

Voltammetric Determination of Sunscreen by Convenient Epoxy-Carbon Composite Electrodes

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ABSTRACT

An electrode composed of an epoxy resin and graphite powder is fast and convenient to fabricate. The performance as a working electrode for cyclic voltammetry measurement of hexacyanoferrate(III) in aqueous and nonaqueous systems is compared with a paraffin carbon paste electrode. Well defined current-potential curves, and well linearity of current-root scan rate and current-concentration system are reported. The electroanalytical studies of the octyl methoxycinnamate, oxybenzone, benzophenone, octyl salicylate, and butyl methoxy dizenzoyl methane, that are often used as sunscreens in commercial cosmetic products, were described at the carbon-epoxy composite electrodes in nonaqueous solvent.

Key words: carbon-epoxy, composite electrode, nonaqueous solution, sunscreens, cyclic voltammetry(CV), differential pulse voltammetry (DPV)

INTRODUCTION

Carbon-based electrodes have been extensively developed and applied for a long time in various electroanalytical regions^(1,2). Usually, the carbon-based composite electrodes are prepared by one of the following procedures: (1) thermomoulding of a homogenized mixture of solid powders^(3,4); (2) compressing a homogenized mixture of solid powders⁽⁵⁾; (3) in-situ polymerization of the monomer properly mixed with carbon, such as carbon-epoxy composites⁽⁶⁾; (4) liquifying by heating the filler, dispersing carbon homogeneously and solidifying the mixture by cooling, such as carbon-paste(wax) composites⁽⁷⁾; and (5) dissolving the polymer in a suitable volatile organic liquid, dispersing carbon thoroughly and allowing the mixture to dry. As is evident, the common factor in all these preparation procedures is how to conveniently construct a homogenous solid composite electrode with high mechanical strength and high compatibility.

Among carbon-based electrodes, carbon pastes are convenient and often used as working electrodes for voltammetric and amperometric measurements because of their attractive properties⁽⁸⁻¹⁰⁾. From an analytical point of view, these electrodes exhibit rather low background currents over a large range of potentials when compared with other solid electrodes, and offer a renewability of their surface as well as a high versatility and simplicity of modification. However, it is also well known that carbon paste electrodes (CPEs) suffer from practical difficulties mainly related to a lack of mechanical and physical stability under hydrodynamic conditions. Additionally, the pastes are dissolved by some non-aqueous solvents, leading to a deterioration of the signal.

Because of their high mechanical strength and high compatibility with non-aqueous solvents, various combinations of carbon and epoxy resin have been used for fabricating conventional or micro sized composite electrodes or biosensors⁽¹¹⁻¹⁷⁾. However, their preparations in most reports require a long period of curing of the epoxy resin from overnight to a week, which is a serious drawback for re-preparation and stability of electrodes, especially in the preparing of biosensors. Nowadays, some commercial products of epoxy resin have been produced for fast curing. These epoxy resins have been suggested as a way to improve the lack of longtime curing for constructing carbon-epoxy composite.

These hydrophobic compounds are widely used in cosmetics as sunscreens. In particular, octyl methoxycinnamate, benzophenone, octyl salicylate, and butyl methoxy dizenzoyl methane are often used in commercial cosmetics. Most of these sunscreens contain the function groups of electroactivity such as the groups of hydroxyl, carbonyl, methoxyl, etc, but electroanalytical studies have not been reported on carbon-based electrodes.

This article reports a method for preparing carbon-epoxy composite electrodes using a fast curing epoxy resin, which aims simply and quickly provide more convenient preparation and gives satisfactory voltammetric characteristics. The voltammetric characteristics of the carbon-epoxy composite electrodes were compared with a carbon paste electrode using paraffin as binding agent, and a commercial glassy carbon electrode in aqueous and nonaqueous solvent. The chronoamperometric characteristics presented in a flow injection analysis system (FIA) with a thin-layer flow cell was consistent with the working electrode of carbon-epoxy composite electrode. The electroanalytical detection of the above-mentioned sunscreens is described at the carbon-epoxy composite electrodes in nonaqueous solvent.

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MATERIALS AND METHODS

I. Reagents

Tetrabutyl-ammonium perchlorate (TBAP), potassium nitrate, nitric acid, acetonitrile (HPLC grade), and octyl salicylate were purchased from Sigma-Aldrich (Madrid, Spain). Potassium hexacyanoferrate (III), dimethyl sulfoxide and N,N-dimethylformamide (A.C.S. reagent) were purchased from Tedia (Ohio, USA). Benzophenone, octyl methoxycinnamate, and oxybenzone were purchased from TCI (Tokyo Chemical Industry, Japan). Methoxy dizonoyl methane was purchased from Roche (Singapore). Epoxy resin (AB glue) was obtained from Red Mount Ent Co., Ltd. All other chemicals were of analytical-reagent grade or HPLC grade, except for benzophenone, octyl methoxycinnamate, and butyl methoxy dizonoyl methane. Cosmetic formula which contain 5% Kowax, 1% stearic acid, 1% cetyl alcohol, 3% sorbitol, 0.3% uniphen P-23, 0.3% unicide U-13, 0.5% lipo320, 1% glycolic acid, 2% mineral oil, and 85.9% (w/w) H₂O was formulated in our laboratory. These cosmetic raw materials were obtained from Lipo (USA). Distilled deionized water with a 17.5 M Ω -cm resistance at room temperature was used throughout.

II. Apparatus

A Princeton Applied Research Model 263 Potentiostat/Galvanostat was used in the Cyclic Voltammetry (CV) and

Differential Pulse Voltammetry (DPV) modes. Voltammetric measurements were performed using a platinum counter electrode, an Ag/AgCl reference electrode purchased from Metrohm and various carbon-based working electrode such as the epoxy-carbon, carbon paste or a glassy carbon disk (5 mm diameter). Anatomic micrographs were made with using a Stemi2000-C apparatus from Zeiss. A scanning electron micrograph was made with using an Zel-840 apparatus from Hitachi, operated at 20 kV.

III. Electrode Preparation

Graphite powder (180 mg) and epoxy resin of A (12 mg) were mixed thoroughly for 2 min, then epoxy resin of B (12 mg) was added to the composite and mixed thoroughly for 1 min. A part of the epoxy-carbon resin was pressed manually into the electrode cavity (5 mm diameter, 2 mm depth) in a PP holder and was then smoothed against a clean flat glass until a flat surface was obtained. The electrode was cured at room temperature for 30 min. Electrical contact to the cured epoxy-carbon was made by pressing a copper o-ring (5 mm o.d., 1 mm i.d., and 2 mm thickness) with connecting copper wire before pressing epoxy-carbon resin. The electrode face was polished with a 0.5 μ m alumina slurry and then washed with a stream of deionization water. Electrodes fabricated in this manner typically had resistance of approximately 25 Ω . Carbon paste electrodes were prepared by manually pressing the carbon paste (90% graphite and 10% paraffin by weight) into the PP holder as above described and the surface was

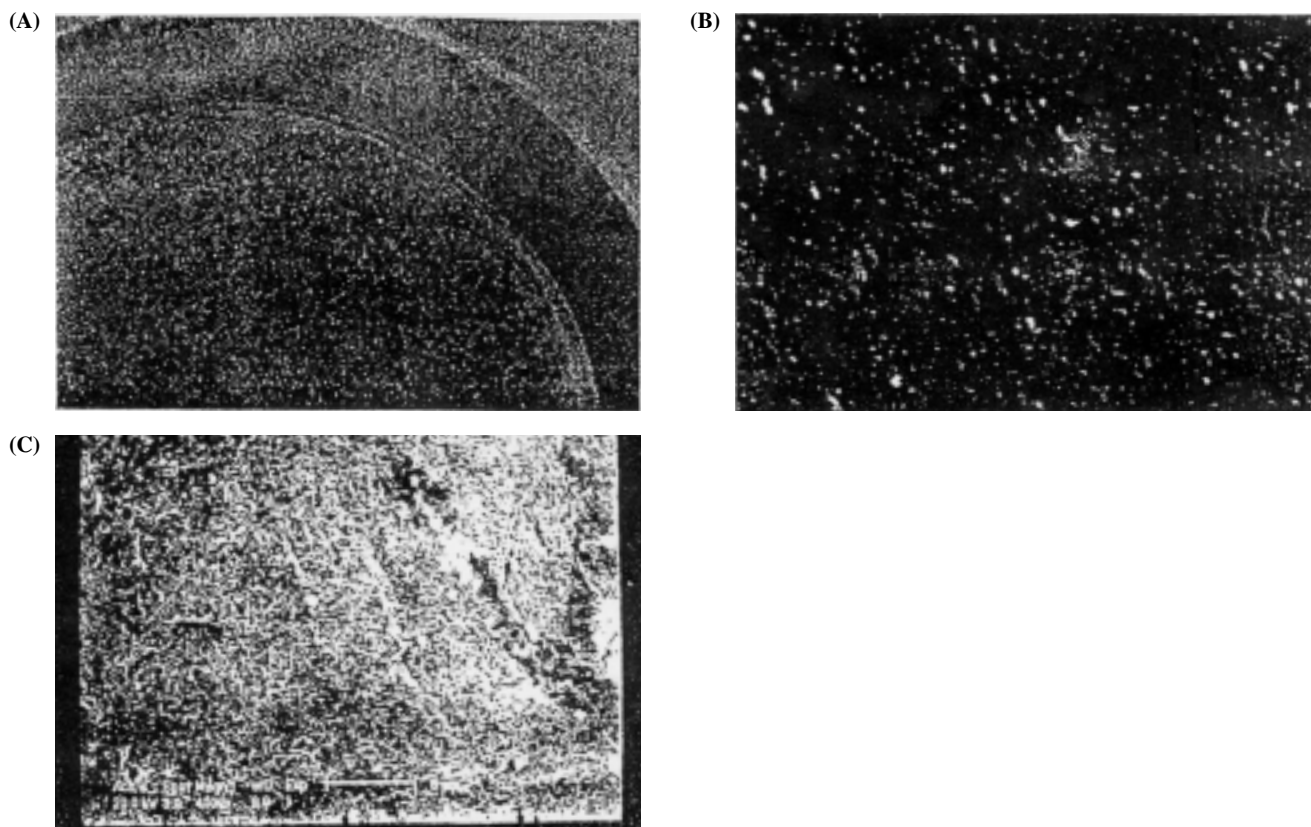


Figure 1. (A) 12 multiple; (B) 25 multiple micrography; (C) scanning electron micrography of epoxy-carbon composite.

smoothed by a weight paper. This fabricated composite had a resistance of approximately 40Ω .

IV. Sample Preparation for Recovery Study

A 9.7 g sample of cosmetic formula, which does not contain sun-screen agent, was placed into a 50 mL beaker. To the cosmetic formula was added 0.30 g sun-screen agent. The mixture was allowed to sit at room temperature for 1 h. A 0.5 g sample of mixture was placed into a centrifuge tube and 5 mL of methanol was added and oscillated for 15 min with an ultrasonic oscillator. The sample and extractant was left together for 10 min, and then centrifuged at room temperature, 4300 rpm for 5 min. The extractant was filtered through a $0.45\ \mu\text{m}$ membrane. A volume of 1.0 mL of the solution was diluted to 10.0 mL in a volumetric flask with supporting electrolyte.

RESULTS AND DISCUSSION

I. Characteristics of the Prepared Composites

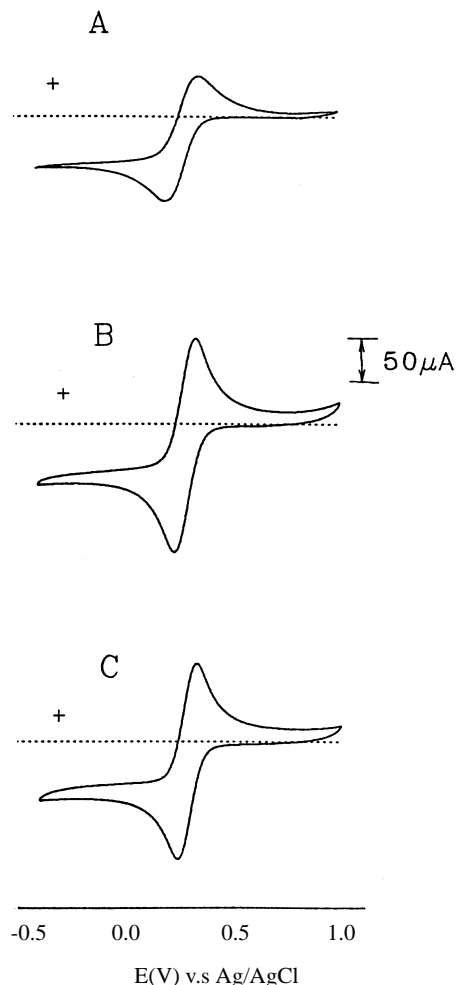


Figure 2. Cyclic voltammograms obtained by using (A) carbon-paste electrode; (B) epoxy-carbon electrode; (C) glassy-carbon electrode in 5 mM hexacyanoferrate(III)/0.1 M KNO_3 /0.01 M HNO_3 aqueous solution.

An epoxy proportion higher than 13% produces a high electrical resistance ($>150\Omega$) for the composite electrode, but lower amounts of epoxy greatly decreases the compactness grade and results in an easily breakable electrode. After the compression step and 30 minutes for curing, the obtained composite electrode showed a very high mechanical strength and a proper electrical resistance (lower than 25Ω). Figure 1 shows the scanning electron micrograph of the surfaces of an epoxy (11.7%)-carbon composite electrodes. The homogeneous surface of the composite can be observed.

II. Cyclic Voltammetric Behavior in Aqueous and Nonaqueous Solutions

The voltammetric response of epoxy-carbon composite electrodes for hexacyanoferrate(III) in various solutions was compared with carbon paste electrodes and commercial glassy carbon electrodes. The measured voltammograms are shown in Figures 2 and 3.

Figures 2 and 3 show the cyclic voltammograms recorded at above three carbon-based electrodes in aqueous and organic (DMSO) solutions, respectively. The background current-potential curves (not shown in this paper) were obtained in an aqueous solution of 0.1M KNO_3 /0.01M

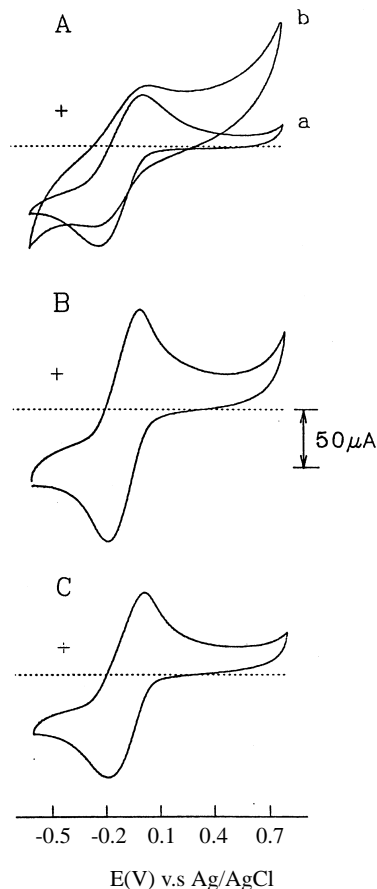


Figure 3. Cyclic voltammograms obtained by using (A) carbon-paste electrode [a] new electrode surface; [b] after used a half hour in DMSO; (B) epoxy-carbon electrode; (C) glassy-carbon electrode in 5 mM hexacyanoferrate(III)/0.1 M KNO_3 /0.01 M HNO_3 in DMSO solution.

HNO₃. The epoxy-carbon electrode exhibits a lower residual current as compared to that of the glassy carbon, but it is slightly higher than that of the carbon paste. The overall potential window of the epoxy-carbon electrode (about 1.6V) agrees well with those reported for most carbon-based electrodes^(1,2). In addition, background current-potential curves were obtained in a DMSO solution of 0.1M KNO₃/0.01M HNO₃. A new carbon paste electrode exhibits a lower residual current than other electrodes. However, after used in a DMSO solution for a half hour, the carbon paste electrode exhibits higher residual current and more narrow potential window as compared to other electrodes. Epoxy-carbon and glassy carbon electrodes offer good reproducibility after used in a DMSO solution for two months. It is quite obvious that the carbon paste electrode exhibits poor reproducibility because the wax in the carbon paste was dissolved in DMSO solution. This effect was also observed in other organic solutions such as acetonitrile and DMF.

The studied redox systems in aqueous and organic (DMSO) solutions are recorded in Figures 2 and 3, respectively. The epoxy-carbon composite electrode in the aqueous system exhibited a good reversible redox's reaction of Fe(CN)₆³⁻/ Fe (CN)₆⁴⁻ since lower peak separation value (ΔE_p) and few different values of anodic (i_{pa}) and cathodic (i_{pc}) peak currents ($i_{pa} / i_{pc} \approx 1$) in magnitude were obtained. In

DMSO solution, the epoxy-carbon electrode exhibits a slightly lower ΔE_p and higher peak currents as compared to that of the glassy carbon and carbon paste electrode. However, ΔE_p values obtained in organic solution were more separated than those obtained in aqueous for three carbon-based electrodes. The higher ΔE_p in organic solution than in aqueous suggests that the lower dielectric constant can result the worse reversible redox's reaction of Fe(CN)₆³⁻/ Fe (CN)₆⁴⁻ in organic solution. In Figure 3(A-b), the CV's plot exhibited the poor redox's reaction of Fe(CN)₆³⁻/ Fe (CN)₆⁴⁻ since wax in the carbon paste electrode was dissolved in DMSO solution .

III. Kinetics and Sensitivity of Epoxy-Carbon Electrode

CV studies of hexacyanoferrate(III) in different solutions using the epoxy-carbon electrode was recorded. Figure 4 shows the result in aqueous solution, but the result in DMSO solution is not shown in this text. The results showed linear dependencies of anodic and cathodic peak currents with the root of scan rate, $r = 0.9999$ and 0.9998 in aqueous solution (in Figure 4B), and $r = 0.9991$ and 0.9987 in DMSO solution. In addition, the results showed linear dependencies of anodic and cathodic peak currents with the concentration, $r = 0.9991$ and 0.9993 in aqueous solution (in Figure 4D), and

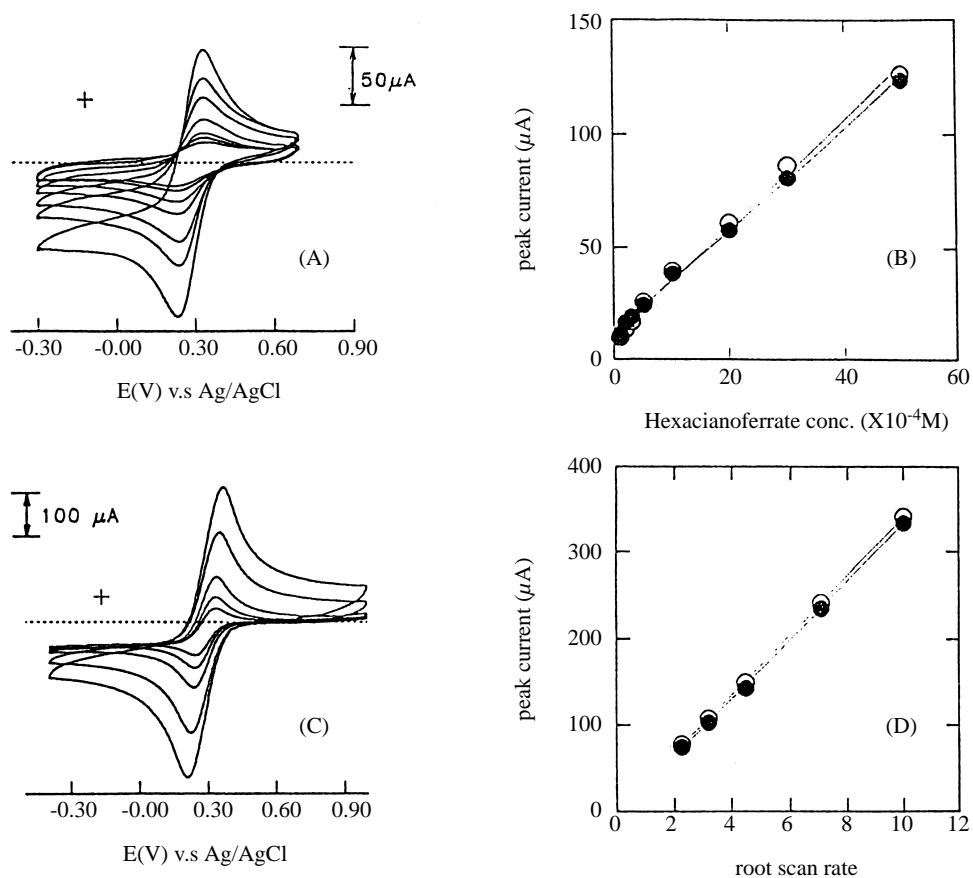


Figure 4. Cyclic voltammograms obtained by using epoxy-carbon composite electrode at various concentrations of hexacyanoferrate(III) from 0.1 to 5 mM in 0.1 M KNO₃/0.01 M HNO₃ aqueous solutions and the scan rate of 20 mV/s (A); peak current–concentration dependence (B). Cyclic voltammograms of 5 mM hexacyanoferrate(III) in 0.1 M KNO₃/0.01 M HNO₃ aqueous solutions at scan rate from 5 to 100 mV/s (C); peak current–root of scan rate dependence (D).

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$r = 0.9997$ and 0.9989 in DMSO solution. The calibration sensitivity of concentration was about $(2.37 \pm 0.05) \times 10^4$ $\mu\text{A}/\text{M}$ in aqueous solution, and $(3.30 \pm 0.08) \times 10^4$ $\mu\text{A}/\text{M}$ in DMSO solution. In the above cases, the linear relationships were not obviously affected by the direction of changes in concentration or sweep rate, indicating the low interaction of reactants with the electrode surface. Finally, a low variability was observed in the response of the epoxy-carbon composite electrode, even after the simple pretreatment was employed, giving relative standard deviation (RSD) values of measured peak current lower than 8% in three replicated experiments. These results indicate that the epoxy-carbon composite electrode is a convenient as a working electrode in an aqueous system. In addition, it is a more convenient application in an organic solvent system than the carbon paste electrode.

IV. Detection of Sunscreen at Epoxy-Carbon Composite Electrodes

Cyclic voltammetry (CV) was applied at the epoxy-carbon composite electrode for sunscreens tested. Most sunscreens which are widely used in cosmetics are hydrophobic compounds. With the aim of easier dissolution and mixing of sunscreens, a simple organic working medium (0.1M tetrabutyl ammonium perchlorate in DMSO) is used. Figure 5 shows the corresponding cyclic voltammograms of five sunscreens, often added in commercial cosmetic products. These cyclic voltammograms of sunscreens indicated that all sunscreens have good characteristics of electroactivity in the potential window. In cyclic voltammograms, the first cathodic peak for oxybenzone, octyl methoxycinnamate, octyl salicylate, butyl methoxyl dibenzoylmethane, and benzophenone

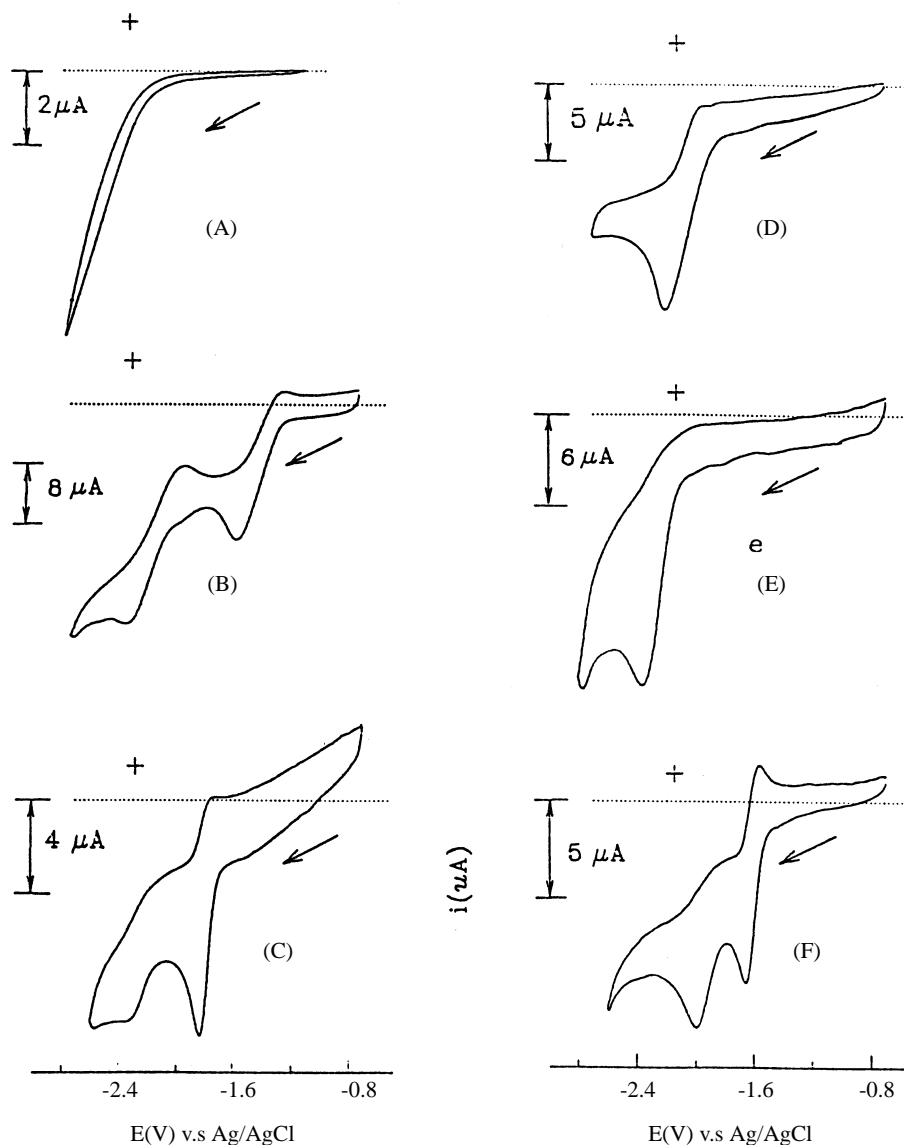


Figure 5. Cyclic voltammograms of the blank solution (A); 200 ppm oxybenzone (B); octyl methoxycinnamate (C); octyl salicylate (D); butyl methoxyl dibenzoylmethane (E); benzophenone (F) obtained by using the epoxy-carbon composite electrode in the blank solution of 0.1 M tetrabutyl ammonium perchlorate in DMSO solution and scan rate 20 mV/s.

were recorded at -1.52V , -1.84V , -2.18V , -2.36V , and -1.62V , respectively. The results indicated that the cathodic reaction of electroactive function groups contained in the sunscreens did occur. Less cathodic potential for the reduction of carbonyl group with diphenyl groups in oxybenzone and benzophenone was reasonable due to the effect of continuous α,β -resonance⁽¹⁸⁾.

The detection of sunscreens was studied at the epoxy-carbon composite electrode using differential pulse voltammetry (DPV). Figure 6 shows the corresponding differential pulse voltammograms of the octyl salicylate in various concentrations from 10 ppm to 500 ppm. The cathodic potential of the octyl salicylate was recorded at -2.15V . The linear dependencies of cathodic peak currents with the concentration was obtained ($r = 0.999$) and the calibration sensitivity of concentration was about $7.2 \pm 0.3 \text{ nA/ppm}$. From other differential pulse voltammograms of oxybenzone, octyl methoxycinnamate, butyl methoxyl dibenzoylmethane, and benzophenone (not shown in this paper), the cathodic potentials were also recorded at -1.48V , -1.92V , -2.23V , and -1.63V , respectively. They are satisfied with the cathodic potential obtained from the cyclic Voltammograms. The linear correlation coefficients were in 0.996, 0.999, 0.991, and 0.998, respectively, and the calibration sensitivity of concentration were about $16.2 \pm 0.5 \text{ nA/ppm}$, $79.8 \pm 0.9 \text{ nA/ppm}$, $3.5 \pm 0.2 \text{ nA/ppm}$, and $8.4 \pm 0.4 \text{ nA/ppm}$, respectively.

The simultaneous detection of mix-sunscreens was also studied. Figure 7 shows the corresponding voltammograms of mix-sunscreens of oxybenzone, and octylmethoxycinnamate in various concentration from 50 to 200 ppm. The simultaneous detection of mix-sunscreens was achieved from the good separation of cathodic potential. The results show the linear relationship between cathodic peak and concentration ($r > 0.996$), and similar calibration sensitivity to the detection of mono-sunscreen.

Recovery studies were performed by adding 3% (w/w)

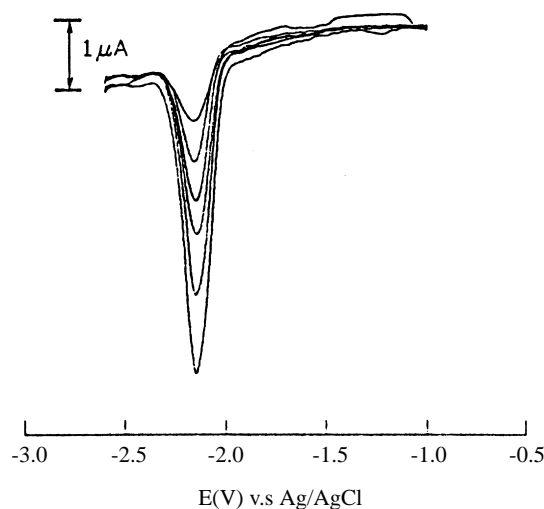


Figure 6. Differential pulse voltammograms of different concentration octyl salicylate from 10 to 500 ppm obtained by using the epoxy-carbon composite electrode in the 0.1 M tetrabutyl ammonium perchlorate in DMSO solution and scan rate 20 mV/s.

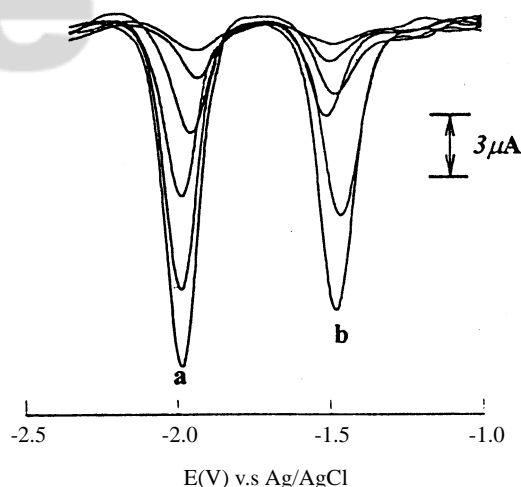


Figure 7. Differential pulse voltammograms obtained using the epoxy-carbon 50 to 200 ppm of the mixture of octyl methoxy-cinnamate and oxybenzone in the 0.1 M tetrabutyl ammonium perchlorate in DMSO solution and scan rate 20 mV/s.

mono-sunscreen in the concentration range of a typical preparation to the cosmetic formula, respectively. The results of the analysis were calculated using the standard addition method. The precision of this method calculated as the RSD of the recoveries ($n = 3$) was smaller than 3.5 % for five sunscreens. Nevertheless, the accuracy of the recoveries was satisfied only with compounds of octyl salicylate (95.5%) and benzophenone(97.3%), in fact with oxybenzone(86.3%), octyl methoxycinnamate (82.7%), and butyl methoxyl dibenzoylmethane (73.8%), it ranged between 73% and 86%. In order to overcome the problem due to a incomplete recovery from the cosmetic formula, we are studying many changes in the extraction mixture, such as changes in buffer composition and ionic strength and change of organic solvent.

CONCLUSIONS

Epoxy-carbon composite electrodes potentially seem to have a high analytical applicability, not only as a working electrode for voltammetry in aqueous and organic systems, but also as an indicator electrode for amperometry in a flowing system. This is due to their suitability for the same electroanalytical application as other carbon -based electrodes, their high mechanical strength, and the simplicity of the electrode preparation and surface regeneration. Finally, the simple procedure of the electrode preparation allows other species to be added easily to construct various modified electrodes. However, it is necessary to research extensively in the application of real sample analysis, because many influences such as efficiency of extraction, coexisting and interferences may be serious and complicated.

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以環氧-碳組成電極伏特安培法測定防晒成份

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摘 要

利用 $\text{Fe}(\text{CN})_6^{3-}$ 測試快速製備的環氧-碳改良電極的電化學性質並與碳糊電極比較其偵測性能。測試結果顯示該環氧-碳電極具有好的可逆性伏特安培關係以及電流對掃描速率 $1/2$ 次方的直線性關係。甲氧肉桂酸辛酯 (octyl Methoxycinnamate)、二-氫氧基,4-氯-雙苯甲酮 (Oxybenzone)、雙苯甲酮 (Benzophenone)、水楊酸辛基酯 (octyl salicylate) 及 4, 4'-正丁基-甲氧基二苯甲酮基甲烷 (4, 4'-n-Butyl Methoxy Dibenzoylmethane) 是防晒化妝品重要防晒成份，我們也利用此種電極來測定這些成份在非水溶液中的電化學行為。並顯示具有好的線性檢量線。

關鍵詞：碳-環氧，組成電極，非水溶液，防晒成份，循環伏特安培法，差式脈波伏特安培法