Short Communication

Determination of Zinc Pyrithione in Hair Care Products on Metal Oxides Modified Carbon Electrodes

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Abstract
A simple electroanalytical method for the determination of zinc pyrithione (ZPT) in commercial cosmetic products has been developed using a metal oxide modified carbon paste electrode. Ingredients in the cosmetic products did not show any interference in the determination of zinc pyrithione. The electrocatalytic behavior in relation to the properties of metal oxides and the mechanism of the oxidation process was investigated using cyclic voltammetry, linear sweep voltammetry , chronoamperometry. and differential pulse voltammetry. Comparison with results obtained from high performance liquid chromatography shows good agreement.

Keywords: Zinc pyrithione, Cyclic voltammetry, Linear sweep voltammetry, Chronoamperometry, Differential pluse voltommetry, Hair care products

The zinc and sodium pyrithiones (Omadine) are broad–spectum antimicrobial agents, effective against both bacteria and fungi [1]. They were used as cosmetic preservatives in the late 1960's and the Procter and Gamble Co. discovered the anti-dandruff properties of zinc pyrithione (zinc 2-pyridinethiol-*N*-oxide or ZPT). ZPT has been established as one of the most effective antidandruff ingredients for use in shampoo, conditioner, rinse and hairdressing formulations through various clinical studies [2]. In 1981 the Food and Drug Administration (FDA) reported that 29 formulations registered with the agency contained ZPT and 7 contained the sodium salt [3]. The Economic Community (EEC) Council Directive allows ZPT to be used in cosmetic products as a preservative in shampoos and conditioners as a antidandruff agent at a maximum concentration of 0.5 % and 1.0 %, respectively [4]. The toxicity of pyrithione salts by various routes of exposure has been studied extensively in several species of animals and has been described previously [5–16].

Several analytical methods for pyrithiones have appeared in the literature [17–30]. In general, they involve titration with Ti(III) ion [17], thin-layer chromatography [4, 18–19], high-performance liquid chromatography [20–26] and polarography [27–30] procedures. Titrimetric methods suffer from a lack of selectivity for pyrthione and interferences in hair care products. Quantitative TLC analysis requires the use of a spectro-densitometry and ZPT decomposes in sunlight on TLC plates. Sodium pyrithione is difficult to quantitate by means of TLC because it reacts with metals in the TLC plate. The normal-phase HPLC conditions in the on-line Cu(II) complex formation technique can damage the analytical column in time. The direct reverse-phase HPLC analysis of ZPT is difficult owing to the interaction with the reverse-phase packing materials or stainless-steel compounds of the liquid chromatography even if Zn(II) is added to the mobile phase.

Although polarography offers greater specificity it is limited to the determination of 2-pyridinethiol and 2-pyridinethiol-*N*-oxide. ZPT is substantially insoluble in water and is present in aqueous-based products as a dispersion of fine solid particles. However, ZPT is soluble in 1 M hydrochloric acid or alkaline solution. ZPT dissolved in 1 M hydrochloric acid showed a degradation of 10 % immediately, 25 % after 24 hours and 93 % after 4 days of storage at room temperature in a light-resistant container. ZPT is stable in alkaline solution [24].

In recent years studies have been initiated to exploit metal oxides dispersed on electrode surface for enhancing the sensitivity of their voltammetric measurement [31–34]. In this work, the electrochemical oxidation of zinc pyrithione using a bare glassy carbon electrode (GCE), carbon paste electrode (CPE) and metal oxide modified carbon paste electrode (M_xO_y/CPE) has been investigated in various alkaline solution by cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA) and differential pulse voltammetry (DPV). The optimum experimental conditions for the determination of ZPT containing cosmetic samples are described in this article.

Pyrithione exists in tautomeric form (thiol and thione). At or below pH 3 the prevailing form is the thione. The thiol form appears as the pH is raised, the equivalence point being about 7.6. Between pH 7.6 and about 10.0 the thiol form (or its salts) is relatively stable, but above pH 10 it is rather easily oxidized to the sulfimic acid anion [3]. In order to achieve the optimum conditions for pyrithione determination, there are several factors such as pH, supporting electrolyte and working electrode which should be considered. In electrocatalytic processes where the rate determining step is the surface reaction, the measured current density depends on both the genuine catalytic activity of the surface and also the real surface area, i.e., the roughness of the surface [35]. Hence in a catalytic electrode design the surface should be as rough as possible to give the highest apparent current density. Electrocatalysts are almost always transition metal species. The catalysts may be expensive, and the best use of metal oxide material disperses the active component in a cheaper matrix. The electrooxidation of ZPT on bare GCE, CPE and M_xO_y/CPE was carried out and the results are shown in Figures 1 and 2. The oxidation of ZPT on a CPE is catalyzed by the metal oxides under optimum conditions. The higher catalytic activities among ten metal oxides dispersed on CPE are shown at SnO_2, ZrO_2 and. Bi_2O_3. The higher oxidation state of M_xO_y is the more favorable for the electrocatalytic oxidation of ZPT. The oxidation in the SnO_2/CPE gives a peak current higher and at less positive potentials as compared with the bare GCE, CPE and

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M_xO_y/CPE. In 2 mM ZPT with 0.1 M tetrabutylammonium hydroxide (Bu_4NOH), SnO_2/CPE is electrocatalytically the most active, much more than the bare GCE or CPE. Chronoamperometry [36–37] and cyclic voltammetry [38] are useful for diffusion coefficient measurements, rates of electrode processes and adsorption parameters. Chronoamperometric curves of ZPT on bare GCE, CPE and SnO_2/CPE are shown in Figure 3. The charging current that flows will then decay exponentially as the double-layer capacitance is charged. A plot of $\ln(i)$ vs. time has a slope of $-(RC_{dl})^{-1}$ and intercept $\ln(\Delta E/R)$. In this way the capacitance and resistance can be measured [38]. The regression equations being $y = 5.113 - 0.261x$ ($r = 0.9940$), $y = 4.316 - 0.366x$ ($r = 0.9953$) and $y = 4.548 - 0.302x$ ($r = 0.9880$) for SnO_2/CPE, bare GCE and CPE, respectively. The adsorption of metal oxide species can therefore give rise to larger capacity currents than bare GCE or CPE. Therefore, the SnO_2/CPE was chosen for use in the determination of ZPT in cosmetic products.

The electrode kinetics and the equilibrium of an electrochemical reaction are greatly affected by the nature of the solvent and electrolyte employed. The structure of the solvent and solvation of the ion affect the structure of the double layer and the specific adsorption of an ion on the electrode surface. The solvation in protic solvent depends on the polarizability of the cation which increases with the size of the cation. Comparative tests of various pH and supporting electrolytes are shown in Table 1. The height of the ZPT wave in solutions of 0.1 M tetrabutylammonium hydroxide was found to be much higher than in the other supporting electrolytes. We have noted that, when a supporting electrolyte of a larger ion is used in place of a smaller ion, e.g., Bu_4NOH in place of NH_4OH. There is a marked

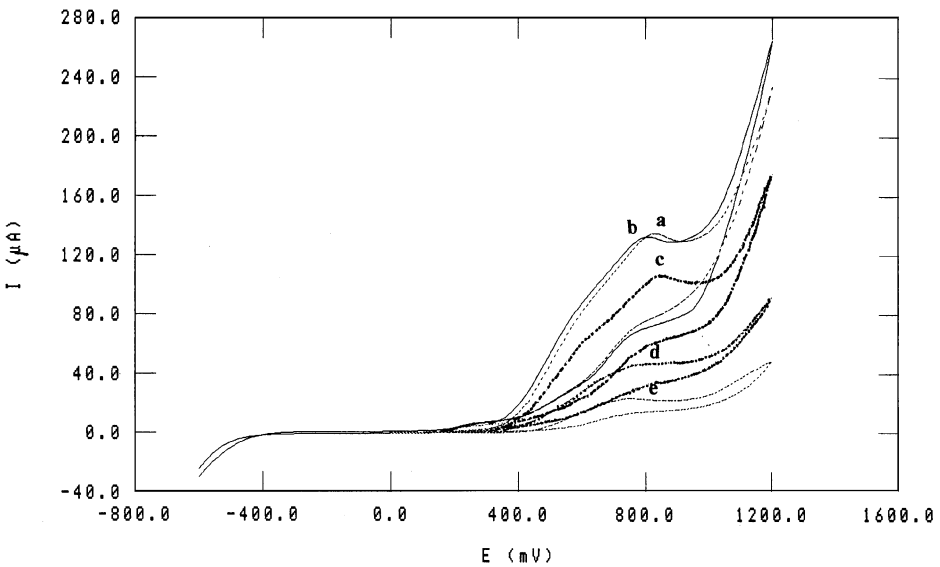

Fig. 1. Cyclic voltammograms of zinc pyrithione (2 mM) in 0.1 M tetrabutylammonium hydroxide (pH 12.47), a) SnO_2/CPE, b) ZrO_2/CPE, c) Bi_2O_3/CPE, d) CPE, e) GCE, scan rate: 10 mV/s, initial potential: 0.0 V, final potential: 1.2 V.

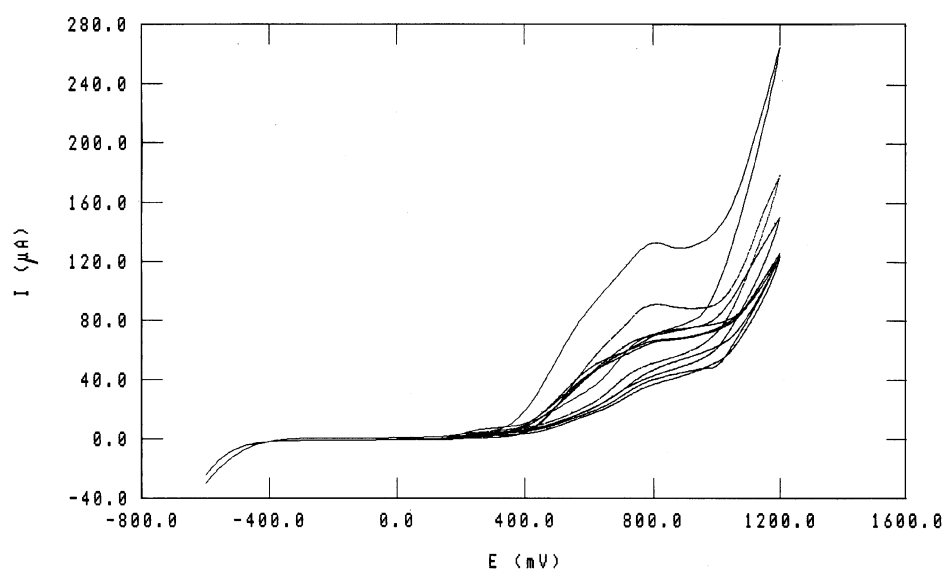

Fig. 2. Cyclic voltammograms of zinc pyrithione (2 mM) in 0.1 M tetrabutylammonium hydroxide (pH 12.47) on metal oxides (SnO_2, CeO_2, Cr_2O_3, PbO, CdO and CuO), scan rate: 10 mV/s, initial potential: 0.0 V, final potential: 1.2 V.

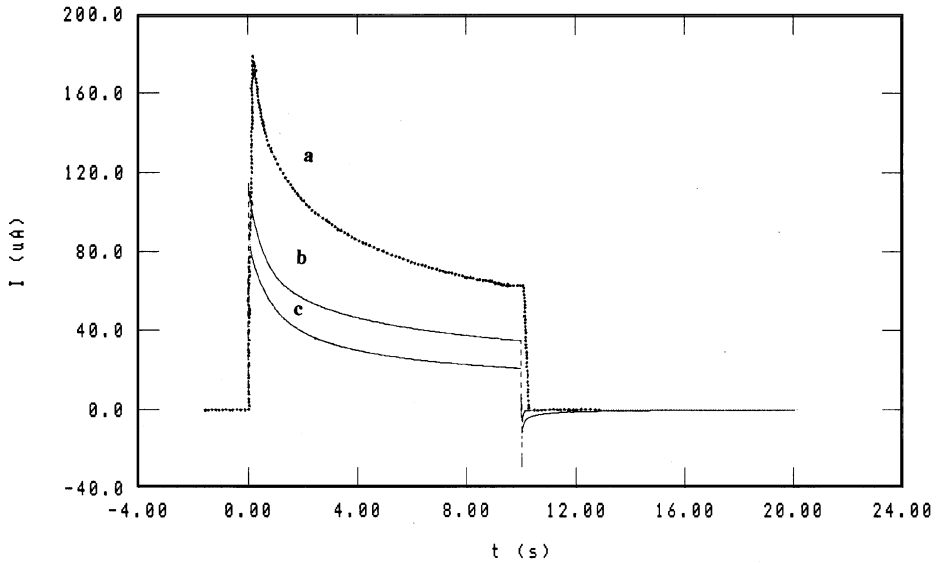

Fig. 3. Chronoamperometric curves for the zinc pyrithione oxidation in 0.1 M tetrabutylammonium hydroxide on a a) SnO_2/CPE, b) CPE, c) GCE.

increase in the apparent transfer coefficient. Hence it is considered that the choice of tetrabutylammonium ion as the solute minimizes the effect of specific adsorption on the kinetics of the electrode reaction.

Table 1. Effect of pH and supporting electrolytes on the differential pulse voltammetry peak current of zinc pyrithione for the stannic oxide modified carbon paste electrode. nm: not measured at this pH and supporting electrolytes.

		Concentration [mg L^{-1}]		
Supporting electrolytes	*pH*	*1.6*	*3.2*	*6.4*
		$i_p \times 10^3$ [nA]		
Robinson buffer	10.26	61.5	117.1	222.7
0.15 M Ammonia	10.54	nm	138.6	265.3
0.1 M Bu_4NOH	12.47	97.0	233.0	464.0

The linear sweep voltammograms of ZPT in 0.1 M Bu_4NOH are shown in Figure 4 at various scan rates on SnO_2/CPE. The $E_p - E_{p/2}$ values of ZPT are found to be around 81.8 mV at SnO_2/CPE. For a reversible charge transfer, $E_p - E_{p/2}$ should be around 60 mV. Hence electrochemical mechanism for the oxidation of ZPT may be concluded as being a diffusion controlled irreversible charge transfer at SnO_2/CPE. For the totally irreversible case at 25 °C, $E_p - E_{p/2} = 0.048/\alpha n_a$, [39] where $E_{p/2} =$ is the half-peak potential, α is the transfer coefficient, and n_a is the number of electrodes in the rate-determining step. Double potential step (DPS) chronoamperometry can play a complementary role to CV in the analysis of electrochemical mechanisms. In combination with the DPS current response (a current–time curve) and CV, both αn_a and D (diffusion coefficient) can be determined. The fundamental equation of chronoamperometry is the Cottrell equation: $I = nFACD^{1/2}\pi^{-1/2}t^{-1/2}$. The chronoamperometric trace of the ZPT is shown in Figure 3

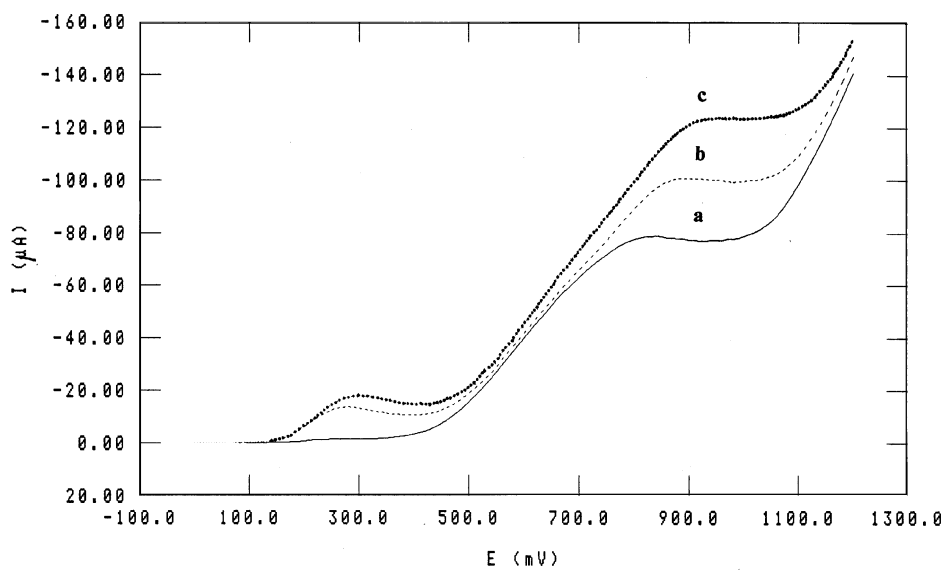

Fig. 4. Linear sweep voltammograms of zinc pyrithione (2 mM) in 0.1 M tetrabutylammonium hydroxide on SnO_2/CPE. Scan rate: a) 10 mV/s, b) 40 mV/s, c) 80 mV/s.

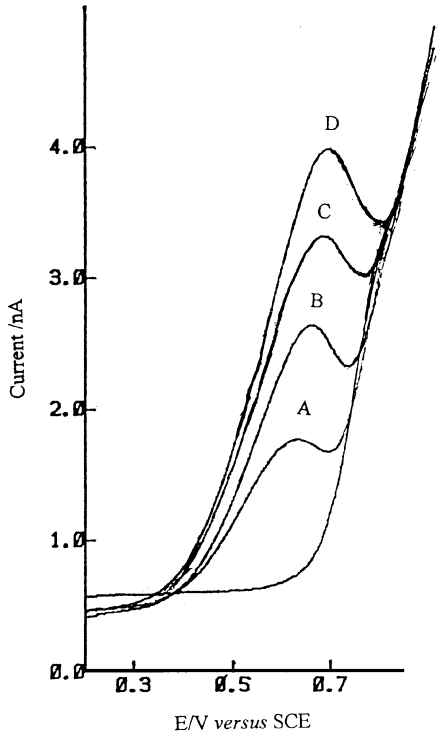

Fig. 5. DPV obtained to produce calibration plot for zinc pyrithione (ZPT) at a SnO_2/CPE. Peak A) 0.620 V, 5.05 (E2) nA (8 ppm ZPT added); B) 0.612 V, 8.05 (E2) nA (16 ppm ZPT added); C) 0.620 V, 1.132 (E3) nA (24 ppm ZPT added); D) 0.628 V, 1.488 (E3) nA (32 ppmZPT added); scan rate: 4 mV/s, pulse height: 0.05 V, initial potential: 0.2 V, final potential: 0.85 V.

along with a current–time curve calculated by allocating ($n = 2$, $C = 2 \times 10^{-3}$ M, $D = 2 \times 10^{-11}$ cm^2 s^{-1}).

Determination of the concentration of ZPT was accomplished by means of a standard addition procedure as shown in Figure 5. The peak height of the wave at +0.620 V increases linearly with the concentration of added ZPT. The calibration plots obtained by plotting the peak current against the concentration of ZPT show good linearity over the range 1.6–32.0 mg L^{-1}, and the regression equations being $y = 163 + 41x$ (correlation coefficient $r = 0.9993$). The relative standard deviation value was 4.3 %. Recovery tests were carried out on cosmetic products to evaluate the reproducibility and accuracy of the proposed DPV method. Three cosmetic products were spiked with the amounts stated in Table 2 and subjected to the whole procedure. As shown in Table 2, excellent recoveries and precision were observed (recoveries ranging from 101 ± 1.5 % to 102 ± 3.1 %).

The effect of the ingredients in cosmetic products on the determination of ZPT was investigated. As shown in Table 3, no interference effects were observed. The proposed DPV method was applied to the determination of ZPT in shampoo, conditioner, rinse and hairdressing products. A representative DPV voltammogram of a commercial shampoo is shown in Figure 6. Analytical results are given in Table 4. These results agreed with those obtained by a high performance liquid chromatographic method.

Table 2. Recovery of zinc pyrithione added to commercial shampoos and rinses by DPV.

	Added [mg L^{-1}]	*Found [mg L^{-1}] N = 3 [a]*	*Recovery [%]*
Shampoo	8.00	8.10	101(1.8 %) [b]
Shampoo and conditioner	10.00	10.17	102(3.1 %)
Rinse	5.00	5.05	101(1.5 %)

[a] Number of determinations; [b] relative standard deviation.

Table 3. Effect of ingredients of cosmetic products on the determination of zinc pyrithione.

Ingredient	*Ingredient added [mg L^{-1}]*	*ZP*		
		Present [mg L^{-1}]	*Found [mg L^{-1}]*	*Recovery [%]*
Sodium lauryl sulfate	80	8.00	7.81	97.6
Sodium lauryl ether sulfate	800	8.00	7.94	99.2
Ammonium lauryl sulfate	80	8.00	8.09	101.2
Ammonium lauryl ether sulfate	120	8.00	8.12	101.6
Trimethylstearylammonium chloride	800	8.00	8.02	100.3
Coconut monoethanolamide	720	8.00	8.23	102.9
Brij 35	800	8.00	8.25	103.5
Triton-X 100	800	8.00	7.98	99.7
Tween 60	800	8.00	7.82	97.7
Monoethanolamine	720	8.00	8.01	100.0
Diethanolamine	800	8.00	8.18	102.0
Triethanolamine	720	8.13	8.01	101.7
Cetyl alcohol	800	8.00	8.06	101.0
Dimethione	800	8.00	8.03	100.3

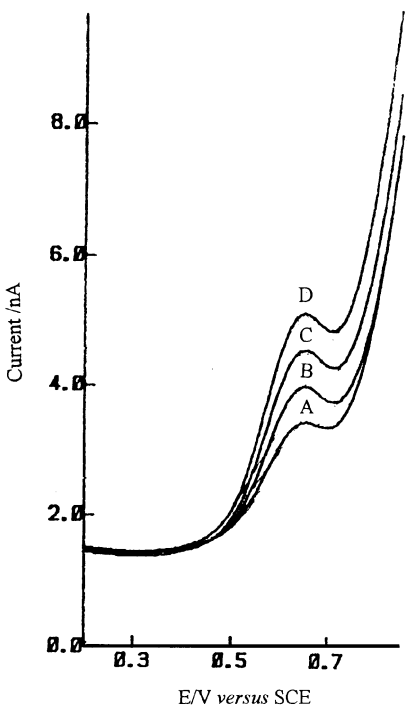

Fig. 6. DPV for zinc pyrithione (ZPT) from commercial shampoo at a SnO_2/CPE. Peak A) 0.648 V, 5.10 (E2) nA (0 ppm ZPT added); B) 0.652 V, 7.94 (E2) nA (8 ppm ZPT added); C) 0.652 V, 1.024 (E3) nA (16 ppm ZPT added); D) 0.652 V, 1.286. (E3) nA (24 ppm ZPT added). Scan rate: 4 mV/s, pulse height 0.05 V, initial potential: 0.2 V, final potential: 0.85 V.

Table 4. Analytical results for the determination of zinc pyrithione in commercial shampoos, conditioner and rinses by DPV and HPLC.

	Concentration [w/w, %]	
	DPV N = 5 [a]	*HPLC*
Shampoo A	0.488(4.0 %) [b]	0.486(4.1 %)
Shampoo B	1.494(4.9 %)	1.562(4.5 %)
Shampoo C	0.474(3.3 %)	0.476(1.7 %)
Shampoo D	0.230(1.7 %)	0.234(1.9 %)
Shampoo and conditioner A	0.758(5.0 %)	0.761(4.2 %)
Shampoo and conditioner B	1.012(5.0 %)	1.016(5.0 %)
Shampoo and conditioner C	0.953(2.4 %)	0.943(0.4 %)
Rinse	0.226(2.6 %)	0.209(2.1 %)

[a] Number of determinations; [b] relative standard deviation.

The carbon paste matrix allows one to make new electrode materials. Modifying the carbon paste matrix with metal oxide powder is very easy. The indicators CPE/M_xO_y can easily be renewed by mechanical polishing with good repeatability and exhibit better stability than CPE and more reproducible than that of GCE. The DPV procedures described here were applied directly to the analysis of cosmetic samples without the need for preceding formation of the Cu(II) complex. The direct determination of ZPT not only offers a higher accurate concentration than the indirect determination but also saves more time.

Experimental

All electrochemical experiments were performed using an EG&G Princeton Applied Research (Princeton, NJ, USA) 384B and 253 polarographic analyzer connected to a Metrohm 628 rotating disk and a Houston Instrument (Austin, TX, USA) Hiplot DMP-40 plotter, respectively. A three-electrode system was employed, consisting of a working electrode (GCE, CPE and M_xO_y/CPE), a platinum counter and a saturated calomel reference electrode (SCE).

The HPLC system consisted of a Model 576 pump (GASUKURO KOGYO, Japan), a Model 7125 injector equipped with a 20 μL sample 1oop and a Model 502 U spectrodetector. Chromatograms and peak areas were obtained with a SISC chromatogram data integrator. Absorbance measurements were recorded with a Cary UV-visible spectrophotometer (Varian Australia Pty Ltd). Matched quartz cells with 1-cm path length were used to hold all solutions for measurement.

Zinc pyrithione (ZPT) and sodium pyrithione were purchased from TCI (Tokyokasei Co. JP) and Aldrich (Milwaukee, WI, USA). Ten kinds of metal oxide, containing tin(IV) oxide (Strem, USA), cerium(IV) oxide (Strem), lead (II) oxide (Strem), zirconium (IV) oxide (Kojundo, JP), γ-aluminum(III) oxide (Balkowski), cobalt(II) oxide (Aldrich), bismuth oxide (Koch, England), cadmium oxide (Koch, England), copper(II) oxide (Strem, USA) and chromium(III) oxide (Strem, USA) were analytical regent grade. Anionic surfactants (sodium lauryl sulfate, sodium lauryl ether sulfate, ammonium lauryl sulfate, ammonium lauryl ether sulfate); cationic surfactant (trimethylstearylammonium chloride) and nonionic surfactants (coconut monoethanolamide; polyoxyethylene[23] lauryl ether or Brij 35, Triton-X 100, Tween 60) were obtained from Sigma and Merck. The ingredients of cosmetic products were monoethanolamine, diethanolamine, triethanolamine, cetyl alcohol and dimethione. All other chemicals were of analytical reagent grade. Samples of shampoo, conditioner, rinse and hairdressing were bought from a number of retail outlets in the south of Taiwan.

Determination of ZPT by DPV: The glassy carbon electrode (3 mm diameter) was polished before each run using two different grades of alumina (1.0 and 0.05 μm) on glass plates before being rinsed. A typical composite metal oxide carbon paste preparation procedure was as follows: 1.2 g of graphite powder (Merck) and 0.015–0.18 g of metal oxides were mixed for 5 min, followed by the addition of 0.8 g of liquid paraffin (Merck) and mixing in a mortar and pestle. The body of the composite metal oxide carbon paste working electrode was fabricated from a PTFE rod (o.d. 7 mm) with a 3 mm deep hole bored (diameter 3 mm) into one side for the composite metal oxide carbon-paste filling. The composite metal oxide carbon paste was placed in the body of the electrode, using a PTFE spatula, and smoothed off.

The pH 10.54 buffer was made by mixing 0.1 M solutions of ammonia and ammonium chloride in deionized water. Briton and Robinson buffer (pH 10.26, 11.78) were prepared by mixing 0.5 M solutions of phosphoric acid, boric acid, acetic acid and 0.2 M sodium hydroxide solution. The supporting electrolytes were 0.1 M ammonia, Briton and Robinson buffer and tetrabutylammonium hydroxide solution.

A 1.0 g amount of cosmetic samples was accurately weighed into a 50 mL beaker, 10 mL of methanol were added and the beaker was heated to 40 °C in a water-bath with stirring until sample dissolution was complete. After cooling and centrifugation, the supernatant was transferred into a 25 mL calibrated flask and made up to volume with dimethylformamide. In order to obtain calibration plots for the zinc pyrithione, 25 mL of supporting electrolyte were pipetted into a voltammetric cell and deaerated with nitrogen for 4 min before voltammetric measurement. By micropipette, aliquots of 1000 mg L^{-1} ZPT solution were added. After each addition voltammograms were obtained; the solution de-aerated for 2 min after each addition before obtaining the voltammogram. Quantative analyses were performed in the differential pulse mode. The potential was set at 0.2 to 0.85 V vs. SCE. The pulse height was 50 mV and the scan rate 4 mV s^{-1} with a drop time of 1.0 s. For sample solution analysis, 1 mL of the solution was pipetted into a 25 mL calibrated flask and diluted to volume with tetrabutylammonium hydroxide solution. This solution was analyzed by DPV using the same condition as for the calibration plot.

Determination of ZPT by HPLC: Stock solution of standards were prepared by dissolving the appropriate amount of ZPT in chloroform and methanol (95 : 5, v/v). A set of standard solutions were produced by diluting aliquots of the stock solutions with chloroform and methanol to 10 mL in calibrated flasks. Taking into account the content of ZPT in the sample, about 0.15–0.50 g of the latter were weighed accurately in a 50 mL beaker, diluted to about 10 mL with methanol and 15 mL buffer solution (0.1 M citric acid and 0.2 M disodium hydrogenphosphate, pH 5.0), dissolved and centrifuged. The supernatant was transferred into a 50 mL beaker and added 6 mL of 1 M copper(II) sulfate solution. The mixture was shaken vigorously for 10 min and centrifuged for 10 min at 1500 rpm. An aliquot of the solution was filtered through a 0.454μm and 0.20 μm membrane filter prior to HPLC analysis. A μ-Bondapak C_{18} (particle size 10 μm, 150 mm × 3.9 mm i.d.) was used for reverse-phase HPLC. The mobile phase was methanol-water (3 : 2) at a flow rate of 1.0 mL/min, the UV detector was at 320 nm. By means of the injection value, 25 μL of the prepared sample solution and standard solution were chromatographed under the operating conditions described above. Quantitation was based on the peak area of the sample.

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References

[1] J.D. Nelson, G.A. Hyde, *Cosm. & Toil*. **1981**, *96*, 87.
[2] A. Babar, C. Kawilarang, A.J. Cutie. F.M. Plakogiannis, *Drug Devel and Indus. Pharm*. **1985**, *11*, 1507.
[3] Jon. J. Kabara, *Cosmetic and Drug Preservation Principles and Pratices*, Marcel Dekker **1984**, p. 117.
[4] N. De Kruijf, M.A.H. Rijk, L.A. Pranoto-Soetardhi, A. Schouten, *J. Chromatogr*. **1987**, *410*, 395.
[5] T. Okumura, S. Hayashi, F. Tokiwa, S. Horin, *Cosmet. Perfum*. **1975**, *90*, 101.
[6] G.A. Nolen, L.F. Patrick, T.A. Dierckman, *Toxicol. Appl. Pharmacol*. **1975**, *31*, 430.
[7] C.D. Klaassen, *Toxicol. Appl. Pharmacol*. **1976**, *35*, 581.
[8] J.H. Wedig, G.L. Kennedy, D.H. Jenkins, R. Henderson, M.L. Keplinger, *Toxicol. Appl. Pharmacol*. **1976**, *36*, 255.

[9] M.D. Adams, J.H. Wedig, R.L. Jordan, L.W. Smith, R. Henderson, J.F. Borzelleca, *Toxicol. Appl. Pharmacol*. **1976**, *36*, 523.
[10] J.H. Wedig, C. Mitoma, R.A. Howd, D.W. Thomas, *Toxicol. Appl. Pharmacol*. **1978**, *43*, 373.
[11] W.B. Gibson, G. Calvin, *Toxicol. Appl. Pharmacol*. **1978**, *43*, 425.
[12] G.G. Cloyd, M. Wyman, J.A. Shadduck, M.J. Winrow, G.R. Johnson, *Toxicol. Appl. Pharmacol*. **1978**, *45*, 771.
[13] A.R. Jeffcoat, W.B. Gibson, P.A. Rodriguez, T.S. Turan, P.F. Hughes, M.E. Twine, *Toxicol. Appl. Pharmacol*. **1980**, *56*, 141.
[14] I.K. Genji, O.M. Kikuhiko, *J. Soc. Cosmet. Chem*. **1983**, *34*, 1.
[15] A.B.G. Lausdown, *Fd. Chem. Toxi*. **1991**, *29*, 57.
[16] N.P. Skoulis, S.J. Barbee, *J. Appl. Toxicol*. **1993**, *13*, 283.
[17] S. Oliveri-Vigh, H.L. Karageozian, *Anal. Chem*. **1976**, *48*, 1001.
[18] R.T. Brooks, P.D. Sternglanz, *Anal. Chem*. **1959**, *31*, 561.
[19] M.D. Seymour, D.L. Bailey, *J. Chromatogr*. **1981**, *206*, 301.
[20] H. Cheng, R.R. Gadde. *J. Chromatogr*. **1984**, *291*, 434.
[21] D. Valdez, J.C. Reier, *J. Lig. Chromatogr*. **1987**, *10*, 2133.
[22] Y.H. Kondoh, S.S. Takand, *J. Chromatogr*. **1987**, *408*, 255.
[23] R.J. Fenn, M.T. Alexander, *J. Lig. Chromtogr*. **1988**, *11*, 3403.
[24] N. Dekruijf, A. Schouten, M.A.H. Rijk, L.A. Pranoto-Soetardhi, *J. Chromatogr*. **1989**, *469*, 317.
[25] N.J. Keiko, Y.U. Toshiko, *J. Chromatogr*. **1990**, *502*, 379.
[26] N. Ferioli, C. Rustichelli, F. Vezzalini, G. Gamberini, *Chromatographia* **1995**, *40*, 669.
[27] D.A. Csejka, S.T. Nakos, E.W. Bubord, *Anal. Chem*. **1975**, *47*, 322.
[28] J.T. Stock, R.E. Larsn. *Anal. Chim. Acta* **1982**, *138*, 371.
[29] J.M. Fernandez-Alvarez, M.R. Smyth, *Analyst* **1989**, *114*, 371.
[30] I. Pardo, M. Angulo, R.M. Galvin, J.M. Rodriguez Mellado, *Electro. Acta* **1996**, *41*, 133.
[31] S.J. Dong, T. Kuwana, *Yingyong Huaxue* **1985**, *2*, 34.
[32] I. Lingvay, I. Galasiu, R. Galasiu, *Rev. Roum. Chim*. **1994**, *39*, 861.
[33] Z. Chen, *Yingyong Huaxue* **1994**, *11*, 33.
[34] Q.G. Mao, S.G. Wu, H.C. Zhang, *Fenxi Huaue* **1995**, *23*, 648.
[35] R. Greef, R. Peter, L.M.D. Pletcher, J. Robinson, *Instrum. Meth. Electrochem*., Ellis Horwood, Chichester **1985**, p. 231.
[36] A.J. Bard, L.R. Faulkner, *Electrochem. Meth. Fundamentals and Applications*, Wiley, New York **1980**, p.138.
[37] J.A. Plambeck, *Electroanalytical Chemistry Basic Principal and Application*, Wiley, New York **1982**, p. 347.
[38] D.K. Gosser, Jr., *Cyclic Voltammetry*, VCH, Weinheim **1993**, p. 57.
[39] A.M. Bond, *Modern Polarographic Methods in Analytical Chemistry*, Marcel Dekker, New York **1980**, p. 186.