

Trace Mercury Determination by Differential Pulse Anodic Stripping Voltammetry Using Polythiophene-Quinoline/Glassy Carbon Modified Electrode

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A Polythiophene-quinoline/glassy carbon (PTQ/GC) modified electrode was developed for the determination of trace mercury in industrial waste water, natural water, soil, and other media. The electrode was prepared by the cyclic voltammetric polymerization of thiophene and quinoline on glassy carbon (GC) electrode by the potential application from -0.6 V to +2.0 V (50 mV/sec) in a solution of 0.1 M thiophene, quinoline and tetrabutyl ammonium perchlorate (TBAP) in acetonitrile. Optimum thickness of the polymer membrane on the GC electrode was obtained with 20 repeated potential cyclings. The redox behavior of Cu(II) and Hg(II) were almost identical on this electrode. The addition of 4-(2-pyridylazo)resorcinol (PAR) to the solution containing Cu(II) and Hg(II) allowed the separation of the components due to the formation of the Cu(II)-PAR complex reduced at -0.8V, which was different from the Hg(II) reduced at -0.5 V on a saturated calomel electrode (SCE). The calibration graph of Hg(II) shows good linear relationship with the correlation factor of 0.9995 and the concentration gradient of 0.33 $\mu\text{A}/\text{cm}^2/\text{ppb}$ down to 0.4 ppb Hg. The method developed was successfully applied to the determination of mercury in samples such as river, waste water, and sea water.

Key Words : PTQ/GC, Mercury, Thiophene, Quinoline, PAR

Introduction

Mercury, one of the most important endocrine disrupters has been reported as poisonous to the human body.¹ Legal control of mercury in industrial waste water should be kept at its lower limit to prevent further environmental pollution. Various determination methods of trace mercury²⁻⁷ have been continuously developed not only for monitoring the component but also for controlling its presence in the environment. Lugowska *et al.*⁴ and Sancho *et al.*⁸ studied the determination of trace amounts of mercury by differential pulse anodic stripping voltammetry (DPASV), using a rotating gold electrode. They refer to the interference of copper and silver in the Hg(II) determination. Gil *et al.*² used gold film electrode for the determination of mercury (0.05-10 $\mu\text{g}/\text{l}$). Chemically modified electrodes for mercury^{9,10} and an electrode based on crown ether for copper¹¹ also have been studied by many researchers. Song *et al.*¹² report that copper and mercury would seriously interfere with the determination of silver, using polypyrene (PPy) film modified glassy carbon electrode because those ions would be extracted onto polypyrrole film. Berchmans *et al.*²⁸ report a determination method of trace mercury(II) by anodic stripping voltammetry using the electrode modified with self-assembled monolayer of 2-mercaptopbenzimidazole film on the surface of a gold electrode. Mercury was deposited at -0.7 V for 10 minutes and swept up to -0.1 V in a solution containing 0.5-3 ppm Hg(II).

A disposable thick film graphite electrode modified with a pyrrolidinedithiocarbamate complex²⁹ was also used for the

determination of mercury by stripping voltammetry.

A carbon paste electrode with mercury film for heavy metals¹³ and a graphite electrode modified with molybdenum (VI) complexes for As(V)¹⁴ have been developed for the determination of trace elements by voltammetric techniques.

Conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PT) have shown superior electrical conductivity^{15,20} due to their delocalized electrons in the polymer chain. The electrical conductivity can also be controlled by doping the polymer with certain kinds of non-redox dopants.

The synthetic polymer materials cannot be uniformly spread on the electrode surface mechanically because of their insolubility in water or organic solvent.²¹ The conducting polymers, however, can be coated on any stable electrode surface by electrolytic polymerization.^{6,29} Santos *et al.*¹⁶ could determine lead by using glassy carbon electrode coated with polyaniline, followed by doping sodium polyvinyl sulfonate (Na-PVS).

Gassy carbon working electrodes have given quite a good response for mercury determination down to 0.1 ppm level but poor reproducibility. PT/GC modified electrodes developed by the previous work³⁰ could not be used for the determination of several metal ions to a few ppb in the absence of mercury.

Polythiophene-quinoline (PTQ) copolymer was coated on the GC electrode, and the electrode was used for the determination of mercury(II) in the presence of Cu(II) by differential pulse anodic stripping voltammetry (DPASV) in this study.

Experimental Section

Apparatus. A three-electrode system of a working SCE

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reference electrode and Pt counter electrodes was used throughout the study. The modified working electrode was prepared by copolymerization of thiophene and quinoline on GC electrode surface by applying the potential cycling (-0.6 V to +2.0 V *vs.* SCE).

Voltammograms of CV and DPASV were obtained by using Potentiostat/Galvanostat (M 273A, EG&G PAR co., USA) coupled with electrochemical software (M 270) and GPIB interface.

Ultrapure water prepared from the Millipore Plus II (Millipore, Molsheim) was used throughout the study.

Chemicals and fabrication of the electrode. The preparation of the PTQ/GC modified electrode was carried out by cyclic voltammetry (CV) in a solution composed of 0.1 M thiophene (>99.9%, Aldrich, Wisconsin), quinoline (>99.9%, Fluka, Buchs), and tetrabutylammonium perchlorate (TBAP) (GR grade, Fluka, Buchs) in acetonitrile (GR grade, Junsei Chemical, Tokyo).

The modified working electrode was used for the determination of mercury by DPASV in 0.1 M KCl (GR grade, OCI, Seoul) supporting electrolyte after removing the dissolved oxygen.

0.01 M stock solution of 4-(2-pyridylazo) resorcinol (PAR) was diluted ten times with water whenever it was used on required.

Results & Discussions

Fabrication of PTQ/GC modified electrode. The PTQ/GC modified electrode was prepared by electrochemical polymerization of a solution composed of 0.1 M thiophene and quinoline in acetonitrile on the glassy carbon electrode.

The fabrication was carried out by removing the dissolved oxygen in the mixture, flowing nitrogen gas for 30 sec followed by potential cycling from -0.6 V to +2.0 V with a scan rate of 50 mV/sec. The typical oxidation peak of

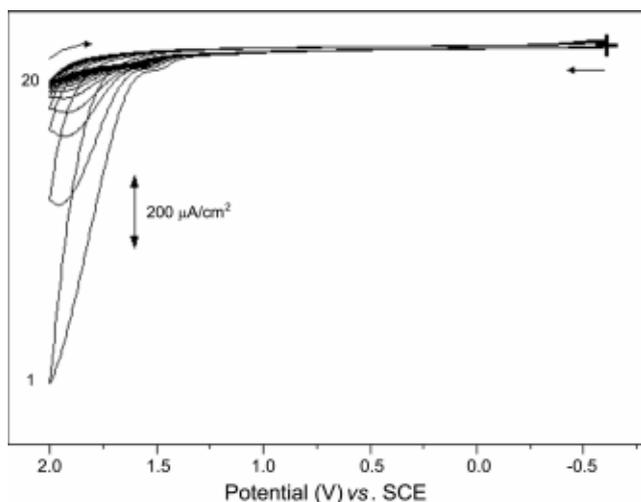


Figure 1. Cyclic voltammograms with GC electrode in a solution containing 0.1 M thiophene and 0.1 M quinoline. The potential was cycled 20 times. Scan rate: 50 mV/s. Supporting electrolyte : 0.1 M TBAP in acetonitrile.

thiophene turned up at +1.8 V *vs.* SCE, which coincides with other workers results¹⁷⁻¹⁹ as can be seen in Figure 1.

Quinoline oxidation at +1.5 V showed a well defined peak for the stabilization process of the modified electrode in 0.1 M KCl solution.

The thickness of the polymer film can be controlled by either cyclic voltammetry or constant current method.

The current density of the oxidation peak at +1.8 V declined remarkably, up to 6 times potential cycle; on the other hand, it was kept constant from 7 to 20 times the potential cycle. The phenomena might be caused by falling conductivity due to increasing thickness of the polymer membrane. The localized non-conducting bonds formed during the copolymerization between thiophene and quinoline molecules inhibit the delocalization of π -electrons by the potential cycling.¹⁸ The most stable polymer membrane used in the study was produced with 20 potential applications.

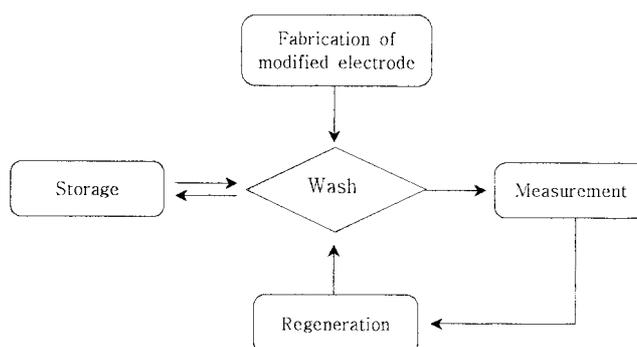
Regeneration of modified electrode. The modified electrode prepared might be contaminated by several metal ions, including copper. The contaminants should be properly removed to determine mercury content successfully.

The electrode was used as shown in Scheme 1. The electrode surface should remain in 0.1 M KCl solution to prevent drying when it is not employed.

The metal contaminants in the modified electrode can be effectively removed in 0.1 M KCl-0.01 M EDTA solution by applying positive potential at +0.5 V for 30 sec.

The electrode can be used about 90 times, cleaning after each use. Damage to the membrane was often observed at 100 times use due to internal or partial destruction of the polymer membrane.

Interference of Cu(II). The differential pulse voltammetric peaks of Hg(II) and Cu(II) appeared at -0.1 V and -0.2 V *vs.* SCE for the electrodes modified, respectively. Anodic stripping voltammograms of the trace ions, however, appeared at +0.02 V for Hg and +0.05 V for Cu which made impossible the determination of those elements simultaneously as can be seen in Figure 2. A trace amount of copper seriously interfered with mercury determination in the coexisting condition by DPASV technique. It was impossible to separate copper and mercury by chelate reaction with EDTA because they have formed very stable complexes with EDTA and given similar stripping peak potentials for the complexes.



Scheme 1. Block diagram of experimental procedure.

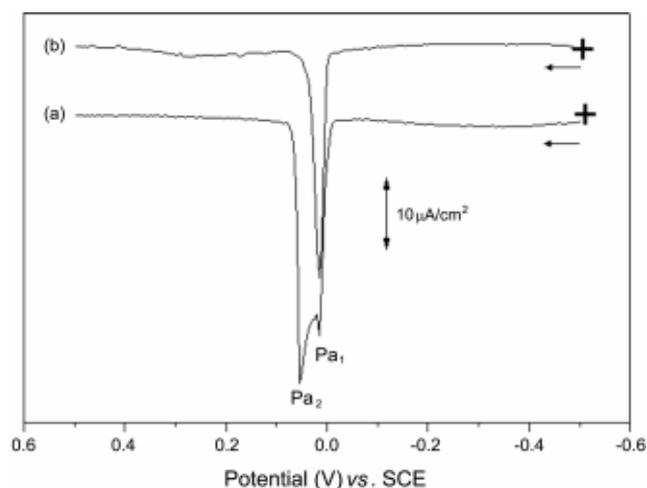


Figure 2. Voltammograms of Hg(P_{a1}) and Cu(P_{a2}) at pH 3 by DPASV in (a) 0.1 M KCl and (b) 0.1 M KCl-0.001 M PAR containing 100 ppb Hg and 100 ppb Cu. Deposition time: 240s at -0.5 V vs. SCE. Scan rate: 50 mV/s.

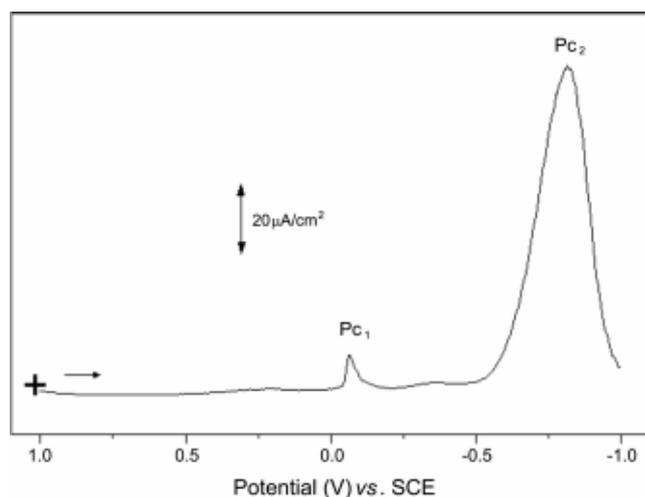


Figure 3. Differential pulse voltammogram of 25 ppb Hg(II)(P_{c1}) and 500 ppb Cu(II)-PAR(P_{c2}) complex in 0.1 M KCl containing 0.001 M PAR at pH 3.

The addition of 4-(2-pyridylazo) resorcinol (PAR) to the solution containing Hg(II) and Cu(II) at pH 3 made it possible to determine mercury without any interference from Cu(II) as can be seen on Figure 2(b). The mercury voltammogram (P_{a1} , DPASV) was obtained from the 0.1 M KCl (pH 3) solution, including PAR by applying the deposition potential, -0.5 V for 240 sec. Anodic peak (P_{a2}) of Cu(II) appeared from the same condition without PAR, but did not appear from the solution including PAR due to the more negative reduction potential of Cu(II)-PAR. Cu(II)-PAR may form a strong complex at the condition, but Hg(II) may not, or may form a complex with a very weak bond with PAR.

The reduction potential of copper(II) may be around -0.05 V, which is similar to that of Hg(II). Differential pulse voltammetric study has ascertained that the reduction peak of Cu(II)-PAR complex appears at -0.8 V (P_{c2}) as can be seen in Figure 3. Mercury can be determined without any Cu(II)

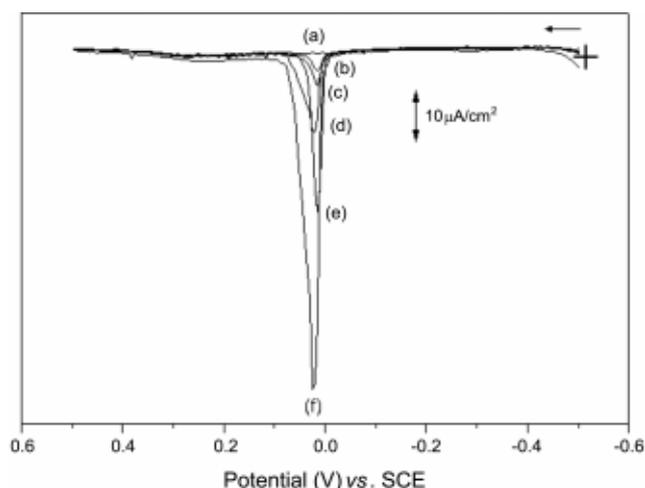


Figure 4. Voltammograms of Hg by DPASV in the mixture of Hg and 1000 ppb Cu in 0.1M KCl containing 0.001 M PAR at pH 3. (a) Blank, (b) 10 ppb Hg, (c) 20 ppb Hg, (d) 50 ppb Hg, (e) 100 ppb Hg, and (f) 200 ppb Hg.

interference in the coexistence situation by DPASV in the solution composed of 0.001 M PAR- 0.1 M KCl at pH 3.

Linear range of Hg. Mercury concentrations in the range of 10 ppb to 200 ppb have been studied to obtain the relationship between current density and Hg concentration by DPASV (-0.5 V \sim $+0.5$ V, scan rate of 50 mV/sec) depositing at -0.5 V for 240 sec.

Figure 4 and 5(a) shows a superior linear relationship for the mercury concentration (10 ppb to 200 ppb) and current densities with the slope factor of $0.33 \mu\text{A}/\text{cm}^2/\text{ppb}$ and a correlation factor of 0.9995.

DPASV peak current density of $2 \mu\text{A}/\text{cm}^2$ could be observed for 1 ppb Hg at the deposition condition of 360 sec. Trace mercury such as 0.4 ppb Hg(II) required longer deposition time (480 sec) than that of higher mercury concentration.

The modified PTQ/GC electrode developed could be used for trace mercury determination at the described condition by controlling the deposition time of the DPASV. A few ppb level of the mercury in some water samples could be

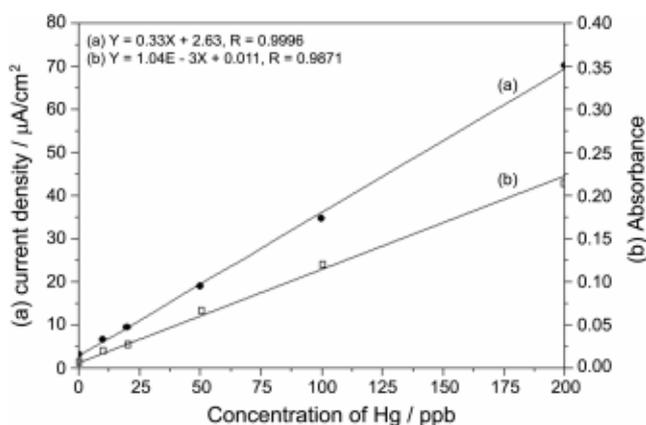


Figure 5. Calibration graphs of Hg by (a) DPASV and (b) cold vapor-AAS.

determined by the method developed.

The cold vapor-AAS method for the determination of mercury recommended by EPA^{22,25-27} was tested in this study, and the linear relationship between concentration and absorbance is illustrated in Figure 5(b). The slope factor of the calibration graph was 1.04×10^{-3} A/Hg ppb, with a correlation factor of 0.9871 for a concentration range of 2-100 ppb Hg. The detection limit (S/N > 5) of 1 ppb Hg recommended by Shimadzu Co. (Japan),²³ and Varian Inc. (USA) could also be obtained by cold vapor -AAS.

Better sensitivity, however, resulted from the voltammetric method, using the PTQ/GC modified electrode developed in this study.

Determination of Hg in real samples. The mercury content in some samples of river water, waste water from an incinerator, and sea water was determined by using the PTQ/GC electrode we developed, and is listed in Table 1. In almost none of the water samples was mercury detected, either by cold vapor -AAS or DPASV using PTQ/GC modified electrode.

In one of the waste water samples, IW-2, however, we determined mercury at 3.5 ppb, which is slightly lower than the allowed level, 5 ppb.

1.0 ppb mercury was determined for sample IW-3 by DPASV, using the modified PTQ/GC electrode for a 10 minutes deposition at -0.7 V. The relative standard deviation of the measured values of the sample was 1.0 ± 0.012 ppb for repeated measurements of $n = 5$. The cold vapor-AAS, however, could not obtain a mercury signal for the sample (IW-3) by direct measurement without a preconcentration process. Successful analytical results of the mercury were easily obtained by voltammetry, using PTQ/GC modified electrode without any interferences in the presence of a large amount of copper.

Table 1. Analytical results of Hg by DPASV and cold vapor-AAS

Sample No.	Concentration of Hg /ppb		Concentration of Cu /ppb
	DPASV	Cold vapor-AAS	
RW* -1	0.0	0.0	23.2
RW* -2	0.0	0.0	45.6
RW* -3	0.0	0.0	28.4
IW** -1	0.0	0.0	66.3
IW** -2	3.5	3.4	42.4
IW** -3	1.0	Tr [†]	79.6
SW***-1	0.0	0.0	23.2
SW***-2	0.0	0.0	16.5
SW***-3	0.0	0.0	8.9

RW*: river water, IW**: industrial waste water, SW***: sea water. [†]Tr: Trace.

Conclusion

The PTQ/GC modified electrode was prepared by cyclic voltammetric polymerization of the chemicals on the glassy carbon electrode. The CV range of -0.6 V to +2.0 V at the scan rate of 50 mV/sec was easily applied to the GC elec-

trode for the polymerization of PTQ in a solution composed of 0.1 M thiophene and 0.1 M quinoline in acetonitrile containing 0.1 M TBAP.

The optimum number of potential cycles for the polymerization were identified to be 20 by the oxidation peak current density of the cyclic voltammograms.

The anodic peak potentials for mercury and copper on the electrode prepared have come at the closed situation of -0.05 V (P_{a1}) and +0.030 V (P_{a2}) for the elements, respectively. Cu(I)-PAR complex was successfully applied to separate the deposition potentials of Hg(II) (-0.5 V) and Cu(II)-PAR (-0.8 V).

The calibration graph of Hg(II) at the condition in the presence of PAR was shown ideally to be a linear relationship from 2 ppb to 100 ppb, with a slope factor of $0.33 \mu\text{A}/\text{cm}^2/\text{ppb}$ and correlation factor of 0.995. The determination of ultra trace levels of mercury (0.4 ppb) can also be done by DPASV, increasing the deposition time.

The modified electrode prepared in this study could be used for the determination of trace mercury in several water samples with good results.

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