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Measuring mercury ion concentration with a carbon nano tube paste electrode using the cyclic voltammetry method

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Abstract

A simply prepared carbon nano tube paste electrode (CNTPE) was utilized for monitoring mercury ion concentration using the cyclic voltammetry (CV) method and the square wave anodic stripping voltammetric (SWASV) method. The CNTPE was compared with various conventional electrodes. The CNTPE method was applied to determine the concentration of trace levels of Hg(II) in several water samples, which yielded a relative error of 0.6% with a concentration of 0.20 mg L^{-1} Hg(II). It was deposited at −0.5 V (vs Ag/AgCl), which was subsequently reduced to +0.20 V to strip it on the CNTPE. The optimal experimental conditions for the analysis were found to be as follows: pH value of 4 for the medium; deposition potential of −0.5 V; deposition time of 210 s; SW frequency of 40 Hz; SW amplitude of 100 mV, and step potential of 25 mV. Given these optimum conditions, a linear range was observed within the concentrations of 1.0–25.0 μg L^{-1} and 40.0–200.0 μg L^{-1}. The detection limit was found to be 0.42 μg L^{-1}.

1. Introduction

Trace mercury detection has a variety of important and practical applications in various fields, particularly in areas where mercury is widely distributed, such as food, agriculture, water, coal, and painting paste [1–6]. Thus, various methods for analyzing Hg(II) and its analogs have been developed in the past. Some examples of these methods are zeeman atomic absorption spectrometry [7], high performance chromatography with UV detection method [8], and flow injection coupled to inductively coupled plasma mass spectrometry [2]. The HPLC-fluorescence spectrometry method [9] and other methods [10, 11] are particularly very sensitive. Most of these methods are considered more complicated than voltammetric analytical methods because they are combined with separation systems, spectrophotometric detection systems, and temperature controlling systems. On the other hand, voltammetric analytical methods are characterized by high sensitivity and low detection limit. Stripping electro analysis is more useful and popular for trace analysis [12–15], since the techniques are compact, efficient, and sensitive. Thus, various voltammetry solutions have been developed, depending on the working electrode technique. For example, dropping mercury electrode [16, 17], glassy carbon electrode [18–20], carbon fiber modified electrode [21–23], and other typical techniques have been used in cases that required more advanced and sensitive methods.

This study made use of a carbon nano tube paste electrode (CNTPE) [24–26] for Hg(II) analysis, employing cyclic voltammetry and square-wave voltammetry in a stripping mode. A carbon nano tube is a new type of carbon electrode with a relatively high surface area and specific chemical properties. It is also less expensive, more convenient, and renewable, compared to the commonly used electrodes. The CNTPE has been successfully applied to low concentration range detection, while the more developed methods have been found useful in analyzing other mercury ion concentration.

2. Experiment

2.1. *Apparatus and reagents*

Experimental systems were conducted using the CHI660A instruments electrochemical workstation (CH Instruments Inc, Cordova TN, USA). A three-electrode system was used to monitor the voltammograms. A small

NTPE measuring 3 mm in diameter and 20 mm in length served as the working electrode, while an Ag/AgCl electrode and a platinum wire served as the reference and the auxiliary electrode, respectively. All solutions were prepared from double distilled water (~18 MΩ cm^{-1}). A 0.1 M CH_3COOH with a pH level of 4.0 served as a supporting electrolyte. The Hg(II) stock solutions were of laboratory grade and were diluted before use, as was deemed necessary. All other reagents were of analytical grade.

2.2. *Preparation of each electrode and the experimental procedure*

The NTPE was prepared by mixing 70% nano tube graphite powder (Nanostructured & Amorphous Materials, inc) with 20% mineral oil. The mixture was homogenized in a mortar for 30 min. The mixed paste was then inserted in a plastic syringe needle using a 3-mm diameter copper wire that connected the measurements to the system [27]. The conventional carbon paste electrode was also made using the same NTPE method [28–30]. A hand made carbon fiber microelectrode 4 mm in diameter and about 15 mm in length was attached to a copper wire via silver paint. Then, the fiber was inserted into a polyethylene tube with a 0.3-mm diameter. The electrode was sealed by heating. This electrode was initially cleaned by sonication for 3 min. It was then cleaned in weak nitric acid, and finally, in double distilled water. The glassy carbon electrode and platinum electrode were conventional types.

All voltammetric measurements were performed using the CHI 660A instruments electrochemical workstation. The NTPE in the three-electrode system was immersed in a stirred solution of 0.1 M acetic acid (pH4.0) containing a known amount of Hg(II). Pre-concentration prior to stripping was carried out at open circuit. The CV and SWASV methods were then performed. The common parameter for CV was a scan rate of 100 mV s^{-1}. On the other hand, the common parameters for the stripping voltammetry were used at optimized conditions. Background voltammograms were recorded with the 0.1 M CH_3COOH in the absence of Hg(II). The electrochemical response of Hg(II) is dependent on the electrolyte solutions and the hydrogen ion activity. Various types of electrolyte solutions were tested (all in 0.1 M) and the acetic acid solution was found to yield the best results.

3. Results and discussion

3.1. *Cyclic voltammetric behavior of Hg(II) on the NTPE and electrode comparisons of stripping voltammetry*

Figure 1(a) shows the row voltammograms of the background electrolytes (0.1 M CH_3COOH with pH of 4.0) and of Hg(II) solutions with various concentrations at a sweep rate of 100 mV s^{-1}, based on the cyclic voltammetric signals tested on the NTPE. During the initial anodic scan of blank and 1 mg L^{-1}, an oxidation peak and a shoulder at 0.2 V appeared. A small reduction peak of 0.1 V was then obtained, which was not well extracted from the background discharge that occurred at a more negative potential. Subsequently, as the concentrations were increased to 2, 3, 4, 5, 6, 7, 8, 9, and 10 mg L^{-1} Hg(II), respectively, the oxidation peaks linearly increased and other peak closely increased, while the reductions responded weakly, even though peak separation from the background did not improve. Nonetheless, a better separation of the oxidation peak

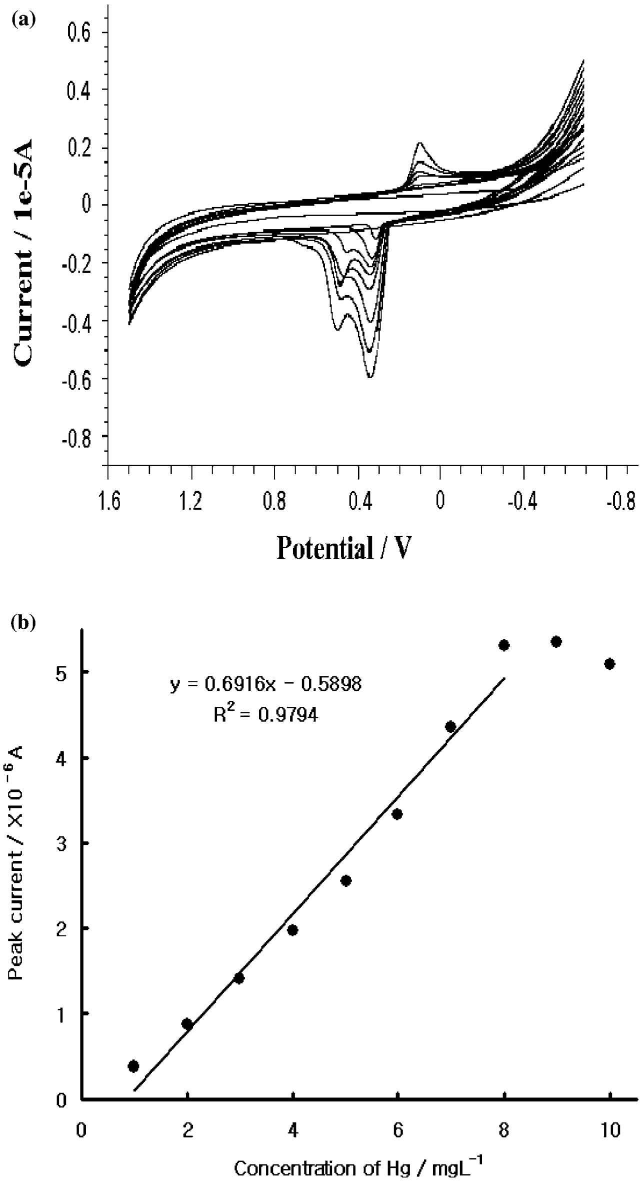

Fig. 1. (a) Cyclic voltammograms on the NTPE at 10 different concentrations of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 mg L^{-1} Hg(II), with a scan rate of 100 mV s^{-1}, initial potential of +1.5 V, and switching potential of −0.9 V. Electrolytes of 0.1 M acetic acid with a pH of 4.0. (b) The peak current (μA) as a function of Hg(II) concentration and the results of regression analysis.

was obtained with the square-wave voltammetry upon anodic stripping of Hg(II). Since the anodic peak was better developed than the cathodic peaks in the CV, the anodic peak currents were used as a function of the Hg(II) concentrations to confirm the linear relationship between the current and the concentration (Figure 1(b)).

A linear regression yielded an equation of $y = 0.6916x{-}0.5898$ (y: current in μA; x: concentration in mg L^{-1}). A correlation of $R^2 = 0.9794$ was obtained. This is useful in analytical applications for mercury analysis. The next sections discuss the more sensitive methods of stripping voltammetry, including NTPE sensitivity.

Figure 2 presents the various electrodes types compared at a fixed concentration of 10 μg L^{-1} Hg(II). The voltammetric parameters used are as follows: 0.1 M CH_3COOH solution with a pH of 4, deposition time of 210 s, accumulation potential of 0.5 V, frequency of 40 Hz, potential step of 25 mV, and amplitude of 100 mV. The voltammograms are shown for the carbon nano tube, carbon paste, carbon fiber, glassy carbon, and platinum electrodes. Identical measurement scales were used, although not all electrodes responded at micro gram ranges. Only platinum and NTPE sensitively responded. Moreover, NTPE exhibited a much sharper increase than the platinum electrode. In the other experimental test, where carbon fiber, carbon paste, and glassy carbon electrodes were tested at a higher concentration, all the signals appeared at very high milligram level concentrations.

3.2. *Experimental optimization for various parameters*

Since electrolyte solutions ionic activity is effectively influenced, various acid and base solutions were tested. The tests yielded good results, particularly for 0.1 M acetic acid solution. Figure 3(a) shows the effect of the hydrogen ionic activity and accumulation times at the peak currents in the horizontal axis within fixed concentrations for 100 μg L^{-1} Hg(II). Various pH strengths of 3.9, 4.5, 5, 5.5, 6, 6.6, 7.1, 7.5, 7.9, 8.9, 10 were applied, respectively. At the pH of 4, high signals appeared. Meanwhile, no response was seen in the pH range > 9–10. Therefore, a pH of 4.0 was deemed as the optimal value for subsequent analysis. Figure 3(a) demonstrates the effects of accumulation time within a range of (10–210 s) at the peak current for the same conditions and fixed Hg(II) concentration of 100 mg L^{-1}. As expected, the peak current increased as the pre-concentration time increased. Specifically, the peak current increased at a fast rate up to about 210 s, then slowed down and started to level off at a range between 210 and 280 s. Thus, 210 s was identified as the optimum accumulation time for the pre-concentration before stripping.

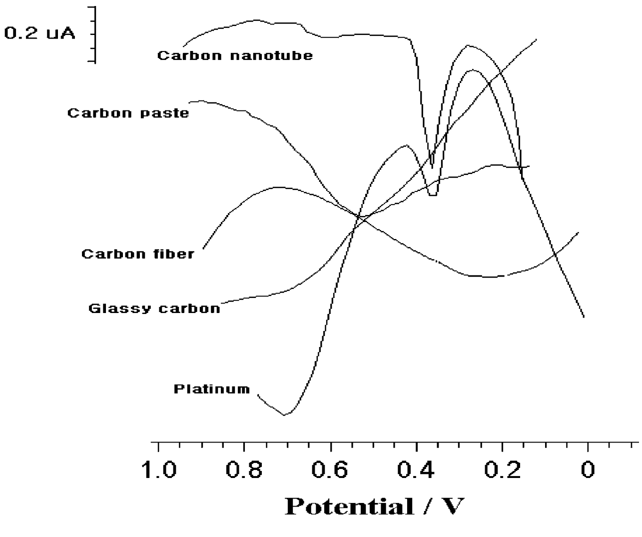

Fig. 2. Comparisons of various electrodes sensitivity for the SWASV peak currents in 10 μg L^{-1} Hg(II), in 0.1 M CH_3COOH with pH of 4, deposition time for 210 s at 0.5 V, frequency of 40 Hz, potential step of 25 mV, amplitude of 100 mV. Other parameters were set at optimum.

Figure 3(b) shows the effect of the accumulation potential on the pre-concentration (hence, the peak current), using various levels of accumulation potentials within the range of (−1.5, −1.3, −1, −0.8, −0.6, −0.5, −0.4, −0.3 V), respectively. The results showed a very slow rate of increase and a linear trend. On the other hand, the ratios were not better than the step potentials. The current increased as the deposition potential approached the positive end of the range from −400 to 0 V. The current reached a maximum value of about 0.27 mA at about 0.0 V, after which the stripping peak current started to decrease. Thus, a pre-concentration potential of 0.0 V was selected as the optimum condition for accumulating Hg(II) on the GPE. A parameter involving the step potential was then tested. Figure 3(b) displays the effect of the step potential on the peak current at the same conditions within a range of 3–30 mV for the 100 μg L^{-1} Hg(II). As the step potential increased, the peak height increased linearly up to 30 mV, after which the effect was not as pronounced. Hence, a step potential in the range > 25–30 mV appeared to be most suitable.

Figure 3(c) shows the dependence of the peak current on the square-wave frequency for 1–40, respectively, and amplitude for 10–100 mV, respectively. Other experimental parameters were held constant using the same conditions. Each peak current exhibited a very rapid and linear rate of increase. As the frequency increased, all the peak ratios identically increased at $1{-}20 \times 10^{-7}$ A, reaching the maximum at about 40 Hz. Thus, the optimal frequency and amplitude was determined at 25.0 Hz and 100 mV amplitude, respectively. However, beyond 40 Hz and 100 mV, peak broadening becomes much larger, making the peak separation worse.

4. Statistics and application

Various concentration effects were studied using optimized conditions. Figure 4 displays the raw

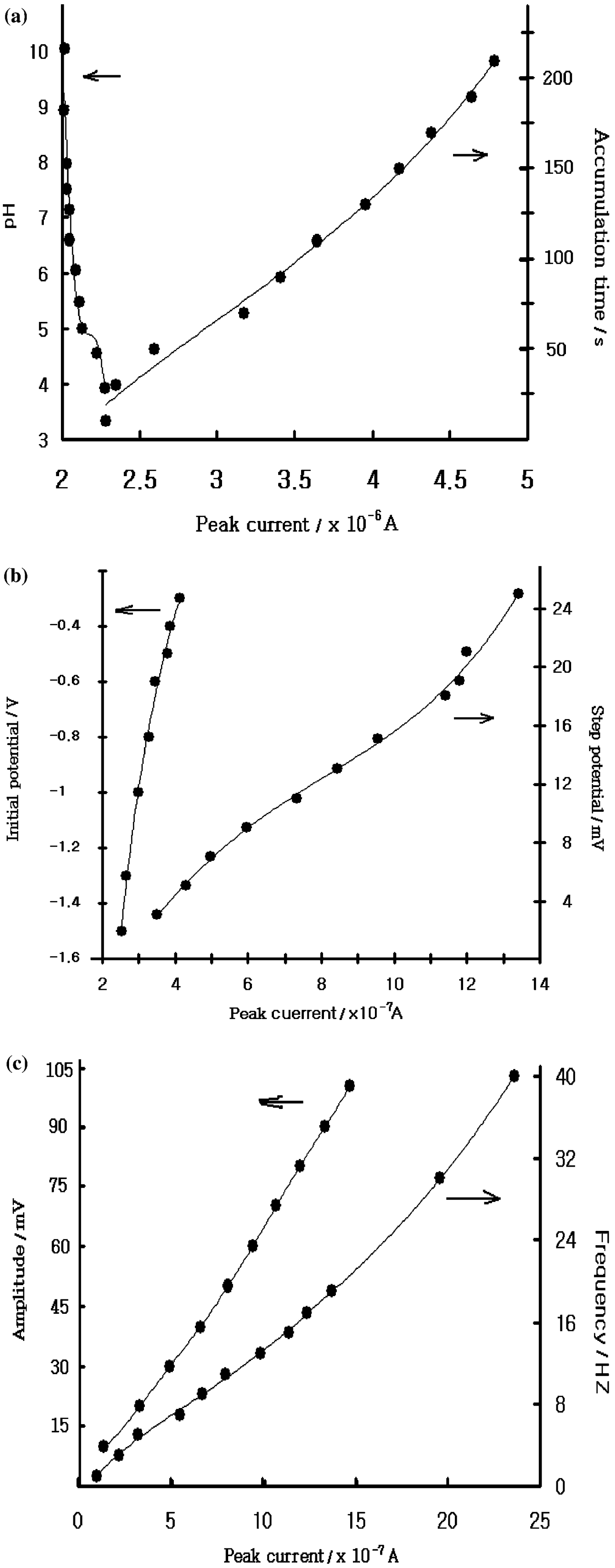

Fig. 3. (a) Square-wave voltammetric peak current (in Amp for horizontal axis scale) at various pH (3.9–10 for left vertical axis) and accumulation times (10–210 s for right vertical axis). (b) Accumulation potential (−1.5 to −0.3 V) and step potential (3–30 mV). (c) Amplitude (10–100 mV) and square-wave frequencies (1–40 Hz) for the 100 μg L^{-1} Hg(II); other conditions in Figure 3 were held constant.

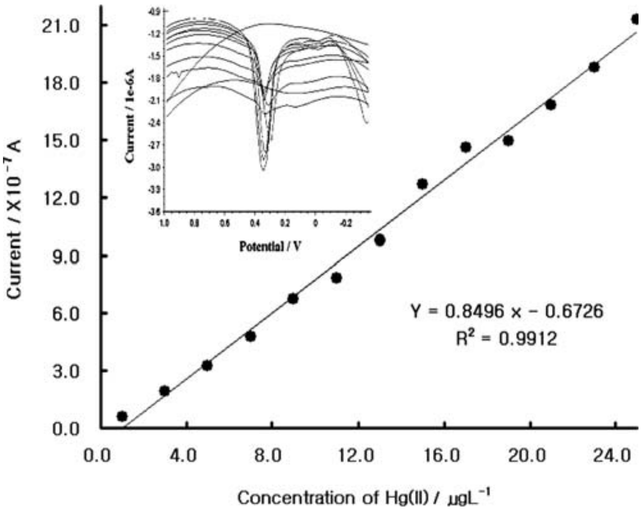

Fig. 4. Square wave stripping voltammograms of Hg(II) at various concentrations ranging from 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23 and 25 μg L^{-1} at optimum conditions, in 0.1 M CH_3COOH solution with a pH of 4, deposition time for 210 s at 0.5 V, frequency of 40 HZ, potential step of 25 mV, amplitude of 100 mV, and the calibration curve with the results of regression. Other parameters were set at optimum.

voltammograms for working ranges of Hg(II) concentrations (1–25 μg L^{-1}) at the linear optimum. After the background current was subtracted from the measured currents, various concentration ranges were tested. Only two ranges appeared as the adjusted currents were plotted. This exhibits the linear range in the concentration range of 1–25.0 μg L^{-1}. A linear regression yielded an equation of $y = 0.8496x–0.6726$ (y: current in μA; x: concentration in μg L^{-1}) with $R^2 = 0.9912$ (R^2: correlation coefficient). At a high concentration range of 40–200 μg L^{-1}, a regression equation of $y = 0.0377x + 4.0278$, $R^2 = 0.9951$ was obtained. The working ranges can be used for determining Hg(II) concentrations in samples. The precision for the 12th determination of 200.0 μg L^{-1} solution yielded a relative standard deviation of 0.14%. The voltammetric current response is highly reproducible. A detection limit of 0.42 μg L^{-1} of Hg(II) per concentration was estimated, based on the signal from the noise characteristics of the data for S/N = 3, given optimum conditions. Analytical applications of various interference elements were then tested. Possible interference of several chemical species during Hg(II) determination was detected at a Hg(II) concentration of 100 μg L^{-1}. The criterion used for the presence of interference was a 5% or greater change in the peak current of Hg(II). The following levels did not show any interference: Ca(II) 300 μg L^{-1}, Cr(III) 300 μg L^{-1}, Cd(II) 300 μg L^{-1}, Ge(IV) 500 μg L^{-1}, Cu(II) 500 μg L^{-1}, and Cd(II) 500 μg L^{-1}. On the other hand, interference ions manifested at 100 μg L^{-1} Hg(II), with 100 μg L^{-1} Ni(II), Ca(II), Ge(IV), Zn(II), Pb(II), Cu(II), Cr(III), and Cd(II), yielding 32.8, 44.8, 12.9, 15.5, 27.6, 34.6, 45.1, and 14.5% of interference, respectively. Subsequently, increased concentrations for 100 μg L^{-1} Hg(II) with 300 mg L^{-1} Ni(II), Ge(IV), Zn(II), Pb(II), and Cu(II) yielded 12.0, 34.5, 108.6, 100.1, and 55.5% of interference, respectively. Further concentrations for 100 μg L^{-1} Hg(II) with 500 μg L^{-1} Ni(II), Ca(II), Zn(II), Pb(II), and Cr(III) yielded 59, 17, 39, 44, and 21% of interference, respectively.

Applying the standard addition method in determining Hg(II) can eliminate the interference of other species. Analytical applications are examined for the determination of Hg(II) ions in laboratory waste solutions for a known amount of 4.5 μg L^{-1}, which was tested five (5) times. Under optimal conditions, this method yielded an amount of 4.427 ± 0.07 μg L^{-1}, with a recovery of 96% ($n = 5$). More expanded applications were examined for the pharmacy and city waste solutions. Good results were obtained from all the previously examined values and known amounts.

5. Conclusions

Using optimum conditions for determining mercury ions, various conventional working electrodes were compared. The NTPE signal was shown to respond better than the other peak currents. The optimum conditions were found to be as follows: a pH of 4.0 for analytical solution; deposition potential of −0.5 V; deposition time of 210 s; SW frequency of 40 Hz; SW amplitude of 100 mV; and, step potential of 25 mV. The SW peak currents exhibited a linear range of 1.0–25.0 μg L^{-1} and 40.0–200.0 μg L^{-1} of Hg(II) and a CV range of 1.0–10.0 mg L^{-1}. Under optimum analytical conditions, the detection limit of Hg(II) was determined to be 0.42 μg L^{-1}, with 0.6% relative error at 0.20 mg L^{-1} Hg(II). Thus, the developed method is a viable technique for monitoring Hg(II) in various fields. It was also confirmed that using NTPE is much more sensitive than using a conventional electrode.

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