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Microchip capillary electrophoresis/electrochemical detection of hydrazine compounds at a cobalt phthalocyanine modified electrochemical detector

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Abstract

This article reports on the use of cobalt(II) phthalocyanine (CoPc)-modified carbon paste amperometric detector for monitoring hydrazine compounds following their microchip separation. The marked catalytic electrochemical properties of CoPc-modified electrode display enhanced sensitivity compared with unmodified carbon pastes at a relatively low detection potential (+0.5 V versus Ag/AgCl). Factors influencing the on-chip separation and detection processes have been optimized. Three hydrazines (hydrazine, 1,1 dimethylhydrazine, and phenylhydrazine) have been separated within 130 s at a separation voltage of 1 kV using a 10 mM phosphate run buffer (pH 6.5). The detection limits obtained from using the CoPc-modified carbon paste electrodes for hydrazine and phenylhydrazine are 0.5 and 0.7 μM, respectively, with linearity over the 20–200 μM range examined. Such miniaturization and speed advantages of microchip CE are coupled to the highly sensitivity and convenient preparation of CoPc-modified carbon paste electrode. The resulting microsystem should be attractive for field monitoring of toxic hydrazine compounds in environmental applications.

Keywords: Hydrazines; Microchip; Capillary electrophoresis; Modified electrodes; Cobalt(II) phthalocyanine; Electrochemical detection

1. Introduction

Since the conception of a microchip-based capillary electrophoresis (CE) system was described, the number of research laboratories developing microchip CE devices has increased dramatically. Miniaturized CE analysis systems have brought numerous advantages of working over large-scale analyzers, including fast analysis, high efficiency, low reagent consumption, and portability. Therefore, microchip systems offer great promise for important applications, such as environmental or industrial monitoring and clinical diagnostics [1–4]. Electrochemical detection is ideally suited for miniaturization, compatible with modern microfabrication and offers high selectivity and sensitivity [5,6].

The focus of this article is a microchip CE/amperometric system for the separation and detection of hydrazine compounds. Hydrazine and its derivatives are important compounds of interests in the chemical industry and pharmaceutical processes. They are applied in many areas, such as fuel cells, herbicides, catalysts or rocket propellants [7–10]. Due to the environmental and toxicological significance of hydrazine compounds, many efforts have been devoted to develop reliable and effective detection methods for this family compounds. Amperometric detection is a powerful technique for monitoring redox species. Unfortunately, hydrazines are difficult to detect electrochemically because of their high overpotentials at ordinary electrodes [11]. In order

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to enhance the amperometric detection of hydrazines, electrochemical flow detectors based on various modified electrodes have been used for monitoring hydrazine compounds in conventional liquid-chromatography [12], flow injection [13], and capillary electrophoresis systems [14]. Chemical modified electrodes can improve the power of amperometric detection in both conventional CE [15,16], and microchip CE [17]. The specific chemical modified electrode that was used here consisted of a conventional carbon paste mixture to which cobalt(II) phthalocyanine (CoPc) was added as modifier. CoPc is well-known for its electrocatalytic capabilities in numerous organic oxidations [14]. The utility for CoPc-modified carbon paste electrodes for CE microchips has not been demonstrated. Here, we combined the attractive performance of microchip CE and the electrocatalytic properties of renewable CoPc-modified electrodes for detecting hydrazine compounds. Utilizing these merits, hydrazine, 1,1 dimethylhydrazine and phenylhydrazine were rapidly separated and detected by CE/amperometry. The performance characteristics of the CE/amperometric microsystem and electrode design are reported in the following sections.

2. Experimental

2.1. Chemicals

Hydrazine sulfate, 1,1 dimethylhydrazine, and cobalt phthalocyanine were obtained from Aldrich. Phenylhydrazine hydrochloride, sodium phosphate monobasic monohydrate, and sodium phosphate dibasic were received from Sigma. Graphite powder was purchased from A Johnson Mallthey. All other chemicals were used without further purification. All solutions were prepared in deionized water and passed through a 0.45-μm membrane filter (Gelman Acrodisc). Standard stock solutions of all analytes were prepared freshly daily in electrophoresis buffer.

2.2. Apparatus

The integrated chip/detection microsystem was depicted elsewhere [18]. Briefly, the glass microchip fabricated by Alberta Microelectronic Company (AMC, Model MC-BF4-001, Edmonton, Canada). The chip consisted of two crossed channels and three reservoirs, including a four-way injection cross (connected to the three reservoirs), and a 72-mm separation channel. The channels were 50 μm wide, 20 μm deep, and side arms of 5 mm long (between the sample reservoir and injection cross). The original waste reservoir was cut off leaving the channel outlet at the end side of the chip, then facilitating the end-column amperometric detection.

The layout of the CE/amperometric microsystem used in this study has been described previously [19]. The CE microchip was placed in a laboratory-built Plexiglas holder fabricated for holding the separation chip and housing the detector and reservoirs. Thus, the setup allows a convenient replacement. Platinum wires were inserted into each reservoir, served as contacts for the high voltage power supply. Short pipette tips were cut and placed in each of the three holes on the glass chip for solution contact between the channel on the chip and corresponding reservoir on the chip holder. The amperometric detector, placed in the waste reservoir (at the channel outlet side), consisted of an Ag/AgCl wire reference, a platinum wire counter, and modified carbon paste working capillary electrode was placed opposite the channel outlet.

2.3. Capillary electrode construction

The unmodified carbon paste was prepared by thoroughly hand-mixing 5 g of graphite powder and 3 mL of mineral oil (Aldrich). The CoPc-modified paste was prepared in a similar pattern except that the graphite powder was mixed with the desired weight of CoPc before adding the mineral oil. Mixing of these two components was accomplished by adding 10 mL of diethyl ether to 5 g of the CoPc/graphite mixture and sonicating until all the diethyl ether evaporated. The CoPc loading in the carbon paste was described in terms of percent basis of the weight of CoPc added to the graphite powder. A copper wire (10 cm long and 0.5 mm diameter) was inserted into a piece of fused silica capillary (5 cm long, 0.53 mm i.d., 0.68 mm o.d.) and a 1.0-cm opening was left in the capillary for the subsequent filling of the paste material. A portion of CoPc/graphite mixture was then packed into one end of a fuse silica capillary. Finally, the surface was smoothed by polishing on a piece of weighing paper to form a disc electrode. Electrical contact was obtained using internal copper wire.

2.4. End-column amperometric detection

The disc-working electrode was placed opposite the outlet of the separation channel through a plastic screw. The 20-μm distance of the working electrode from the chip outlet was controlled by plastic screw. The high voltage power supply had switchable voltage ports between running buffer and sample injections with adjustable voltage range between 0 and 4000 V. Amperometric detection was performed with an Electrochemical Analyzer 621A (CH Instruments, Austin, TX) using the "amperometric *I–t* curve" mode. The electropherograms were recorded with a time resolution of 0.1 s while applying a detection potential at +0.5 V versus Ag/AgCl wire. Sample injections were performed after stabilization of the baseline. The raw data of electropherograms were digitally filtered using built-in 15-point least-square smoothing by CHI Version 3.27 software (CH Instruments).

2.5. Electrophoresis procedure

Before to use, the channel was treated with deionized water, 0.1 M sodium hydroxide and deionized water for 10, 20, and 5 min, respectively. The running buffer is 10 mM phosphate buffer (pH 6.5), prepared by dissolving the required

amount of sodium phosphate monobasic and sodium phosphate dibasic in deionized water. Each of the reservoirs in the chip holder and corresponding pipette tips on the microchannel chip were filled with their respective solutions. The sample reservoir was filled with the mixture of hydrazines, while the "buffer" reservoirs were filled with the CE running buffer solution. A potential of 1000 V was applied to the "sample" reservoir for 3 s with the detection reservoir grounded and other reservoirs floating. The separation was performed by applying 1000 V to the running buffer reservoir with the detection reservoir grounded and other reservoirs floating. By switching the high voltage contacts, the separation potential was subsequently applied to the "running buffer" reservoir for the separation of the hydrazine compounds. All experiments were carried out at room temperature.

Safety considerations: The high voltage power supply and associated open electrical connections must be handling with extreme care.

3. Results and discussion

3.1. Comparison of an unmodified and CoPc-modified carbon paste capillary electrodes

Hydrazines are difficult to oxidize at conventional/bare carbon electrodes because of their large overpotentials. The use of various chemically modified electrodes has been explored to overcome this problem. We found a simple modification of the carbon paste electrode matrix with CoPc to be effective for minimizing the oxidation potential of hydrazines and facilitating their amperometric detection. Fig. 1 compares typical electropherograms for hydrazine (a), 1,1 dimethylhydrazine (b), and phenylhydrazine (c) at the unmodified (A) and CoPc-modified (B) carbon paste detectors. The marked electrocatalytic activity of CoPc-modified electrode towards to hydrazines offers enhanced sensitivity, low noise, and well resolved peaks. The three peaks can be separated within 130 s with well-defined peaks with CoPc-modified carbon paste electrodes. The sensitivity of hydrazines detection at CoPc-modified carbon paste electrodes is much higher than at the unmodified electrode under the same conditions. Such accelerated anodic detection is attributed to mediation or catalysis by Co(II) state of the modifier [20]. Hence, the electron-transfer rate on the electrode occurred fast. The flat baseline and low noise level at this separation voltage showed an effective isolation from the high separation voltage. These, along with the well-defined peaks, indicated convenient quantitation down to the micromolar level (see data in Fig. 1).

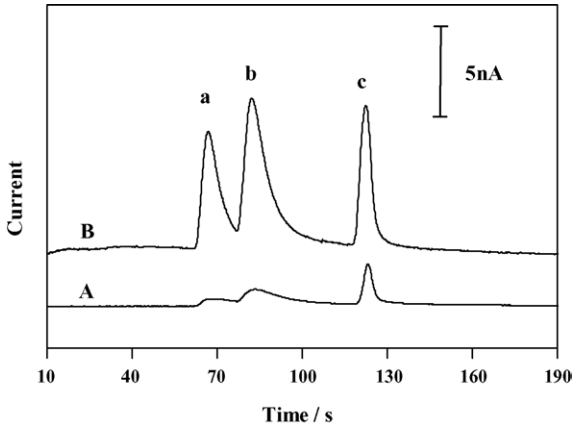

Fig. 1. Electropherograms for a mixture containing 50 μM hydrazine (a), 100 μM 1,1 dimethylhydrazine (b), and 100 μM phenylhydrazine (c), obtained at unmodified (A) and 5% CoPc-modified (B) carbon paste electrodes. Separation and injection voltages, +1000 V; injection time, 3 s; detection potential, +0.5 V (vs. Ag/AgCl). Phosphate buffer (10 mM and pH 6.5) was used as running buffer.

3.2. Capillary electrophoresis optimization

In any CE separation, the buffer pH had a significant impact on the ionization and electrophoretic mobility of each analyte. A pH optimization was carried out for the separation of hydrazine compounds. The pH values on the migration time were examined in the pH range 6.2–7.6, as shown in Fig. 2. All buffers contained a 10 mM phosphate buffer. Hydrazine, 1,1 dimethylhydrazine and phenylhydrazine could not be well separated at pH ≥ 6.8. This is may attributed to the low ionization of hydrazine, while pH approaching to

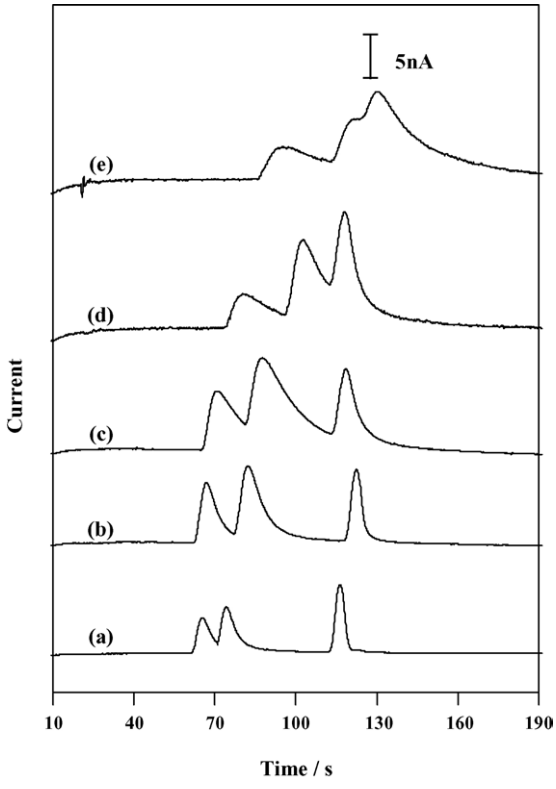

Fig. 2. Influence of the pH value of 10 mM phosphate run buffer on the separation and detection for mixture at the 5% CoPc-modified carbon paste capillary electrodes pH 6.2 (a), pH 6.5 (b), pH 6.8 (c), pH 7.3 (d), and pH 7.6 (e); other conditions, as in Fig. 1.

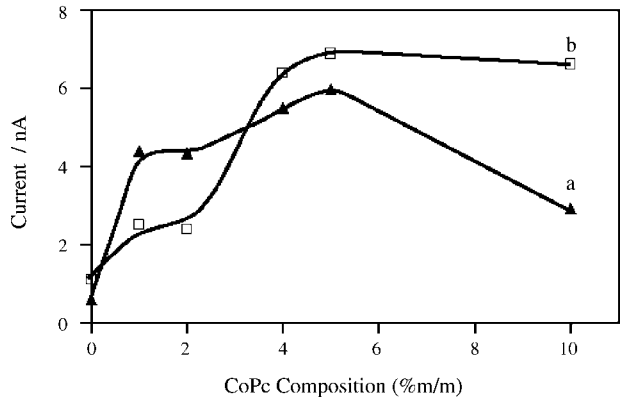

Fig. 3. Effect of CoPc loading in carbon paste on the current response of 50 μM hydrazine (a) and 100 μM phenylhydrazine (b); other conditions, as in Fig. 1.

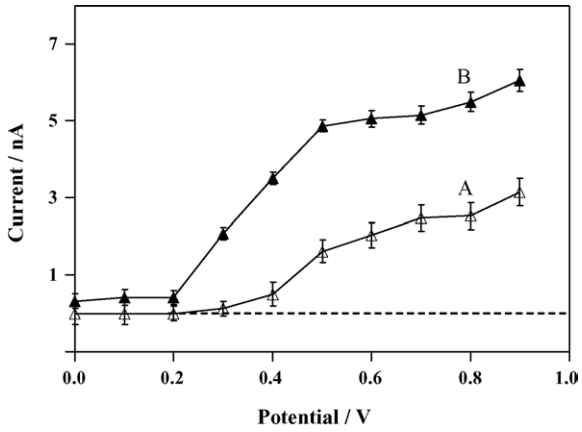

Fig. 4. Hydrodynamic voltammograms for 50 μM hydrazine at unmodified (A) and 5% CoPc-modified (B) carbon paste electrodes; other conditions, as in Fig. 1.

the pK_a (pK_a = 8.0, 7.7, 5.21 for hydrazine, 1,1 dimethylhydrazine and phenylhydrazine, respectively) leading to more neutral form of each analyte. From the results, the pH 6.5 buffer was found to be optimal because it leads to the good resolution of the first two peaks when compared to buffer pH 6.2 (for pH 6.5, R_s = 0.86 and pH 6.2, R_s = 0.76). Moreover, it is evident that a pH 6.5 buffer exhibited the highest current signal using CoPc-modified carbon paste electrodes. Accordingly, this buffer was selected for all subsequent work.

3.3. Influence of CoPc loading

The effect of the CoPc loading on the analytical performance of modified capillary electrode was investigated over the 1–10% range. Shown in Fig. 3 is the current response versus CoPc composition of 50 μM hydrazine and 100 μM phenylhydrazine using 10 mM phosphate run buffer (pH 6.5). As this figure illustrates, the hydrazine oxidation currents are enhanced between 1 and 5% of modifier and then decrease when the amount of the modifier is increased. The highest sensitivity was obtained using a loading of 5% modifier. The lower loading than 5% also enhanced peak currents; however, the electrode-to-electrode reproducibility was significantly inferior (%R.S.D. (n = 6) > 15% for hydrazine and phenylhydrazine). Overall, a 5% modifier loading offered the most favorable performance and hence was used throughout this study.

3.4. Hydrodynamic voltammetry

As expected, the detection potential affects the sensitivity and detection limits of this system. Fig. 4 illustrates the enhanced electrocatalytic activity of the CoPc-modified carbon paste electrodes in comparison with the unmodified carbon paste electrodes. It depicts the hydrodynamic voltammograms for the oxidation of 50 μM hydrazine at unmodified (A) and CoPc-modified (B) carbon paste electrodes. The curves were recorded step by step (in steps of 0.1 V) over the 0.0 to +0.9 V range, using a separation voltage of 1000 V. At the CoPc-modified carbon paste electrode, hydrazine displays defied wave starting around +0.0 V and leveling of above +0.5 V. The half-wave potential for hydrazine at the unmodified (A) and CoPc-modified (B) carbon paste is +0.48 and +0.35 V, respectively. The electrocatalytic property toward the investigated analyte pronounced as the half-wave potential on the CoPc-modified carbon paste electrode has decreased by approximately 130 mV in comparison with that on unmodified electrode. These voltammograms indicate that the CoPc-modified carbon paste-based detector provides a greatly improved performance, with a substantially higher sensitivity over the entire potential range and a moderate lowering of the operating potential (the geometric areas of both electrodes are the same). Because of the low background current at the lower potentials, the stability of the electrode can be enhanced so that the reproducibility is improved. All subsequent amperometric work employed a constant potential of +0.5 V. Higher operating potential would be required while working with higher separation voltages that may shift the voltammetric profile to the anodic direction.

3.5. Analytical figures

The CoPc-modified carbon paste-based detector offers a well-defined concentration dependence. Electropherograms for mixtures containing increasing levels of hydrazine (a) and phenylhydrazine (b) in increments of 20 and 40 μM, respectively, are shown in Fig. 5. Defined peaks with current proportional to the analyte concentration are observed. The resulting calibration plots are linear with the sensitivity of 173 and 85 nA/mM for hydrazine and phenylhydrazine, respectively (correlation coefficients, 0.9977 and 0.9981). The detection limits, based on signal-to-noise ratio (S/N) of 3, were found to be 0.5 μM for hydrazine and 0.7 μM for phenylhydrazine.

Good precision is another attractive feature of the chemically modified electrodes. The precision of microchip CE/CoPc-modified carbon paste electrodes was examined from a series of six repetitive injections of a sample mixture

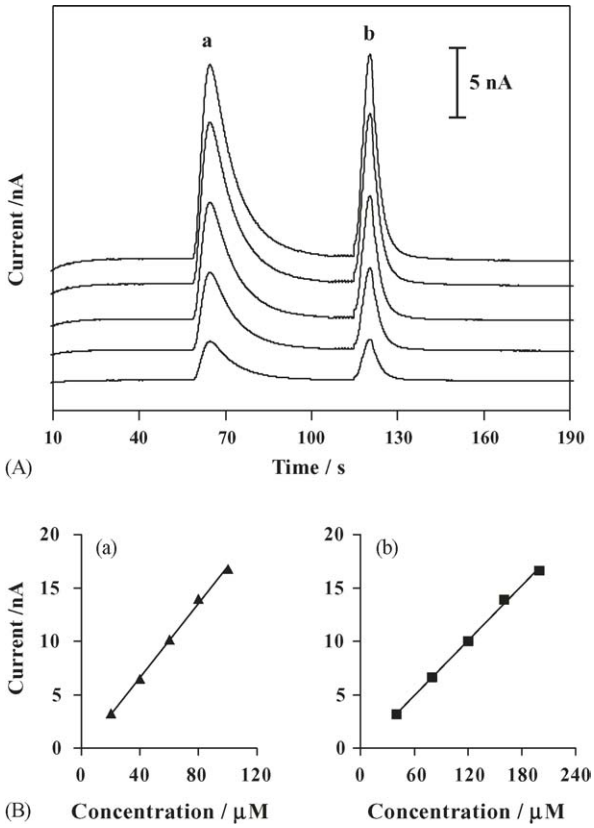

Fig. 5. (A) Electropherograms detailing the current response to increasing concentrations of hydrazine (a) and phenylhydrazine (b) in steps of 20 and 40 μM, respectively. (B) The resulting calibration plots; other conditions are same as Fig. 1.

containing 50 μM hydrazine and 100 μM phenylhydrazine. Reproducible signals were obtained with relative standard deviations (%R.S.D.) of 4% and 7% for the peak current of hydrazine and phenylhydrazine, respectively. Such good precision indicates negligible surface fouling of the CoPc-modified carbon paste electrode. An inferior precision, with R.S.D. of 20%, was observed for prolonged operation ($n \geq 10$), possible due to a gradual loss of CoPc from the electrode surface. The paste design allows rapid renewal. Different electrode surfaces after surface renewal also displayed a good precision, with R.S.D. between electrode-to-electrode of 2.53% for hydrazine and 2.55% for phenylhydrazine ($n = 3$).

4. Conclusions

We demonstrated the first utility of CoPc-modified electrodes for detecting hydrazines in microchip CE devices. The above results show that the hydrazines can be successfully separated and detected with proposed method. The electrocatalytic activity of CoPc-modified carbon paste electrode allows low-potential detection of this group of hydrazines when compared with the unmodified carbon paste electrodes. Moreover, these CoPc-modified electrodes exhibit a good stability in flowing system, enhanced of sensitivity, and good reproducibility in amperometric detection. Combining the accelerated anodic detection with renewability, bulk modification, and versatility of CoPc-modified electrodes to the advantages of the microchip CE format, offers attractive analytical applications. The resulting microchip CE holds great promise for rapid field screening of hydrazine contaminants and other pollutants. The negligible solvent/sample consumption of microchip CE makes it suitable for on-site environmental detection. Other types of catalytic modifiers are currently being examined for improving the microchip detection of different classes of compounds.

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