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Determination of Mercury at a Modified Carbon Paste Electrode Containing Picolinic Acid N-Oxide

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Abstract

Modified carbon paste electrodes (CPEs) for the analysis of the Hg(I) ion have

been constructed by incorporating picolinic acid N-oxide (PICN) into graphite powder with nujol oil. Simple immersing of the PICN-modified CPE into the measuring solution led to the chemical deposition of Hg(I) ion onto the electrode. The linear sweep and the differential pulse voltammetry were used to characterize the modified electrode that responded to the Hg(I) ion. The analysis of the Hg(I) ion was carried out with the CPE in the K_2SO_4/H_2SO_4 aqueous solution. The response, to the 1.0×10^{-7} M Hg(I) ion, reproduced about 5.8% in the relative standard deviation using differential pulse stripping voltammetry. The detection limit for the Hg(I) ion was 1.0×10^{-9} M for 25min of the deposition time. Our results obtained in the determination of mercury are verified using a certified standard urine reference material, SRM 2670 (trace elements in urine).

Key words : Modified electrode, Analysis of mercury, Carbon paste electrode, Picolinic acid N-oxide.

I. Introduction

Stripping voltammetry is known as a very sensitive and selective electroanalytical method[1,2]. This method is used to analyze traces of organic and inorganic substances through the preconcentration from the solution followed by stripping analyte into the solution. The stripping method often employs chemically modified electrodes (CMEs) to preconcentrate the analyte selectively on the surface via chemical reactions[3-8]. Thus, using CMEs in the stripping method give a versatile preconcentration range with little interference compared to conventional stripping voltammetry. Another advantage using a CME is exchanging the sample solution with a clean electrolyte before the stripping step, so that one may effectively bypass the host of electroactive interferences. To determine metal ions using a CME, the deposition

of test ions take place by reacting with the test ions through the complexation or adsorption processes on the modified electrode surface. This usually forms sparingly soluble complexes on the electrode surface in an aqueous solution. Of these CMEs, CPEs were used occasionally to analyze metal ions with the stripping method because they have the following unique advantages. CPE can be readily prepared and easily regenerated to a new electrode surface. A review paper was presented dealing with the use of CPEs for electrochemical sensors[9].

There are several studies for CMEs to determine the Hg(II) ion[10-30], a simultaneous determination of Pb(II), Cu(II) and Hg(II) ions with the CPE containing humic acid[31], and a simultaneous determination of Hg(II) and Ag(I) ions with glyoxal bis(2-Hydroanil)[32]. Anodic stripping voltammetry using Kryptofic-222 modified electrode exhibited a similar sensitivity toward Hg(I) and Hg(II) ions[28]. Therefore, it yields the total levels of mercury ions in a sample. To the best of our knowledge, there aren't any studies on the determination of Hg(I) ion only using a CME. We found that PICN-modified CPE react with both Hg(I) ion and Hg(II) ion. With the 30% PICN-modified CPE, while the response to 1.0×10^{-5} M Hg(I) ion apparently could be seen at 0.65V, the response to 1.0×10^{-5} M Hg(II) ion couldn't be seen at the same potential. It indicates that PICN-modified CPE have higher sensitivity toward Hg(I) ion than Hg(II) ion in an aqueous solution. Thus we studied a method to determine the Hg(I) ion in an aqueous solution using the PICN-modified CPE. PICN is a complexing agent to form a 1 : 1 binary chelate compound with Co(II) ion[33], and mixed-ligand complexes with Eu(III) and Tb(III)[34].

This work characterizes the analytical performance of the CPE and optimizes various experimental parameters affecting the response of the CPE in the following : the pH dependence, deposition time, electrode composition, deposition temperature, the effect of interference etc. We described the detection limits by using the differential pulse voltammetry and the linear sweep method under the optimum

conditions determined in these experiments. We made analysis of mercury species in a real standard sample and verified with the urine standard sample.

II. Experimental

1. Reagent

The organic reagent, PICN (Sigma Co.), was recrystallized twice from bezene and dried under vacuum at room temperature. Mercurous nitrate (Allied Chemical) and reductant, hydroxylamine hydrochloride, were used without further purification. Potassium nitrate (Junsei Chemical Co., Ltd.) was used after twice successive recrystallization procedures from deionized water. Potassium sulfate (Yakuri Pure Chemicals Co., Ltd.) was recrystallized with deionized water and dried under vacuum before use. We used deionized water to conduct experiments.

2. Electrode and Apparatus

After washing the graphite powder in 96% ethanol with stirring well, the solvent was evaporated away under vacuum for several hours at 90℃. The graphite powder was mixed with PICN in various composition, which were 0, 10, 20, 30, 40, 50 and 60%(w/w) in content of PICN to graphite powder. A carbon paste electrode(CPE) was made by the addition of 3㎖ nujol oil into the 5g mixed powder. The electrode body was assembled by cutting the edge of a 1㎖ polyethylene syringe with a razor. The piston of the syringe was used to support the paste. A copper wire through the flank of the piston was established to connect the carbon paste and the potentiostat. Before using the CPE in each measurement, the electrode surface was rubbed with a clean paper until its surface had become smooth and shinning.

The potentiostat used in the linear sweep and the differential pulse voltammetry was the BAS 100B MF-9062 from Bioanalytical Systems Inc.. Measurements were done with a three electrode system using the Ag/AgCl reference electrode connected with a 0.1M KNO_3 bridge to prevent the interference of Cl^-. A platinum wire was used as an auxiliary electrode. The test solution was thermostated at 23± 0.1℃.

3. Process of Analysis

The stock solution (1.0×10^{-3}M) of Hg(I) ion, made by dissolved $HgNO_3$ in the deionized water, was diluted to adequate concentration and used immediately before each measurement. After immersing the PICN-modified CPE in the test solution for a given period while stirring to deposit Hg(I) ion on the electrode surface, it was taken out and rinsed thoroughly with deionized water. Voltammograms were recorded after the CPE was transferred into the vessel containing only a supporting electrolyte solution. The voltage scan range of voltammetry was from -0.2V to +0.8V. The voltage scan rate was 100mV/s and 5mV/s for the linear sweep and the differential pulse voltammetry, respectively.

4. Determination of Mercury in Urine

After transferring the standard urine sample of 2.5mℓ in a pyrex beaker, it was decomposed in a boiling 5mℓ HNO_3 solution. All the mercury ions were converted into the Hg(I) ion with treating it by the reductant, $NH_2OH\cdot HCl$, and deionized water were added to the sample solution to 25mℓ. A CPE was used to preconcentrate the test ion in the solution by stirring for 20min. After preconcentration of the test ion on the CPE, it was taken out from the sample solution, and then washed with deionized water thoroughly. Next, stripping voltammograms were obtained in the blank solution of 0.1M K_2SO_4/H_2SO_4 or 0.1M KNO_3.

Ⅲ. Results and Discussion

1. Electrochemical Behavior for CPEs

LSSVs for the PICN-modified CPE predeposited with 1.0×10^{-5}M Hg(I), Ag(I), Hg(II) ions are shown in Fig. 1. With 30% PICN-modified CPE, while there was sharp anodic peak current in the Hg(I) ion (Fig. 1a), any anodic peak current correspond to the Hg(II) ion couldn't be found (Fig. 1b). With 50% PICN-modified CPE, the response to the Ag(I) ion (Fig. 1d) was about one-third in comparison with that of Hg(I) ion (Fig. 1c). Following the above observation, Hg(I) ion showed most sensitive anodic peak current. It is difficult that a simultaneous determination of Hg(I) ion and Ag(I) ion, because they interfered each other (we will discuss it in detail later). If there existed Ag(I) ion over 3 times of Hg(I) ion mole concentration in a sample solution, the two anodic peaks, Hg(I) ion anodic peak at +0.65V and Ag(I) ion anodic peak at +0.48V, appeared single peak at +0.57V. Thus we decided to determine Hg(I) ion.

Figure 2 shows the LSSVs obtained for the PICN-modified CPE predeposited in a 1.0×10^{-5}M Hg(I) ion containing solution (Fig. 2d) and in the electrolyte (0.1M KNO_3) only (Fig. 2c), respectively. While the LSSV in Fig. 2d has the stripping peak at 0.65V, the LSSVs in Fig. 2a and 2b have no peak in the case of the deposition of test ions with the unmodified electrode. The anodic stripping peak of the Hg(I) ion appeared at 0.65V. To identify the mechanism of the analysis, we obtained various LSSVs from following conditions ① a sloution containing Hg(II) ion only, ② oxidant

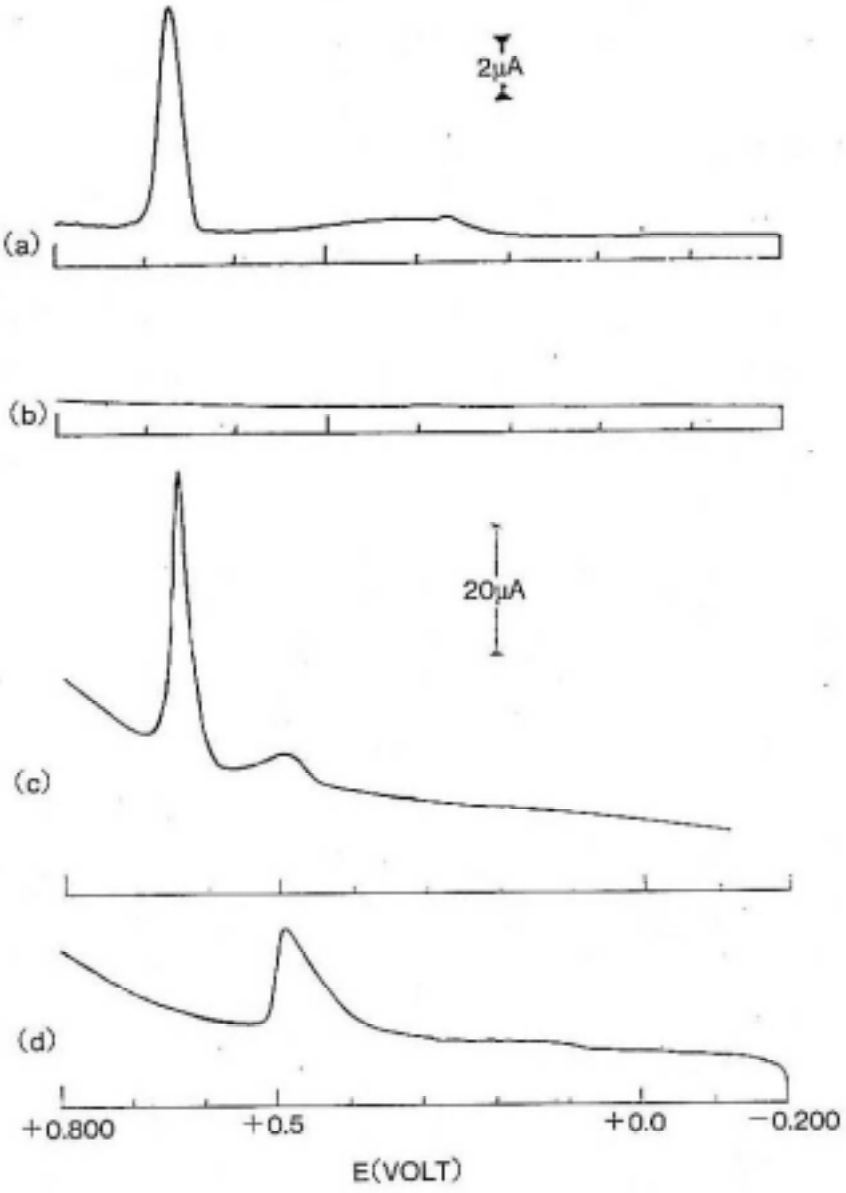

Fig. 1. Linear sweep stripping voltammograms of the carbon paste electrodes : (a and b) : the chemically modified electrodes (30% PICN), (c and d) : the chemically modified electrodes (50% PICN). Electrodes were exposed for 10min to 1.0×10^{-5}M Hg(II) ion solution (b), 1.0×10^{-5}M Hg(I) ion solution (a and c), and 1.0×10^{-5}M Ag(I) ion solution (d), respectively.

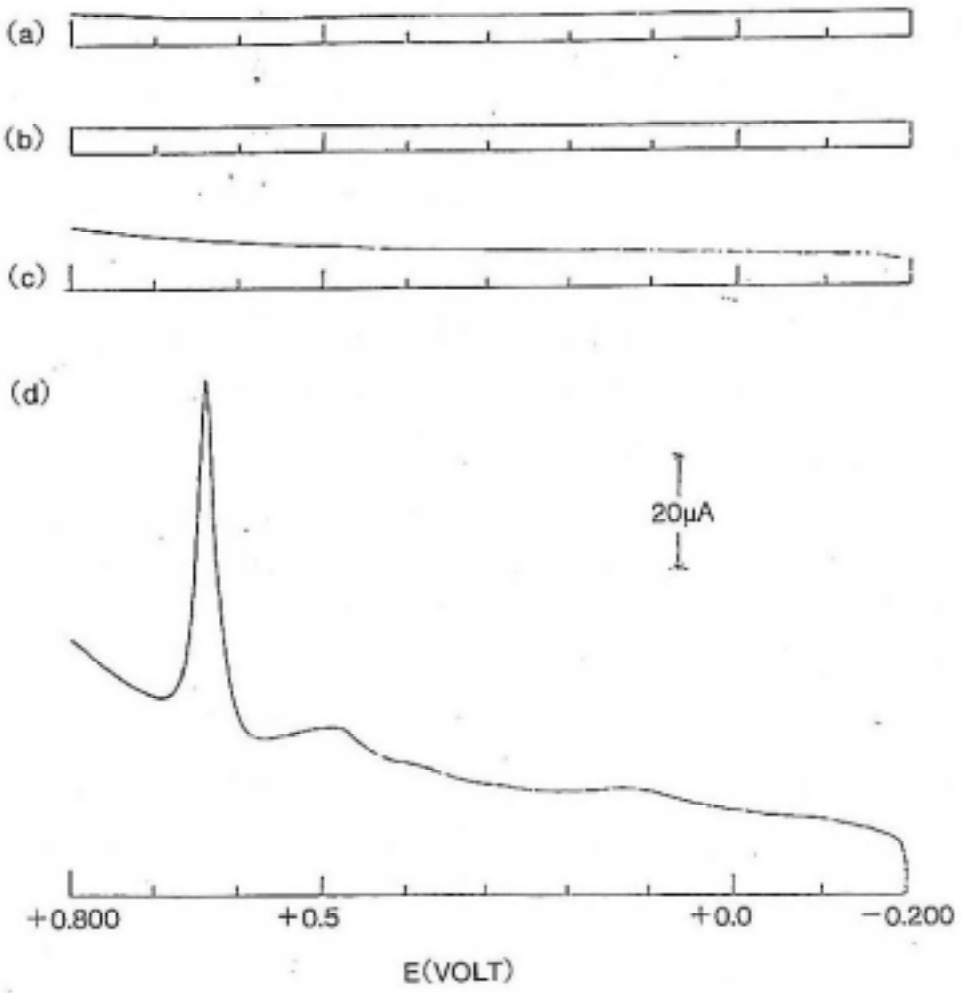

Fig. 2. Linear sweep stripping voltammograms of the carbon paste electrodes : (a and b) : the plain carbon paste electrodes, (c and d) : the chemically modified electrodes. Electrodes were exposed for 10min to (a and c) : blank, and (b and d) : 1.0×10^{-5}M Hg(I) ion solution.

was added to the solution containing Hg(I) ion, ③ a solution containing Hg(I) ion only, ④ reductant was added to the solution containing Hg(II) ion, ⑤ variation of Hg(I) ion concentration. Sharp anodic peak current could be seen for methods ③ ④, and negligible anodic peak current for methods ① ②. In the method ⑤, the anodic stripping peak currents were linearly increased with the increase of Hg(I) ion concentration. Thus, the mechanism of the analysis might be as follows :

$Hg(I) + PICN(CPE) \rightarrow Hg(I)-PICN(CPE)$ complex : deposition

$Hg(I)-PICN(CPE)$ complex $\rightarrow Hg(0) + PICN(CPE)$: reduction of the complex

$Hg(0) + PICN(CPE) \rightarrow Hg(I) + PICN(CPE)$: stripping

We optimized the experimental conditions for the determination of test ion using the above peak potential analytically. The modified CPEs were prepared in various ratio of PICN weight content with respect to the carbon powder, which were 10, 20, 30, 40, 50, 60% (w/w), respectively.

Figure 3 shows a plot for the variation of the anodic peak current according to the change of PICN contents. The peak current reached a maxium value, when the PICN content was 50% (w/w), until the ratio of weight content became 50%, the peak current increased due to the increase of the quantity of the PICN compared to graphite contents, and eventually a resistance of the modified CPE was quite high. Thus, the optimum ratio of the electrode composition was 50% (w/w) PICN.

Figure 4 shows a variation of the peak current of LSSVs according to the pH change of a test solution. To deposit the Hg(I) ion, CPEs were immersed in the buffer solution containing 1.0×10^{-5}M Hg(I) ion for 10min. The pH range of buffer solution was from 1.0 to 6.1. We observed the decrease of the anodic peak current with the increase of pH above 2.0. Then we conducted experiment in the pH 1.0 buffer solution, but the peak current was lower than any other results. Following above results, the pH of the deposition solution was adjusted to pH 2.0 made of 0.1M K_2SO_4/H_2SO_4 solution.

We obtained the result of the effect of scan rate on the anodic peak height of

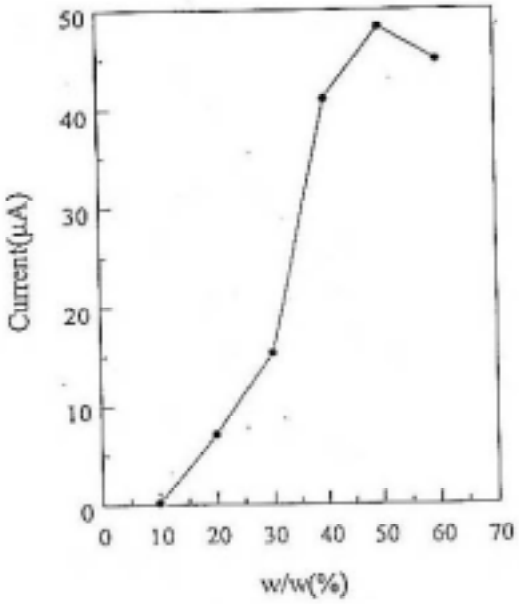

Fig. 3. The variation of the anodic peak current of the Hg(I) ion deposited on the PICN-modified CPE according to the ratio of contents of PICN to the graphite powder composited of the CPE.

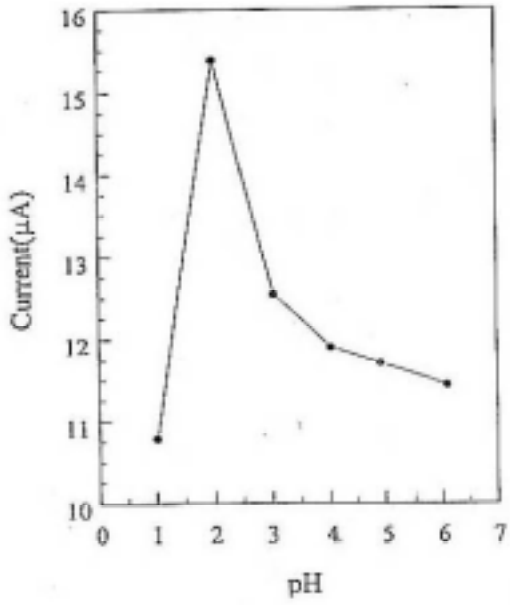

Fig. 4. Effect of pH of the solution on the anodic peak currents of the Hg(I) ion. The concentration of the Hg(I) ion was 1.0×10^{-5}M. The deposition time was 10min, and the scan rate was 100mV/s.

the test ion. The anodic peak current was linearly proportional to the scan rate, indicating a diffusional-controlled process (Fig. 5). This process is typical in stripping voltammetry with a CPE.

Figure 6 shows a plot for the deposition time dependence of the peak current in 1.0×10^{-5}M Hg(I) ion solution. As the deposition time was longer, the peak current gradually increased but it almost appeared constant at a certain time later. This might have been resulted from the saturation of active sites with the test ion deposited on the electrode surface. The peak current slowly increased over 20min for 1.0×10^{-5}M Hg(I) ion solution, little further variation of the peak current size was observed.

A plot for the variation of the peak current of the Hg(I) ion was obtained with the change of the complex formation temperature (not shown). The deposition time was 10min. The peak current increased to 27℃ of the solution temperature, and decreased over 27℃. This might occurred because the electrode surface ran down slowly into the solution above 27℃.

Interference effects were investigated for several metal ions, which would be expected to disturb the determination of the test ion by complex formation with PICN. Metal ions tested in this experiment were Pb(II), Cd(II), Fe(II), Ti(Ⅳ), Mn(II), Bi(II), Se(Ⅳ), Zn(II), Ni(II), Co(II), Tl(I), Cu(II), Al(Ⅲ), Ba(II), Mg(II), Ag(I), Hg(II). In the results, Ag(I) and Hg(II) ions interfered the determination of the Hg(I) ion. In the case of coexistence of the Ag(I) ion in a sample solution, it is impossible to determine the Hg(I) ion at more than 3 times of Hg(I) ion mole concentration, because Ag(I) ion anodic stripping peak merged into the Hg(I) ion anodic peak. Oxidation signals of the Hg(I) ion anodic peak were reduced by 67% at 2 times of Hg(I) ion mole concentration, and 33% at the same. In the case of coexistence of the Hg(II) ion, oxidation signals of the Hg(I) ion anodic peak were reduced by 24% at one-fifth of Hg(I) ion mole concentration, 35% at a half, 80% at the same, and 50% at 3 times. We also conducted

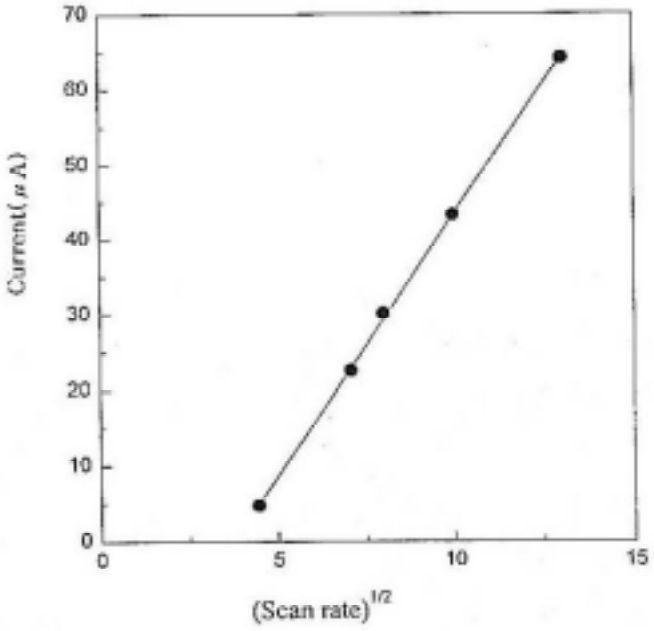

Fig. 5. A plot of the peak height according to the change of the root mean square of scan rate : the deposition time was 10min, pH 2.0. The concentration of the Hg(I) ion was 1.0×10^{-5}M.

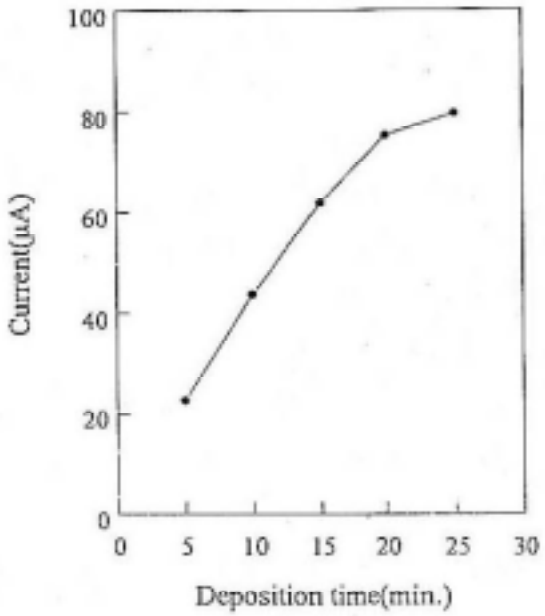

Fig. 6. Effect of the deposition time on the peak height of the Hg(I) ion. pH : 2.0, scan rate : 100mV/s, The concentration of the Hg(I) ion was 1.0×10^{-5}M.

experiments following conditions to identify the increase of signals ① a solution containing 1.0×10^{-5}M Hg(II) ion only, ② addition of oxidant into the solution containing 1.0×10^{-5}M Hg(I) ion, ③ a solution containing 1.0×10^{-5}M Hg(I) ion and 1.0×10^{-5}M Hg(II) ion. All of the three cases, we found the same size of the anodic peak. So we concluded that the PICN-modified CPE responded only Hg(II) ion over the same mole concentration, that is, Hg(II) ion is more selective than Hg(I) ion to make a complex with PICN, but it is hard to detect Hg(II) ion at lower ion concentration. Following above results, we could conclude that Hg(I) ion is less selective, but more sensitive to the PICN-modified CPE in comparison with Hg(II) ion. For the other metal ions, interference effects could not be observed in a real urine sample(SRM 2670 ; NIST of USA) including several metal ions and anions, such as Al, As, Be, Cd, Ca, Cl, Cr, Cu, Au, Pb, Mg, Mn, Hg, Ni, Pt, K, Se, Na, S, V.

Figure 7 shows the calibration plot by LSSV. There are good linearities between 1.0×10^{-6}M and 1.0×10^{-5}M, and 1.0×10^{-5}M and 5×10^{-5}M. For 4 or 5 runs, the relative standard deviation of the current for each scanning was about 5.7%. In the deposition time of 30min, the detection limit was 2.0×10^{-7}M.

Differential pulse voltammograms were obtained in the blank electrolyte solution after preconcentration, immersing the PICN-modified CPE into 1.0×10^{-7}M Hg(I) ion solution for 20min. Figure 8 shows the differential pulse voltammogram for the Hg(I) ion and the calibration plot found by DPV. There is a good linearity between 3.0×10^{-8}M and 1.0×10^{-7}M. The DPV measuring conditions were as follows : scan rate : 5mV/sec ; pulse height : 25mV ; pulse width : 80msec ; deposition time : 20 min and pH : 2.0. In this case, the relative standard deviation was about 5.8%. In the deposition time of 25min, the detection limit was 1.0×10^{-9}M. The detection limit was taken at a concentration where the peak current is twice as large as that of the noise.

Table 1 shows analytical results of mercury by using the PICN-modified CPE

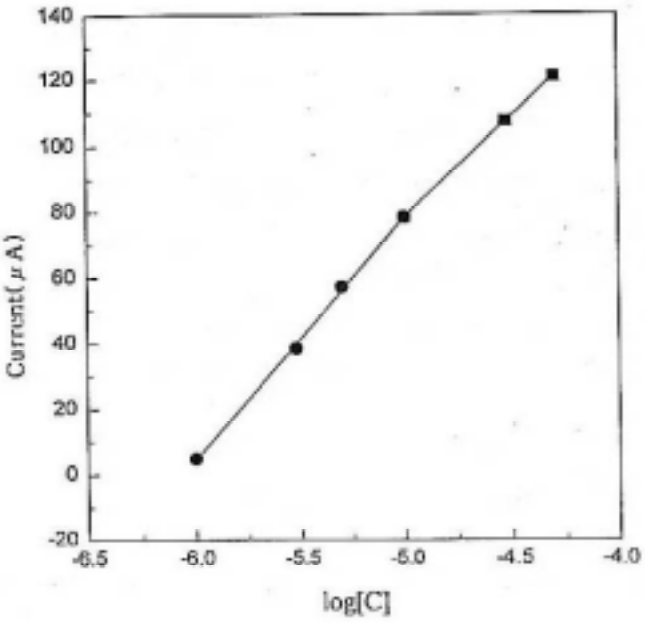

Fig. 7. Calibration plot of the Hg(I) ion from the standard solution.

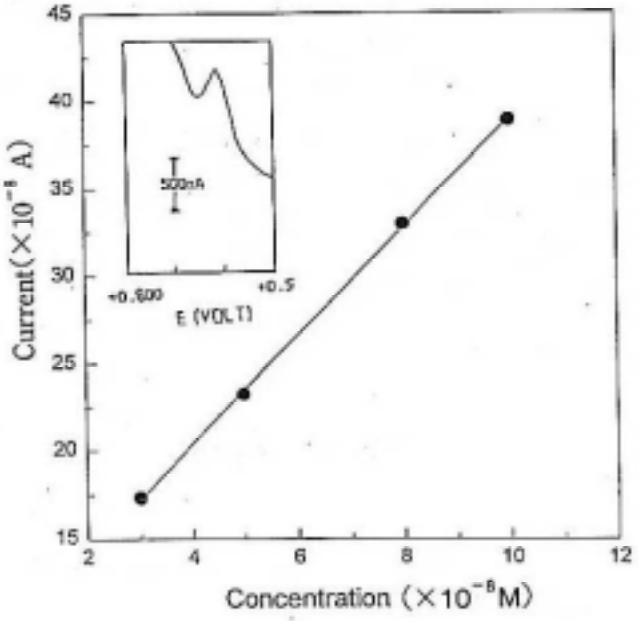

Fig. 8. The differential pulse voltammogram obtained with the PICN-modified CPE during preconcentration of 1.0×10^{-7}M Hg(I) ion for 20min, and the calibration plot for the Hg(I) ion standard solution.

after wet ashing of a real urine sample (SRM 2670 ; NIST of USA). The analysis of the mercury concentration using the urine standard material of American National Institute of Standards and Technology was lower than that of the real concentration. This is due to the loss of weight during wet ashing by using nitric acid or shortness of deposition time. If the deposition time is longer, the error may be even smaller.

Table 1. Analytical results of mercury in certified sample (Urine, SRM)

Substance analyzed	No. of determination	Deposition time(min)	Metal found ± SD/ppb
Urine sample	3	20	9.94± 0.09
Certified sample			10.50

Ⅳ. Conclusion

In this study, optimum experimental conditions were as follows : the ratio of PICN and graphite was 50%(w/w), the pH of the solution was 2.0, and the deposition time was 20min. While the detection limit of the Hg(I) ion was 2.0×10^{-7}M using linear sweep method, with differential pulse voltammetry, the detection limit was 1.0×10^{-9}M.

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