

Determination of Mercury in Cosmetics on Electropolymerized Film-modified Electrodes

LAI-HAO WANG*, HUO-MU YAI AND MING-TYAN CHEN

Department of Applied Chemistry, Chia Nan Junior College of Pharmacy, Tainan, Taiwan 71710

ABSTRACT

Electropolymerized film-electrodes modified with a film consisting of N-ethyl-N-(p-hydroxyphenethyl) amine, tyramine and tri-n-octylphosphine oxide, in a 0.5% Nafion or 0.02% poly(vinyl chloride) matrix were used for an anodic stripping determination of mercury in cosmetics. The most important parameters include thickness of the modifying film, the modifier-to-matrix ratio in the modifying film and the base electrolyte composition. These parameters were investigated in this study. Comparison with results obtained from atomic absorption spectrophotometric analysis (AAS) showed good agreement.

Key words: Mercury determination, cosmetic bleaching agent, electropolymerized film-modified electrodes.

INTRODUCTION

The efficacy of ammoniated mercury as a skin bleaching agent has been described by Nealon⁽¹⁾. A bleaching cream usually contains 3% (w/w) ammoniated mercury. Bidstrup explained the mechanism by which mercury interferes with the dopa (dihydroxyphenylalanine) enzyme which is found in the skin and is vital to the formation of pigment⁽¹⁾. There is evidence that mercury also specifically inhibits other enzyme systems. Ammoniated mercury can cause irritation in persons with sensitive skins.

There are few reports in which characterize the determination of mercury and its compound⁽²⁻⁴⁾. These existing studies have however relied entirely on the use of atomic absorption spec-

trophotometry (AAS) which requires reduction conditions with a mercury-hydride system. The preparation and electrochemical properties of a gold film modified with GC electrode and gold electrode had been described in an earlier paper⁽⁴⁾. This type of determination has many advantages, particularly its sensitivity and its low detection limit (0.04 ppb), but its organic interferences comparatively large. In order to improve the detection, the working electrode was coated with a permselective membrane to protect the surface from these interferences.

Organic compounds have previously been applied to modify electrodes⁽⁵⁻¹⁴⁾. In order to increase mechanical stability, we have used a Nafion or poly(vinyl chloride) matrix in the preparation of our electrode. The electropolymerized

film-modified GC electrodes were described for the preconcentration and subsequent voltammetric measurement of mercury in cosmetics.

EXPERIMENTAL PROCEDURES

I. Reagents

Three kinds of pearl cream and skin lighteners were purchased from commercial cosmetic formulations. A stock solution of Hg(II) (1000 ppm Hg, Merck) was diluted (accordingly) with 1.5% HNO₃ to yield a working solution of Hg(0 ~40 ppb). The N-ethyl-N-(p-hydroxyphenethyl) amine (NEA) was synthesized by the same procedures as paper⁽⁷⁾. The solutions for electrode modification were prepared by dissolving tri-n-octylphosphine oxide (TOPO) in tetrahydrofuran, tyramine and NEA in ethanol-water (1:1, v/v) and adding 0.5% Nafion solution respectively.

II. Apparatus

An EG&G Princeton Applied Research 384B polarographic analyzer was connected to a Metrohm 628 rotating disk electrode and to a Houton Instrument Hiplot DMP-40 plotter. A Perkin-Elmer 3100 AAS was equipped with a MHS-10 (mercury-hydride system) and the Perkin-Elmer mercury hollow cathode lamp. The absorption line and lamp current measured 253.7 nm and 6 mA. A CEM MDS-81D microwave digestion system used was fitted with Teflon digestion vessels and pressure-relief valve.

III. Preparation of Electrochemically Synthesized Polymers Modified Electrodes

The glassy carbon electrode (3 mm diameter) was coated by one drop of the modification solution ($0.5 \times 10^{-4} \sim 6 \times 10^{-4}$ mol L⁻¹) containing 0.5% Nafion solution to the electrode surface. Several Nafion films of different thickness were investigated. The solvent was evaporated at 70°C under an infrared lamp, and the electrode heated at 70°C for 5 minutes. Each pre-formed polymers elec-

trode was rinsed, dried and subsequently immersed in 10 ml of 0.1 mol L⁻¹ perchloric acid solution for 5 min. The polyNEA-Nafion, polytyramine-Nafion and polyTOPO-Nafion composites were synthesized by applying +0.8 V (versus SCE) to a GC electrode coated with 1 μ L of 0.5% Nafion in an electrolyte of 0.1 mol L⁻¹ perchloric acid and 3×10^{-4} mol L⁻¹ NEA, tyramine and TOPO in alcohol, respectively.

IV. Determination of Mercury by SWASV

Sample digestion procedure and determination of mercury by cold-vapor AAS were carried out as described previously⁽⁴⁾. For mercury determination, a composite polymers modified electrode, a platinum electrode and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. Aliquots of 5 mL of the sample solution were added to a flask and the volume made up to 10 mL with 0.1 mol L⁻¹ perchloric acid. This solution was introduced into the cell and deaerated with nitrogen for 4 min. The cell voltage was scanned from -0.2 V to +0.8 V and the deposition time was 240 s.

RESULTS AND DISCUSSION

I. Electropolymerized Film Formation

Electrooxidation of NEA and tyramine onto an electrode surface from 0.1 mol L⁻¹ hydrochloric acid were +0.262 V and +0.286 V respectively. The peak current decreased with the number of scans, due to polymerization of the NEA and tyramine, via the -OH group, onto the surface of the electrode. The conducting polymer films of NEA and tyramine had been serially grown on the glassy carbon electrode. These conducting polymer derivatives modified electrodes were capable of determining mercury (Fig. 1 and 2) with detection limits (triple the standard deviation) at 5.8 ppb (ng/ml) for NEA and 4.6 ppb for tyramine. The steric effects play an important role in film formation⁽¹⁵⁾. The TOPO in which

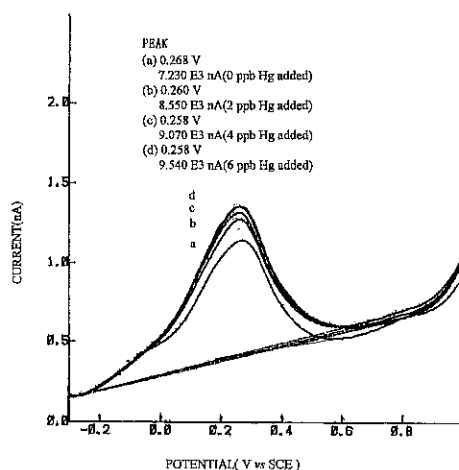


Figure 1. SWASV traces of mercury in 0.1 M HCl determined with a conducting NEA polymers modified electrode at conditions set as scan rate, 200mV s⁻¹; pulse height, 20 mV; equilibration time, 30 sec; frequency 100 Hz.

substituted tri-octyl groups are attached to the phosphine exhibit the largest steric effect that TOPO does not produce films. Many potential technological applications of conducting polymers require the films to be both strong and flexible. The mechanical properties of NEA and tyramine can be enhanced by forming composite polymers. This method involves electrochemically polymerizing NEA and tyramine into a Nafion

Table 1. Effect of pH and supporting electrolytes on the square wave anodic stripping voltammetry (SWASV) peak current of mercury for the NEA modified electrode

Supporting Electrolyte (0.1 M)	pH	$i_p \times 10^3$ (nA)
HCl	1.03	1.320
HNO ₃	1.02	1.150
HClO ₄	0.97	3.220
Acetate Buffer	4.50	-----*
NH ₃ /NH ₄ Cl Buffer	8.47	-----*

* Mercury not measured at this supporting electrolyte.

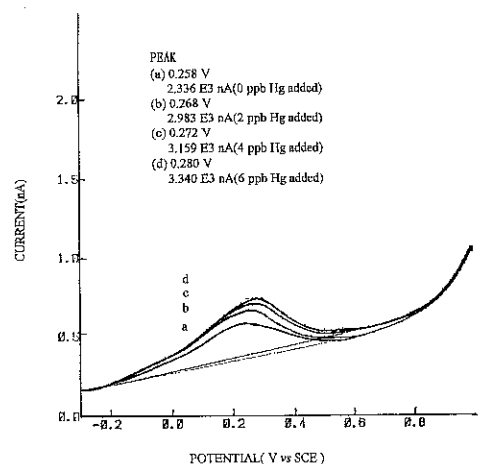


Figure 2. SWASV traces of mercury in 0.1 M HCl determined with a conducting tyramine polymers modified electrode at conditions set as scan rate, 200 mV s⁻¹; pulse height, 20 mV; equilibration time, 30 sec; frequency 100 Hz.

matrix with superior mechanical properties⁽¹⁵⁾.

II. Choice of Experimental Conditions

The choice of electrolyte is an important consideration for optimal film formation⁽¹⁵⁾. Electrolytic salts need to be highly soluble so as to form solutions of sufficient conductivity to maintain current flow between the electrodes. Comparative tests of various supporting electrolytes such as HCl, HNO₃, HClO₄, acetate buffer and NH₃-NH₄Cl solution were conducted. The pH and supporting electrolytes of analyte solution were studied and shown in Table 1. The NEA modified electrode showed an optimum performance when pH was about 1.0. The peak current (i_p) of mercury was the largest in 0.1 mol L⁻¹ HClO₄. The effect of the thickness of the NEA-Nafion layer was examined by coating the GC electrode with 1 μL of modification solution between 0.5x10⁻⁴ mol L⁻¹ and 6.0x10⁻⁴ mol L⁻¹. The regression equations of NEA in 1x10⁻⁴, 3x10⁻⁴ and 6x10⁻⁴ mol L⁻¹ were $y=1669+100851x$ ($r=0.9946$), $y=1685+309809x$ ($r=0.9999$) and $y=1794+105355x$ ($r=0.9903$), respectively. The 3.0x10⁻⁴ mol L⁻¹ NEA was used for coating since the slope of calibration graph obtained by the standard for addition method was the largest. In

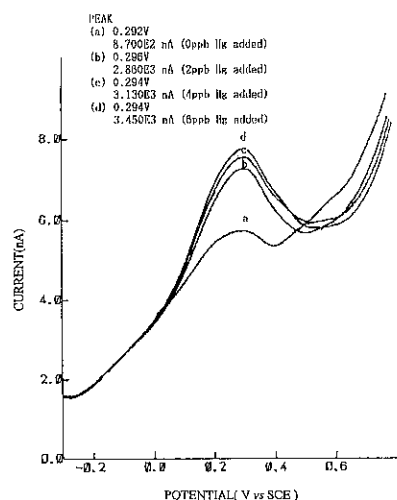


Figure 3. SWASV traces of mercury in 0.1 M HClO_4 determined with a polyNEA-Nafion composite polymers modified electrode at conditions set as scan rate, 200 mV s^{-1} ; pulse height, 20 mV; equilibration time, 30 sec; frequency 100 Hz.

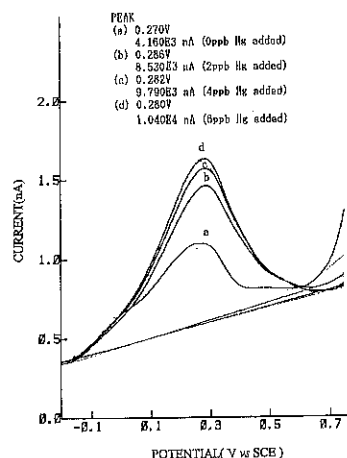


Figure 4. SWASV traces of mercury in 0.1 M HClO_4 determined with a polytyramine-Nafion composite polymers modified electrode at conditions set as scan rate, 200 mV s^{-1} ; pulse height, 20 mV; equilibration time, 30 sec; frequency 100 Hz.

this study, three kinds of polymers modified electrodes were investigated and shown in Fig. 3, 4, and 5 respectively. The TOPO-Nafion modified electrode showed the lowest background current (Fig. 5). The average slope ($n=3$) of polyNEA-Nafion and TOPO-Nafion electrodes were 449616 and 281000 respectively. The sensitivity of NEA-Nafion electrode was higher than TOPO-Nafion electrode and therefore used for mercury determination in the present study.

III. Reproducibility and Accuracy

Determination of the concentration of mercury was accomplished by means of a standard addition procedure as shown in Fig. 3. The peak height of the wave at +0.296 V increased lineally with the concentration of added mercury. Calibration graph was linear in the range of 2~80 ppb of mercury. The correlation coefficient was 0.9993. Recovery tests were carried out on cosmetic preparations to evaluate the reproducibility and accuracy of the proposed SWASV method. Three commercial creams were spiked with the amounts of mercury reported in Table 2. As shown in Table 2, excellent recoveries and precision were observed.

IV. Application to Cosmetic Formulations

The mercury content in the cosmetic formulation was determined by the square wave anodic

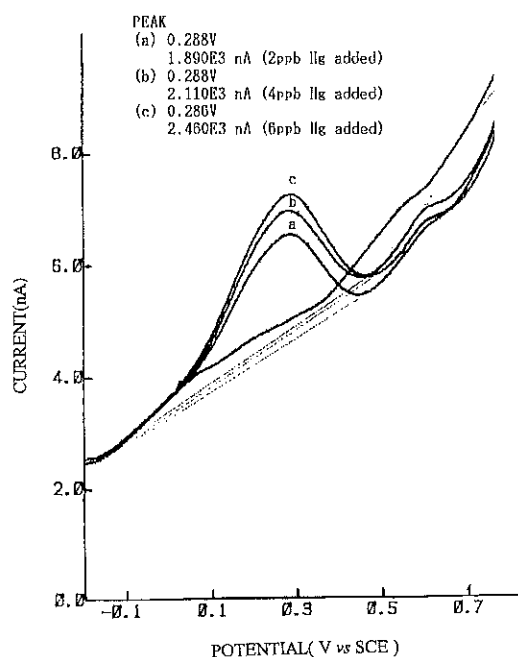
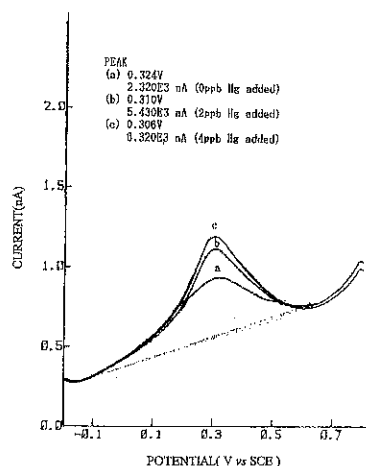


Figure 5. SWASV traces of mercury in 0.1 M HClO_4 determined with a GC electrode modified with a film of 0.1 m mol TOPO in a PVC matrix at conditions set as scan rate, 200 mV s^{-1} ; pulse height, 20 mV; equilibration time, 30 sec; frequency 100 Hz.

Table 2. Recovery and reproducibility in the analysis of commercial cosmetics by SWASV at polyNEA-Nafion composite modified electrode in 0.1 M HClO₄

Hg			
Sample	Added ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$)	Recovery(%) $n=3^a$
Skin lightener	4.00	3.99	99.8 ± 0.14^b
Pearl cream 1	2.00	2.00	100.0 ± 0.16
Pearl cream 2	2.00	1.98	99.6 ± 3.40

^a Number of determinations^b Standard deviation**Figure 6.** SWASV traces of mercury from pearl cream in 0.1 M HClO₄ determined with a polyNEA-Nafion composite polymers modified electrode at conditions set as scan rate, 200 mV s⁻¹; pulse height, 20 mV; equilibration time, 30 sec; frequency 100 Hz.

stripping voltammetry (SWASV) as mention above. A representative SWASV voltammogram of a commercial pearl cream was shown in Fig.6. The results of the SWASV determination were then compared with those of an AAS determination. The results are presented in Table 3.

V. Conclusions

The electrochemical preparation of several new conducting polymers modified electrode

Table 3. Analytical results for the determination of mercury in commercial cosmetics by SWASV at polyNEA-Nafion composite modified electrode in 0.1 M HClO₄ and cold-vapor AAS

Sample	SWASV (mg L^{-1}) $n=5^a$	AAS (mg L^{-1}) $n=6^a$
Skin lightener	2.49 ± 0.13^b (5.4) ^c	2.30 ± 0.12^b (5.2) ^c
Pearl cream 1	1.47 ± 0.05 (3.1)	1.36 ± 0.05 (3.5)
Pearl cream 2	1.40 ± 0.07 (5.0)	1.40 ± 0.02 (1.1)

^a Number of determinations^b Standard deviation^c Relative standard deviation

have been described. Copper(II) is generally considered as a major interference in determination of mercury(II) on gold electrode⁽¹⁶⁾. For polyNEA-Nafion modified electrode, the results showed that less than 100-fold concentration of copper(II) and lead(II) did not interference the mercury response. This technique is relatively simple and reproducibility. The polyNEA-Nafion modified electrode might be used for the routine

analysis of clinical, environmental and cosmetic samples.

ACKNOWLEDGEMENT

Financial support of this work by the National Science Council of the Republic of China is gratefully acknowledged. No. NSC 83-0117-C-041-013 M.

REFERENCES

1. Balsam, M.S. and Edward, S. 1972. *Cosmetics Science and Technology*. Vol.1. p. 228, Wiley, N.Y.
2. Wang, C.H. and Song, P.X. 1988. Determination of Traces of Mercury, Arsenic and Lead in Cosmetic by Atomic-absorption Technique. *Riyoung Huaxne Gougye*. 5: 257-259.
3. Max, X.J., Tiang, R.F., Yang, H.Q. and Luo, Y.B. 1990. Determination of Trace Amount of Mercury in Cosmetics by Cold Atomic Absorption Method. *Fienxi Huaxue*. 18(8): 721-725.
4. Wang, L.H. and Tien, H.J. 1994. Determination of Lead, Arsenic and Mercury in Cosmetic Formulations at Modified Electrodes. *Int. J. Cosmet. Sci*. 16: 29-38.
5. Inside, M.D. O'Riordan, D.M.T. and Wallace, G.G. 1988. Metal Ion Uptake and Voltammetry on a Dithiocarbamate Containing Polymer Modified Electrode. *Anal. Lett.* 21(11): 1969-1986.
6. Lubert, K.H., Schnurrbusch, M. and Thomas, A. 1982. Preconcentration and Determination of Uranyl Ions on Electrodes Modified by Tri-n-octylphosphine Oxide. *Anal. Chim. Acta*. 144: 123-136.
7. Liu, K.Z., Wu, Q.G. and Liu, H.L. 1990. Application of a Nafion-Schiff Base Modified Electrode in Anodic Stripping Voltammetry for the Determination of Trace Amounts of Mercury. *Analyst*. 115: 835-837.
8. Jiri, L. and Karel, S. 1986. Determination of Bismuth by Electrochemical Stripping Analysis. *Talanta*, 33(1): 11-16.
9. Jiri, L. and Karel, S. 1985. Preparation of a Mercury Film Electrode Modified by Tri-n-octylphosphine Oxide and the Electrochemical Properties of This Electrode. *Talanta*, 33(11) : 1027-1033.
10. Jiri, L. and Karel, S. 1989. Preparation of a Gold Electrode Modified with Tri-n-octylphosphine Oxide and Its Application to Determination of Mercury in the Environment. *Talanta*, 36(8) : 843-848.
11. Lubert, K.H. and Schnurrbusch, M. 1986. The Mechanisms of Preconcentration and Voltammetric Behaviour of Uranium (VI) at Glassy Carbon Electrodes Modified by Trioctylphosphine Oxide. *Anal. Chim. Acta*. 186: 57-69.
12. Kosuke, I., Toshio, N. and Toshiyuki, A. 1983. Voltammetric Determination of Uranium in Sea Water after Preconcentration on the Trioctylphosphine Oxide-coating Glassy Carbon Electrode. *Anal. Chim. Acta*. 152: 285-288.
13. Torres, J.M., Losa, H.R., Schorb, K. and Ache, H.J. 1988. Stripping Voltammetry Determination of Traces of Technetium with a Glassy Carbon Electrode Coating with Tri-n-octylphosphine Oxide. *Anal. Chim. Acta*. 211: 317-323.
14. Kosuke, L., Toshio, N., Rituso, T. and Hiroshi, H. 1983. Voltammetry at a Trioctylphosphine Oxide-coating Glassy Carbon Electrode and Its Use for the Determination of Trace Uranyl Ions after Preconcentration. *Anal. Chim. Acta*. 149: 147-155.
15. Linford, R.G. 1987. *Electrochemical Science and Technology of Polymers*. Vol.2. Chapter 3. Preparation and Properties of Electrochemically Synthesized Polymers. pp.97-108. Elsevier Applied Science, London and N.Y.
16. Ingemar, G. 1986. Determination of Mercury in Sea Water by Stripping Voltammetry. *J. Electroanal. Chem*. 214: 31-36.

化妝品中汞於電聚薄膜修飾電極的測定方法之研究

王來好* 戴火木 陳銘田

嘉南藥專應用化學科

摘 要

分別將電極修飾劑N-乙基-N-(對羥基苯乙基)胺、對羥基苯乙基胺和三正辛基氧化膦，以0.5%Nafion或0.02%聚氯乙稀為基質，電合成薄膜修飾電極當工作電極。以陽極

剝除法測定化妝品中汞的含量，並探討修飾薄膜的厚度、修飾劑對基質之比值和電解液組成等重要參數。將分析結果與原子吸光法比較，發現很一致。

關鍵詞：汞測定，化妝品漂白劑，電聚薄膜修飾電極。