zone electrophoresis was employed to rapidly separate sugars, sugar alcohol, and sugar acids according to their electrophoretic mobilities in a strong alkaline solution containing a cationic surfactant, cetyltrimethylammonium chloride. Sample zones were monitored electrochemically using amperometric detection at a constant potential of 0.7V (vs. Ag/AgCl) with a copper-disk microelectrode (30 $\mu$ m in diameter). The copper microelectrode in strong basic solutions with a cationic surfactant showed about two-times the electrocatalytic oxidation currents for carbohydrates and related compounds compared to those without a cationic surfactant. A sample mixture of carbohydrates and related compounds was separated in less than 15min, being one third compared with that of the conventional method. The detection limits for the samples studied were about 2.5fmol (S/N=3), being about one twentieth compared with that of the conventional method.

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[Lab. of Pharm. Analytical Chemistry]

**Development of a Determination Method for Acetylcholinesterase Activity  
by FIA with Electrochemical Detection.**

Masashi GOTO\* and Mikio KOBAYASHI

A new method using flow-injection analysis (FIA) with electrochemical detection for determining acetylcholinesterase activity was developed by using micro-enzyme electrode. The micro-enzyme electrode was made by directly cross-linking choline oxidase using glutaraldehyde vapor on micro-platinum disk (diameter 200 $\mu$ m). The detection limit of acetylcholinesterase was 0.005U/ml (S/N=3) and the relative standard deviation of its activity measurement at 0.1U/ml level was  $\pm 1.6\%$  (n=6). The present method was superior to the conventional methods with respect to the detection limit and precision.

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[Lab. of Pharm. Analytical Chemistry]

**On-line Electrochemical Detection of Carbohydrates Coupled with the Periodate Oxidation.**

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A new concept of an amplified electrochemical detection of carbohydrates is proposed, where carbohydrates are oxidized by periodate ion ( $\text{IO}_4^-$ ) in acidic solutions to yield iodate ion ( $\text{IO}_3^-$ ) which would be electrochemically reduced into iodide ion ( $\text{I}^-$ ) under suitable conditions. This scenario allows highly sensitive detection of carbohydrates, for example, as 30 electrons per aldohexose molecule. Our cyclic voltammetric study revealed that  $\text{IO}_3^-$  is reduced at much lower overpotentials than  $\text{IO}_4^-$  at gold, platinum and carbon-based electrodes despite the fact that the standard redox potential of the  $\text{IO}_3^-/\text{I}^-$  couple is more negative than that of the  $\text{IO}_4^-/\text{I}^-$  couple. In the electrochemical reduction of  $\text{IO}_3^-$ ,  $\text{I}^-$  is considered to function as a mediator. Stable flow-through detection of  $\text{IO}_3^-$  in the presence of  $\text{IO}_4^-$  was realized at glassy carbon electrodes. This method was coupled with the  $\text{IO}_4^-$  oxidation of carbohydrates and the experimental conditions were partially optimized on a flow injection system. The  $\text{IO}_4^-$  oxidation-coupled electrochemical detection of carbohydrates was applied to ligand-exchange high-performance liquid chromatography in a post-column mode. Sub-nanomole order of carbohydrates were successfully detected on this system.

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[Lab. of Pharm. Analytical Chemistry]

**Sodium Dodecyl Sulfate-Tween 20 Mixed Micellar Electrokinetic Chromatography for  
Separation of Hydrophobic Cations: Application to Adrenaline and Its Precursors.**

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Separation of hydrophobic cations in capillary electrophoresis under the mixed micellar system composed of SDS and Tween 20 was investigated from the viewpoints of thermodynamics and practical application. Hydrophobic cations interact strongly with the anionic SDS micelle, and this often lead to predominant dissolution of the analytes into the micellar phase, resulting in poor resolution. The ionic interaction was evaluated to be close in strength to the hydrophobic interaction between benzenes and the SDS micelle. Tween 20 as a component to the mixed micelle was found to weaken the attractive ionic interactions between the cationic solutes and SDS. In addition, the polyether chain of Tween 20 serves also as a hydrogen acceptor to cause the attractive hydrogen-bonding interactions with hydrogen-donating analytes. The two different functions of Tween 20 improve the separation of hydrophobic cations remarkably. Separation patterns are well controlled by varying the mixing ratio of the two surfactants. Adrenaline and its six precursors were successfully separated with this mixed micellar system. The improved separation efficiency was not affected by the presence of bovine serum matrix.