result of nucleophilic attack by triphenylphosphine.

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Copper Oxide-Modified Polymeric Composite Electrodes for Amperometric Detection of Carbohydrates in LCEC Analysis

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Modified polymeric composite electrodes having highly dispersed CuO particles through the electrode matrix were prepared for LCEC or flow injection analysis of carbohydrates. The composite electrodes were prepared by incorporating carbon black and highly dispersed copper oxide particles in polystyrene matrix cross-linked with divinylbenzene. The analytical characteristics of the electrodes for LCEC and flow injection analysis of carbohydrates were evaluated. Improved performance in LCEC and flow injection analysis of carbohydrates is demonstrated in terms of sensitivity, reproducibility, stability and surface renewability. It was possible to get improved performance of the electrodes as well as adaptability of the electrodes for practical applications by employing highly dispersed catalyst particles through the electrode matrix and robust polymeric electrode matrix.

Introduction

Detection of carbohydrates after HPLC separation has been of great research interest to analytical chemists because of their importance in physiological, clinical, medicinal, food and nutritional aspects. Due to the lack of a functional group absorbing light in most carbohydrates cumbersome pre- or post-column derivatizations are required in

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using common UV/visible or fluorescence detectors. Electrochemical detection techniques following anion exchange chromatographic separations have been studied extensively because of its versatility for the detection of carbohydrates.[1-15] Pulsed amperometric detection technique using gold or platinum electrodes was developed and optimized for high sensitivity and reproducibility by Johnson and his coworkers.[1,2,7,16] This technique has been widely adopted by many analysts with commercially available detection system. However, the detection system requires sophisticated instrumentation and optimized pulse sequences for the best performances.

Simple constant potential amperometric detection techniques utilizing various catalyst-modified electrodes showing high sensitivity have been demonstrated by many analytical chemists.[3,4,6,8-15] Cobalt phthalocyanine (CoPc)-modified electrode shows high catalytic activity in carbohydrate oxidation.[3,9] Nevertheless, the catalytic activity of CoPc decreased gradually due to deactivation of the catalyst so that stability of the electrode was not good enough to be used in practically long term experiments. Oxides or hydroxides of metal such as Ni, Cu, Co and Ru are also known as catalysts for the electrochemical oxidation of carbohydrates in alkaline media.[4,6,8,10-15] Electrochemically generated metal oxide hydroxides (MOOH) at oxidizing potential catalyze the oxidation of carbohydrates. The electrochemical reactions take place between +0.3V and +0.6 V *vs.* Ag/AgCl. Copper-based chemically modified glassy carbon electrodes were studied for the detection of carbohydrates in terms of modified layer formations, characteristics and its applications with great interest by Baldwin and his workers.[12,13] Nickel and cobalt oxides were also studied as catalytic modifiers on the surface of glassy carbon electrodes for the detection of scarcely oxidizing polyols including carbohydrates by others.[8,10,15] High sensitivity of the electrodes resulting from catalytic activity of metal oxides deserves the utilization of the electrodes for the detection of carbohydrates by constant potential amperometry in alkaline media. Nevertheless these surface-modified electrodes are mostly lack of reproducibility, stability and renewability for the practical routine analysis. Modified carbon paste electrode technique is one of the alternative ways to utilize the electrocatalytic properties of metal oxides in carbohydrate oxidation.[4,11,14] Hydroxides or oxides of various metals such as Cu, Ni, Ru and Co could be mixed into carbon paste electrode matrix as modifiers to get improved surface renewability and reproducibility. Nevertheless, cumbersome preparation procedure of the modified carbon paste electrodes is still embarrassing analysts fronting day-to-day analysis of many samples. Yet it requires further improvement in many aspects for practically long term experiments. Recent report on Ni-Ti alloy electrode for LCEC analysis of carbohydrate described the excellent analytical performances of the electrode in terms of sensitivity, reproducibility and stability especially in organic solvent system. Nevertheless the metal alloy electrode had to be conditioned for more than two hours until the oxide surface stabilized.[17]

In this circumstance we devoted to develop reliable metal oxide-modified electrodes for practical carbohydrate detection by adopting modified polymeric composite electrode technique.[18] Improvements in durability, surface renewability and adaptability for practical use as well as sensitivity, stability and reproducibility were targeted. Polymeric modified composite electrodes can be prepared by incorporating conductive carbon black and modifiers into monomeric mixtures of composite matrix followed by polymerization. A wide range of modifiers such as monomers, molecular catalysts, inorganic solids, etc., can be incorporated easily into the electrode matrix. The modified composite electrodes are robust and the surface can be renewed by simple polishing whenever contaminated or deactivated. In the present work copper oxide highly dispersed through electrode matrix was chosen as modifier which reveals high catalytic activity in carbohydrate oxidation.[11-13] The preparation methods and analytical characteristics of CuO-modified polymeric composite electrodes for LCEC analysis of carbohydrates are described.

Experimental Section

Materials. All chemicals were reagent grade and used as received otherwise mentioned. Ketjen black 600JD carbon black (semigraphitic carbon from Akzo Chemie) was ground well with a mortar and pestle, then stored in a sealed bottle. Styrene was from Junsei (Japan) and divinylbenzene (55%) was from Wako (Japan). The monomers were vacuum distilled and stored in a freezer before use. Radical initiator, azodiisobutyronitrile[(AIBN) 2,2-azobis(2-methylpropinonitrile)] (Aldrich) was without further purification. Carbohydrate reagents were from Sigma and used without further purification. Fresh stock solutions of carbohydrates were prepared everyday and stored in a refrigerator. The solutions were diluted to appropriate concentrations with carbonate free sodium hydroxide solution. The solutions for LCEC experiments were prepared by filtering with 0.45 μm Millipore filters. Deionized water (18 MΩ) was used for the preparation of solutions. Practical samples were prepared by adjusting concentration of NaOH same as mobile phase and filtering with 0.45 μm Millipore filters. They were diluted appropriately for LCEC analysis.

Apparatus. BAS 100W Electrochemical Analyzer was used for voltammetric measurements. Pharmacia LKB HPLC pump 2150 dual head pump was used for mobile phase delivery. BAS amperometric detector LC-4C and thin layer flow cell were used for constant amperometric detection. Ag/AgCl reference electrode from BAS was employed for voltammetric measurements. However, the electrode was not stable in NaOH solution for long term LCEC experiment so that a homemade Hg/HgO (0.10 M NaOH) reference electrode was used. Rheodyne injector with 20 μL loop was used for sample injection. CarboPac™ PA1 (4× 250 mm) anion exchange column with CarboPac™ PA guard column from Dionex was used for carbohydrate separation. Rigaku D/MAX II X-ray diffractometer was used for analysis of CuO powder.

Electrode Preparation. Electrode preparation method was adopted from the reported works elsewhere.[18-20] The electrode was prepared by modifying polymeric composite electrode matrix with CuO as follow; appropriate amount of Ketjen black 600JD (usually about 2 g) was dispersed thoroughly in 200 mL of ethanol using a ultrasonicator for 2 hours. Pre-estimated amount of $Cu(NO_3)_2 \cdot 6H_2O$ was dis-

solved in 300 mL of ethanol, then mixed with the carbon black dispersed solution. Appropriate amount of deionized water was added to make the alcoholic content to 30% approximately. The mixture was titrated with 2 M NaOH slowly to get colloidal $Cu(OH)_2$ precipitates. Cautious addition of NaOH were required to get uniform black mixture of $Cu(OH)_2$ and carbon black without separated precipitation. If blue color of $Cu(OH)_2$ precipitates is observed, satisfactory precipitate mixture was regenerated with NaOH after dissolving $Cu(OH)_2$ with acid. The mixture was filtered and washed with deionized water thoroughly. The carbon black/$Cu(OH)_2$ mixture was dried at 110 °C overnight, then ground thoroughly with a commercial coffee bean grinder into fine powder. $Cu(OH)_2$ was converted into CuO by heating at 250 °C overnight in a convection oven. The mixture of carbon black/CuO was ground again well, then stored in a sealed container to prevent from moisture. Powder X-ray diffraction analysis was performed to confirm the conversion of $Cu(OH)_2$ into CuO and only the characteristic peaks of CuO were observed.

Finely ground carbon black/CuO mixture was added to the solution containing pre-determined amounts of styrene, divinylbenzene and radical initiator AIBN (see Table 1). Then the paste of the mixture was polymerized in a sealed glass tubing at 60-80 °C for 4 hours to get CuO-modified polymeric composite electrode material. The electrode material was fabricated into proper types of electrode for voltammetric measurements or LCEC experiments. Silver paste was used for electrical contact between the electrode material and copper lead wire. The composite electrode materials were sealed in glass tubing with commercial epoxy resin for voltammetric measurements. The electrodes for LCEC experiments were fabricated by molding the electrode materials with commercial polyester resin. The diameter of the electrodes were 3.0 mm. The electrodes were ground with 1000 grit SiC paper, polished with 0.05 μm alumina, and then sonicated to remove residues on the surface. The electrodes were rinsed thoroughly with copious amount of water in each step. The preparative compositions of the electrodes used in this work are shown in Table 1.

Results and Discussion

The CuO-modified composite electrodes were mostly hard and suitable for machining and polishing. The polished surface of the electrode was reflective and smooth. Generally high content of modifier in electrode matrix was desirable to get high catalytic activity (see Figure 3). However, CuO loading should be compromised with proper mechanical strength of the electrodes. Large loading of CuO resulted in weak physical strength of the composite electrode materials. The physical strength of the electrodes having CuO content higher than 35% was not good enough to insure the applicability of the electrodes for long term experiments. The range of 20 to 35 wt% of CuO loading was suitable to get reliable electrodes having good physical strength and analytical characteristics.

Table 1. Preparative compositions of CuO-modified composite electrodes

electrode	styrene (wt%)	divinylbenzene (wt%)	AIBN (wt%)	carbon black (wt%)	CuO (wt%)
1	69.0	18.7	1.0	5.0	6.3
2	63.9	17.4	0.9	5.1	12.7
3	59.1	16.3	0.8	5.0	18.8
4	54.4	14.8	0.7	5.0	25.1
5	49.5	13.4	0.7	5.0	31.4

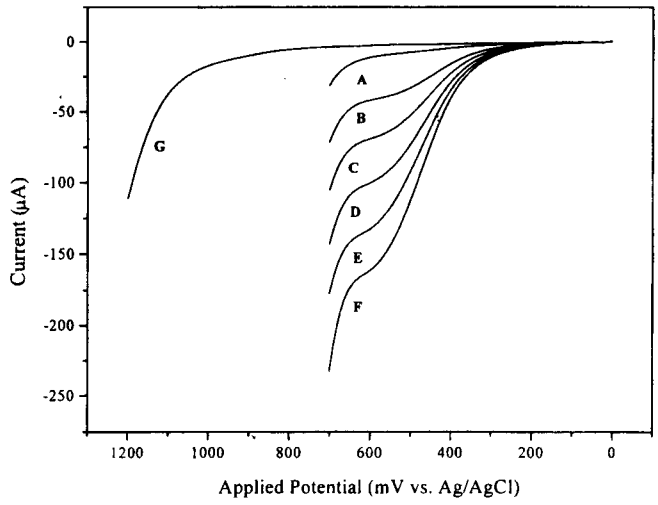

Figure 1. Linear sweep voltammetric behavior of 31.4 wt% CuO composite electrode. A: blank solution, B: 1.0 mM glucose, C: 2.0 mM glucose, D: 3.0 mM glucose, E: 4.0 mM glucose, F: 5.0 mM glucose, G: glassy carbon electrode in 5.0 mM glucose, supporting electrolyte: 0.10 M NaOH, scan rate 50 mV/s *vs.* Ag/AgCl.

Figure 1 shows the effect of catalytic oxidation of glucose by the CuO-modified composite electrode containing 31.4 wt% of CuO. Curve A is a linear sweep voltammogram in 0.10 M NaOH blank solution. The potential scan started from 0 V to the positive direction. The anodic current increased gradually due to the oxidation of Cu(II) to Cu(III) without any distinct peak in the potential range of +0.3 V to +0.7 V until anodic background oxidation started. Moiety of the active Cu(III) is known to be responsible for catalytic oxidation of carbohydrates.[11] Upon the reversal of potential scan at +0.7 V a broad cathodic peak current at +0.53 V due to reduction of Cu(III) to Cu(II) was observed which is not shown in the figure. This result is very similar to the results of Cu_2O-modified carbon paste electrode reported by Huber and his colleague.[11] When the potential window of scan was extended toward to more negative direction the voltammetric behavior was complicated. Large oxidation state change, *i.e.* (Cu(0) ↔ Cu(I) ↔ Cu(II) ↔ Cu(III)), accompanying with surface morphology change occurred during repeated scans. Details in the change of the surface morphology during repetitive scanning of potential are under investigation. Curve B through F shows the catalytic oxidation of glucose by the CuO-modified composite electrode in various concentrations. The catalytic oxidation currents of glucose were observed clearly starting from +0.30 V and showing broad peaks near +0.6 V. In contrary oxidation of glucose on a glassy carbon electrode occurred near +1 V overlapping with background oxidation (curve G). The currents sampled at +600 mV were linearly propor-

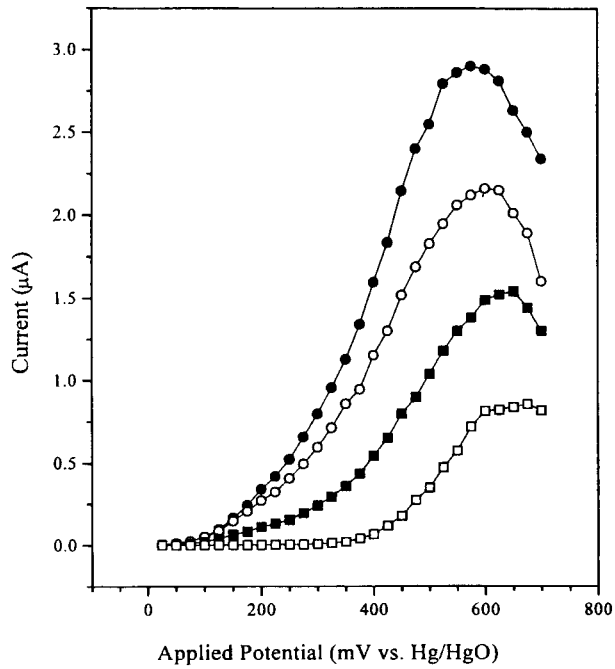

Figure 2. Hydrodynamic voltammograms of carbohydrates. Glucose (●), fructose (○), maltose (■), sucrose (□), electrode D (31.4 wt% of CuO), E_{app} *vs.* Hg/HgO (0.10 M NaOH), 20 μL/injection, 0.10 mM of carbohydrate, 0.10 M NaOH mobile phase, 0.50 mL/min, without column.

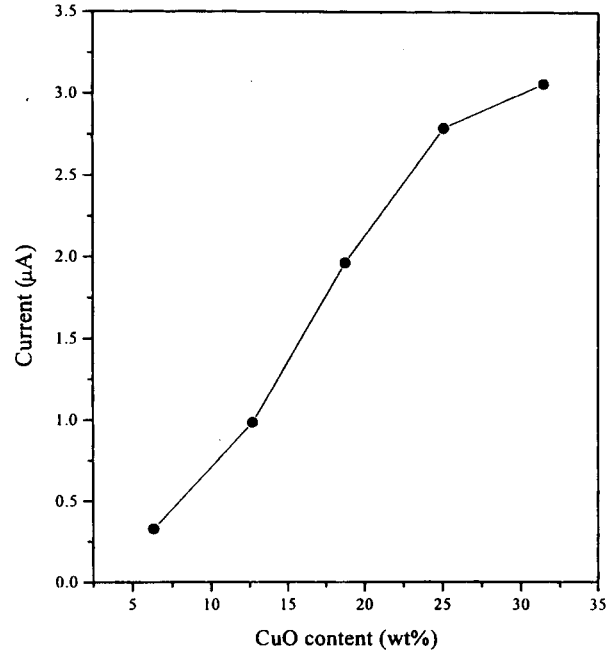

Figure 3. Effect of CuO content on the electrode response in flow injection analysis: 0.10 mM glucose, E_{app}=+550 mV *vs.* Hg/HgO (0.10 M NaOH), mobile phase 0.10 M NaOH, flow rate 0.5 mL/min, 20 μL/injection, without column.

tional to the concentrations of glucose assuring the applicability of the electrode in quantitative analysis of carbohydrates.

Hydrodynamic voltammograms of some typical carbohydrates are shown in Figure 2. Twenty microliter of 0.10 mM carbohydrates were injected for flow injection analysis. Catalytic oxidation of carbohydrates started between +0.1 V and +0.4 V. Maximum currents of these were mostly observed between +0.50 and +0.65 V, then the currents decreased slowly. Oxidation of sucrose was observed starting about +0.4 V and very sluggish. The current decrease above +0.65 V was due to competitive background oxidation, which was mainly oxygen evolution. Background current was stable below this potential, but it became to increase abruptly then unstable above this potential. So the potential of +0.550 V *vs.* Hg/HgO (0.10 M NaOH) was chosen as E_{app} for constant potential amperometric detection of carbohydrates in LCEC or flow injection analysis experiments. High catalytic oxidation of carbohydrates was possible and the background was still low and stable at this potential.

In order to optimize the catalyst content in the electrode matrix the effect of CuO content on catalytic oxidation of carbohydrates was studied by comparing amperometric responses of the electrodes for 0.10 mM glucose at 0.550 V and shown in Figure 3. Presumably due to increase of the active surface concentration of the catalyst enhanced amperometric response was achieved at higher CuO content. Although higher content of CuO in the electrode matrix was preferred, physical strength of the electrode was not affordable for practical application when CuO content was higher than 35 wt%. The electrode containing 31.4 wt% of CuO was chosen for the evaluation of the analytical charac-

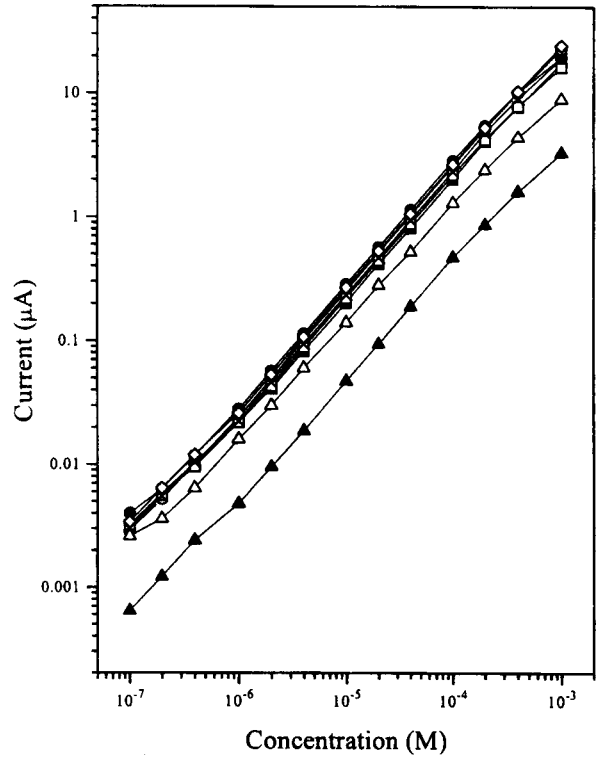

Figure 4. Log plots of flow injection analysis response *vs.* concentration of carbohydrates : (●) glucose, (■) fructose, (○) ribose, (□) mannose, (×) galactose, (◇) arabinose, (▲) sucrose, (△) maltose, 31.4 wt% CuO-modified composite electrode, E_{app}= +550 mV *vs.* Hg/HgO (0.10 M NaOH), mobile phase 0.10 M NaOH, flow rate 0.5 mL/min, 20 μL/injection, without column.

Table 2. Analytical characteristics of CuO-modified composite electrode for carbohydrates

Compound	linear range* (μM)	detection limit** (μM)
glucose	0.4-400	0.04
fructose	1~400	0.06
sucrose	1~1000	0.06
maltose	2~1000	0.3
arabinose	1~1000	0.04
ribose	0.2~1000	0.05
mannose	0.4~400	0.05
galactose	1~1000	0.05

*Linear ranges were estimated by the criteria of ±10% of average response factor. **Detection limit (D.L.) were determined for S/N=3 from 2 μM concentration.

teristics.

Flow injection analysis of carbohydrates was performed at +0.550 V *vs.* Hg/HgO for the wide range of carbohydrate concentration in order to evaluate linear dynamic working ranges. The standard calibration curves are shown in Figure 4. The amperometric response factors for given carbohydrates were constant in the range of more than three order of magnitude. The correlation coefficients of calibration curves ranged between 0.9991 and 0.9999. The sensitivity of the CuO-modified composite electrode for glucose was 365 μA/(mM·cm^2) which was higher than that reported for the electrochemically pretreated Cu_2O-modified carbon paste electrode (215 μA/mM·cm^2)[11] and Cu-modified electrode on the surface of a glassy carbon electrode (120 μA/mM·cm^2 estimated from Figure 4 in reference 13). Presumably high sensitivity of CuO-modified composite electrode resulted from the high catalytic activity of fine CuO particles exposed at the surface of electrode which were also highly dispersed through electrode with high active surface area. The analytical parameters of the CuO modified composite electrode in flow injection analysis are abbreviated in Table 2.

One of the advantages of modified composite electrodes is surface renewability. The electrodes contain highly dispersed CuO modifier particles through the matrix, so the surface can be renewed easily by simple grinding and polishing whenever it is contaminated or deactivated. In order to test surface renewability the surface of the electrode was renewed by simple grinding and polishing for ten trials, then responses of the electrode were measured at +550 mV *vs.* Hg/HgO reference electrode by injecting 20 μL of 0.10 mM glucose ten times each. The relative standard deviation of the average signals was 2.0% for 10 trials of polishing, which proves distinction of the CuO-modified composite electrode in surface renewability. The reproducibility of the electrode response was also evaluated by pooling the data obtained during surface renewability test. The relative standard deviation of the pooled data (n=100) was only 0.7%. Improvements in reproducibility and surface renewability might be resulted from high uniformity of CuO particle distribution through the electrode matrix and physical stability of the polymeric matrix binding modifier and carbon black strongly.

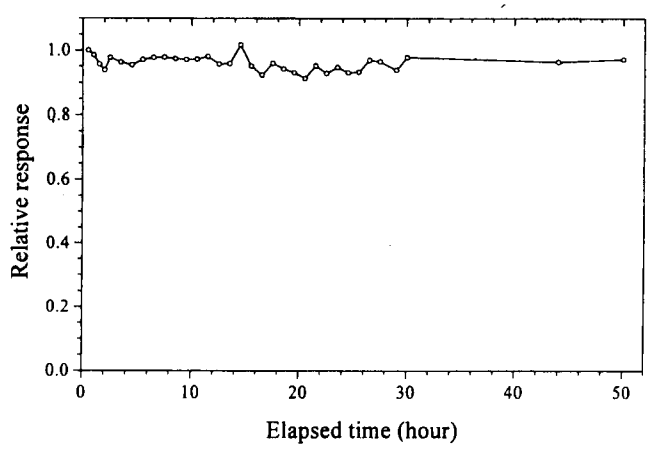

Figure 5. Chronogram of the electrode response for glucose. Electrode D (31.4 wt% of CuO), 0.10 mM of glucose, 20 μL/injection, 0.10 M NaOH, 0.50 mL/min, E_{app}=+550 mV *vs.* Hg/HgO (0.10 M NaOH).

Since one of the requirements of chromatographic detectors in long term experiments is stability, the response of the electrode was monitored under continuous operation for

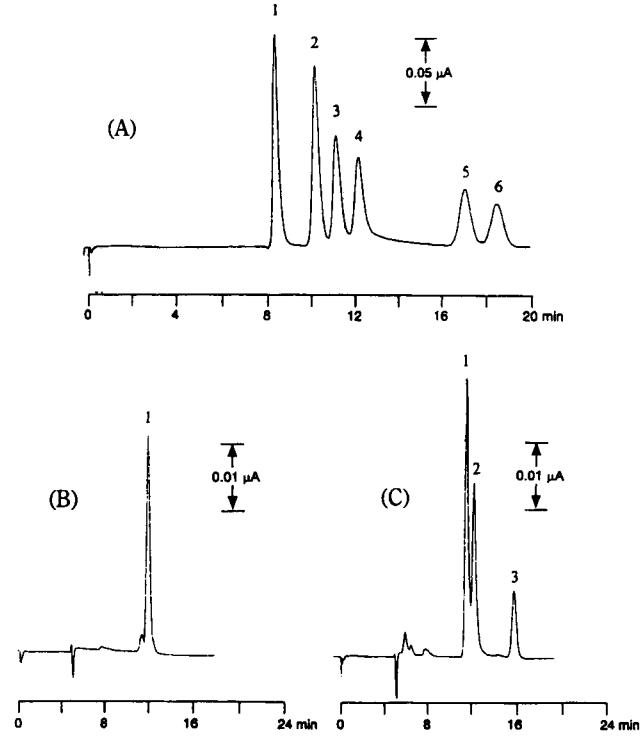

Figure 6. Some examples of carbohydrate separation and detection. CarboPac™ PA1 (4×250 mm) anion exchange column with CarboPac™ PA guard column, E_{app}=+550 mV vs. Hg/HgO (0.10 M NaOH), chromatogram A: synthetic mixture of 1.0×10^{-4} M of arabinose (1), glucose (2), fructose (3), sucrose (4), ribose (5) and lactose (6), mobile phase: 0.10 M NaOH, 0.4 mL/min., 5 μL/injection, chromatogram B: diet soft drink, diluted 14,000 times, peak (1) fructose, mobile phase: 0.10 M NaOH, 0.25 mL/min. 20 μL/injection, chromatogram C: unsweetened orange juice, (1) glucose, (2) fructose, (3) sucrose, sample was diluted 12,000 times, mobile phase: 0.10 M NaOH, 0.25 mL/min., 20 μL/injection.

50 hours. Twenty microliter of 0.10 mM glucose was injected ten times each, then the responses were averaged for every data point in Figure 5. The electrode response was decreased gradually during the first two hours, then stabilized. Although there were some fluctuations of the response, the electrode was rarely deactivated during the experiment. The average response reached 96% of the initial response with a relative standard deviation of 2.2%, which represents the degree of response fluctuation. The significant stability of the electrode might be due to the stable polymeric matrix binding active catalyst particles strongly. It affords practical applicability of the CuO-modified composite electrode in practically long term carbohydrate analysis.

Some examples of LCEC analysis of carbohydrates using the CuO-modified composite electrode are shown in Figure 6. Figure 6a shows an example of separation and detection of a synthetic mixture of six carbohydrates. Carbohydrates having 0.10 mM concentrations were successfully separated and detected. Figure 6b and c are chromatograms of a diet soft drink and an unsweetened orange juice respectively, which were simply diluted to appropriate concentration with mobile phase and filtered with 20 μm filters before injection.

In summary we have developed CuO-modified composite electrodes having improved analytical characteristics in carbohydrate LCEC analysis. It is worthwhile to stress the advantages of simple constant current amperometric detection technique of carbohydrates using the CuO-modified composite electrode in the sense of the performance, simplicity and convenience over other detection techniques such as UV detection or pulsed amperometric detection. It was possible to improve reproducibility, stability and surface renewability of the CuO-modified electrode significantly by adopting modified polymeric composite electrode technique. High sensitivity of the electrode resulted from the catalytic activity of highly dispersed CuO particles in the matrix of the electrode. The results obtained in this work ensure practical applicability of the CuO-modified composite electrode in LCEC analysis of carbohydrates. Further utilization of metal oxide-modified composite electrodes in detection of other organic compounds is under investigation.

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