Determination of Hg_2^{2+} Ions Using the Specific Reaction with a Picolinic Acid N-Oxide Modified Electrode

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A modified carbon paste electrode that specifically reacts with Hg_2^{2+} ions in a Hg^{2+} and Hg_2^{2+} mixed solution has been constructed by incorporating picolinic acid N-oxide into graphite powders. After a preconcentration in a Hg_2^{2+} and Hg^{2+} ion solution (pH 2.0), this electrode shows a well-defined anodic stripping peak for only Hg_2^{2+} ion and a linear response between 3.0×10^{-8} M and 1.0×10^{-6} M of Hg_2^{2+} ion. The electrode has been successfully applied to the selective determination of trace Hg in the human urine sample.

Various methods for a determination of the total mercury content have been reported.[1–3] Additionally, there have been reports on the determination of Hg^{2+} ions with the carbon paste electrode (CPE) containing *l*-sparteine,[4] a simultaneous determination of Pb^{2+}, Cu^{2+} and Hg^{2+} ions with humic acid,[5] and a simultaneous determination of Hg^{2+} and Ag^{+} ions with glyoxyal bis(2-hydroxyanil).[6]

However, there have been no reports on the application of CPE on the specific analysis of Hg_2^{2+} in the coexistence of Hg^{2+} ions. Picolinic acid N-oxide (PICN) has been previously known as a complexing agent[7–9] that forms a 1 : 1 binary chelate compound with Co^{2+} ion and mixed-ligand complexes with Eu^{3+} and Tb^{3+}. In our preliminary work, the PICN-modified CPE had an electrochemical response for the 1.0×10^{-5} M Hg_2^{2+} ion at +0.65 V, but the response for the 1.0×10^{-5} M Hg^{2+} ion couldn't be observed in the same experimental conditions. These results indicated that PICN-modified CPE gives higher specific reaction, toward an Hg_2^{2+} ion than an Hg^{2+} ion in an aqueous solution. Thus, we studied a method to selectively determine the Hg_2^{2+} ion in an aqueous solution using the PICN-modified CPE by voltammetric techniques. The present study characterizes the analytical performance for the PICN-modified CPE and optimizes various experimental parameters affecting the response of the CPE such as: electrode composition, pH dependence, deposition time, deposition temperature, and effects of interference, etc. We also analyze the Hg species in a real standard urine sample.

PICN (Sigma Co) was recrystallized twice from benzene and dried in a vacuum at room temperature. The stock solution of Hg_2^{2+} ion, made by dissolved $HgNO_3$ in the deionized water, was diluted to adequate concentration and used immediately before each measurement. PICN-modified CPE was made by the addition of 3 ml nujol oil into 5 g carbon paste and PICN mixed powder. Electrochemical measurements were done with a three electrode system using the Ag|AgCl reference electrode connected with a 0.1 M KNO_3 bridge to prevent the interference of Cl^{-}. After the preconcentration process, the PICN-modified CPE was taken out from the test solution and washed with distilled water thoroughly. Then, the PICN-modified CPE was transferred to the vessel containing only a supporting electrolyte solution. In every voltammetric measurement, an initial potential of −0.2 V was applied for one minute to reduce Hg_2^{2+}-complex to Hg^0 on the electrode surface. After the electrochemical reduction, the potential was scanned from −0.2 V to +0.8 V with 100 mV s^{-1} and 5 mV s^{-1} for the linear sweep voltammetry (LSV) and the differential pulse voltammetry (DPV), respectively.

Figure 1 shows the linear sweep voltammograms (LSVs) recorded for the PICN-modified CPE after preconcentration in a blank solution (curve-a) and in a 1.0×10^{-5} M Hg_2^{2+} solution (curve-b), respectively. As shown in Figure 1-b, PICN-modified CPE shows a well-defined anodic stripping peak at +0.48 V and +0.65 V. The standard reduction potential of Hg_2^{2+} and Hg^{2+} to Hg^0 was +0.792 V and +0.854 V (vs. NHE), respectively.[10] Thus, the first small anodic peak corresponds to the oxidation of reduced Hg^0 to Hg_2^{2+} species and the second does to Hg^{2+}. A simultaneous oxidation of Hg to Hg^{2+} and Hg_2^{2+} to Hg^{2+} can occur on the electrode surface, because the standard potential of Hg to $Hg^{2+}$and Hg_2^{2+} to Hg^{2+} are close to each other. Thus, two oxidation process partially overlap together and the peak height at 0.6 V might be larger than that at 0.48 V.

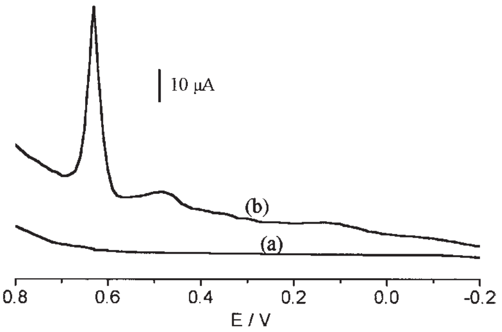

Figure 1. Linear sweep voltammograms for the PICN-modified CPE in 0.1 M K_2SO_4/H_2SO_4; (a) after preconcentration in a blank solution, and (b) after concentration in a 1.0×10^{-5} M Hg_2^{2+} solution. Temperature: 27 °C, preconcentration time: 20 min, and scan rate: 100 mV s^{-1}.

The anodic stripping peak current observed at +0.65 V was directly proportional to the concentration of Hg_2^{2+} ions and preconcentration time. However, the same experiment in a 1.0×10^{-5} M Hg^{2+} solution yielded no stripping peaks of Hg^0. It indicates that PICN-modified CPE gives a highly specific complexation toward Hg_2^{2+} ion than Hg^{2+} ions. The deposition and stripping mechanism is as follows:

Hg_2^{2+} + PICN(on the CPE)

→ Hg_2^{2+} − PICN complex(on the CPE):Deposition step

Hg_2^{2+} – PICN complex(on the CPE)

$\rightarrow$ Hg^0 + PICN(on the CPE):Electrochemical reduction step

Hg^0 + PICN(on the CPE)

$\rightarrow$ Hg_2^{2+} + PICN(on the CPE)

Hg^{2+} + PICN(on the CPE):Stripping steps

In order to determine the optimum conditions for the analysis of Hg_2^{2+} ions with the PICN-modified CPE, we investigated various experimental parameters affecting the analytical signal, such as content ratio of the PICN, preconcentration time, temperature, and pH of the media.

The dependence of the anodic current on the deposition time is shown in Figure 2. As the deposition time was longer, the peak current gradually increased but it almost appeared constant at a certain time later. This might be the result of the saturation of active sites on the electrode surface with the deposited test ion. The peak current slowly increased by 20 min for the 1.0×10^{-5} M Hg_2^{2+} ion solution, and a small increase in the peak current was observed over 20 min.

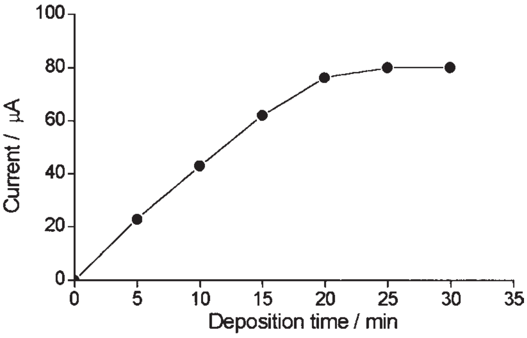

Figure 2. Effect of the preconcentration time on the stripping peak current of Hg_2^{2+} ions using the PICN-modified CPE. Hg_2^{2+} ions concentration: 1.0×10^{-5} M, pH: 2.0, temperature: 27 °C, and scan rate: 100 mV s^{-1}.

The changes in the anodic peak height were examined as a function of the pH of the deposition solution over 1.0 to 6.0. Maximum peak height was achieved when the preconcentration had been done at pH 2.0. Following above results, the pH of the deposition solution was adjusted to pH 2.0 made of 0.1 M K_2SO_4/H_2SO_4 solution.

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. The presence of Pb, Fe, Cd, Ti, Ni, Co, Mg, Al, Mn and Zn did not interfere in the analysis of the Hg_2^{2+} ion. However, the coexistence of Ag^+ ion (1.0×10^{-5} M) in a test solution showed a decrease by about 33% in the anodic current of Hg_2^{2+} ion. Moreover, in the case of the coexistence of Hg^{2+} ion (1.0×10^{-5} M), anodic peak was reduced by about 20% when compared to that in the absence of Hg^{2+} ion. It might be due to the decrease of Hg_2^{2+} concentration by oxidation in air.

Figure 3 shows the calibration plot obtained from data of DPV with PICN-modified electrode into 1.0×10^{-7} M Hg_2^{2+} solution for 20 min preconcentration. The calibration plot for DPV yields linearity between 3.0×10^{-8} M and 1.0×10^{-6} M.

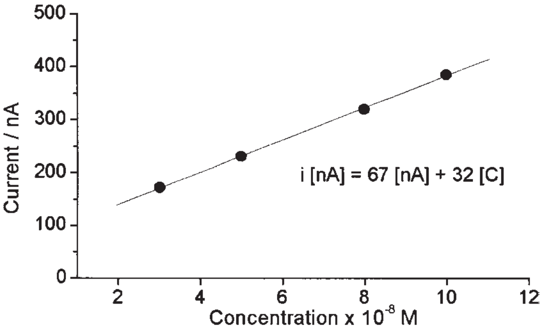

Figure 3. The calibration plot for the analysis of Hg_2^{2+} ions with the PICN-modified CPE using a differential pulse voltammetry. Preconcentration time: 20 min, scan rate: 5 mV s^{-1}, pulse amplitude: 50 mV, and pulse width: 50 ms.

The least-square treatment of DPV data produced an equation of I[nA] = 67[nA] + 32[C] with r = 0.998.

To demonstrate the availability of this analysis method for a real sample with PICN-modified CPE, we attempted to determine Hg in a well-characterized real sample (SRM 2670; NIST of USA). The determined concentration of the Hg with the PICN-modified CPE was 80 ppb from six times DPV measurements. The analytical results obtained from the reference urine material shows that observed value has a good agreement with the certified value (84 ppb) of the urine sample without any interference from the diverse metal ions.

Conclusively, to distinguish the oxidation states of a species in a sample is very important and attractive in a certain experiment. To do that, ESR and XPS have been used. However, these techniques are not easy and are limited to get some information about separate oxidation states of metal ions. Therefore, specific detection of Hg_2^{2+} ion with the PICN-modified electrode is a great advantage, because this study can be applied to specific determination of Hg_2^{2+} in a Hg^{2+} coexisting sample solution.

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References and Notes

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