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Arbutin Flow-Injection Analysis Using a Printed Circuit-Board Waste Modified Screen-Printed Electrode

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A copper-metal enriched printed-circuit board waste modified screen-printed electrode has been demonstrated for the sensitive electroanalysis of a tyrosinase biosynthesis-inhibiting cosmetic agent, arbutin by flow-injection analysis.

Arbutin (4-hydroxyphenyl β-D-glucopyranoside, Fig. 1A) is the most competitive cosmetic skin-lightening agent used in the 21st century. The hydroquinone formed in the intermediates upon arbutin sunlight exposure serves as an inhibitor to cellular tyrosinase production, and in turn to control of skin-melanin biosynthetic activities.[1–3] Inhibitory compound/s not only act as a skin-lightening agents, but also as a remedy for disturbances in hyperpigmentation, such as melasma, lentigo, and melanosis.[4,5] Arbutin containing a natural resource, *Bearberry leave* is used as a drug for urinary-track infections.[6] Furthermore, arbutin is also used as an antioxidant for some food and pharmaceutical products.[7,8] Thus, arbutin detection and determination are potentially important in cosmetics, phamaceutical and cellular mechanistic studies. Most of the existing methods were oriented only with the UV absorption method.[9] Our group recently reported square-wave voltammetric (SWV) determination of arbutin on a clay-modified screen-printed electrode (SPE).[10] In this report, we introduce a new flow injection analysis (FIA) method using copper-enriched printed circuit board (Cu_{PCB}) waste modified disposable screen-printed electrode (designated as Cu_{PCB}/SPE) for sensitive arbutin analysis in skin-lightening cosmetic products (gel and cream). Disposables of electronic waste products have been serious problem in industrialized countries like Japan, Taiwan, United States of America, and United Kingdom. In this report, we are introduce a new strategy for waste recycling to chemical sensor applications.

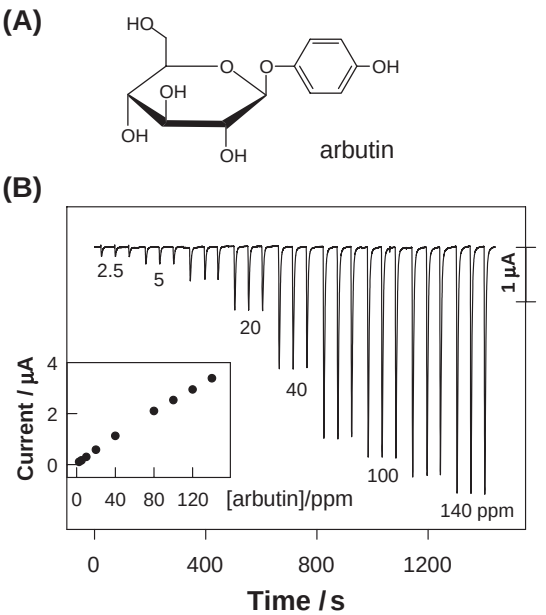

Fig. 1. (A) Chemical structure for arbutin. (B) FIA response of Cu_{PCB}/SPE with increasing standard [arbutin] using 0.1 M NaOH as a carrier solution at an applied potential of 0.6 V vs Ag/AgCl. Flow rate = 0.4 mL/min. Insert Fig. 1B is a plot of FIA's peak current against the [arbutin].

The printed circuit board (PCB) waste removed as an environmental pollutant from cleaning and surface preparation, electro-less copper plating, pattern printing, and etching etc processes were composed of copper as the major component; aluminium, lead, nickel, and chrome were minor elements along with other organic compounds.[11] After recovering some of the metal ions, the waste products were usually disposed of a cinder by pre-smelting it at $\sim$1200 °C in treatment plants. In this study, we utilized those waste cinders as an electrode material to prepare a Cu_{PCB}/SPE and for sensitive arbutin detection. Our initial cyclic voltammetric (CV) experiments of Cu_{PCB}/SPE in a potential window of -0.50 to $+0.65$ V vs Ag/AgCl with a 0.1 M NaOH solution didn't show any faradic response (data not enclosed). On the other hand, the Cu_{PCB}/SPE with a 100 ppm of arbutin showed a profound oxidation characteristic with a shoulder-like anodic peak at about 0.5 V vs Ag/AgCl due to the electrocatalytic function of the Cu_{PCB} system. The existence of a very low concentration of catalyst ([catalyst]) in the waste-matrix is a possible reason for the absence of any peak-like behavior of the Cu_{PCB}/SPE in the blank solution. Continuous CV experiments of the Cu_{PCB}/SPE didn't show any appreciable loss in the peak-current signals, while unmodified SPE yielded a feeble catalytic signal with unstable behavior. The catalytic function with the Cu_{PCB}/SPE was further utilized to the FIA for sensitive arbutin analysis.

The hydrodynamic FIA conditions were systematically optimized in the detection of a 50 ppm of arbutin concentration ([arbutin]) at Cu_{PCB}/SPE with a 0.1 M NaOH carrier buffer solution. The applied potential was 0.6 V vs Ag/AgCl and the flow rate was 0.4 mL/min. Figure 1B shows the typical FIA response for the increasing [arbutin] at Cu_{PCB}/SPE under the optimal working conditions. The calibration plot is linear over the range of 2.5–140 ppm with sensitivity and regression coefficient values of 0.024 μA/ppm and 0.99904, respectively. The

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Table 1. Arbutin Assays for Skin-Lightening Cosmetic Products Using Cu_{PCB}/SPE by FIA

Sample	[arbutin]/ppm				Recovery
	Found	Original	Standard	Detected after standard	
Gel (3%)	28.03	29.45 ± 0.14	20	49.79 ± 0.26	101.70 ± 1.49
			40	69.91 ± 0.09	101.15 ± 0.41
			60	88.25 ± 0.84	98.00 ± 1.41
Gel (2%)	18.36	18.34 ± 0.02	20	38.25 ± 0.17	99.55 ± 0.84
			40	57.91 ± 0.81	98.92 ± 2.03
			60	76.93 ± 0.75	97.64 ± 1.25
Cream (2%)	20.09	20.61 ± 0.29	10	31.48 ± 0.23	108.63 ± 1.83
			20	41.35 ± 0.20	103.67 ± 0.88
			40	60.82 ± 0.74	100.52 ± 1.33
Cream (2%)	37.48	39.42 ± 0.42	20	58.99 ± 0.15	97.88 ± 2.23
			40	77.27 ± 0.78	94.61 ± 2.21
			60	95.80 ± 0.55	93.96 ± 1.55

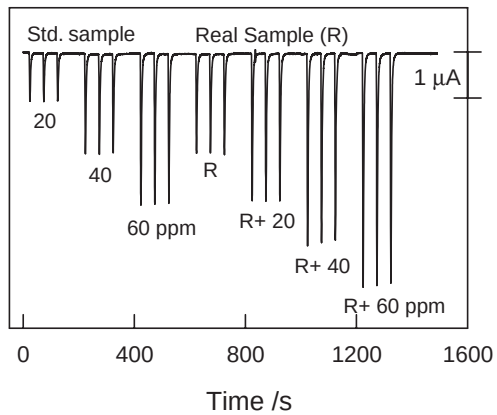

Fig. 2. FIA response of Cu_{PCB}/SPE for the real sample analysis of a skin-lightening cream (4th sample's data in Table 1). All other FIA conditions were as in Fig. 1B.

RSD value for 11 successive FIA injections of 10 ppm [arbutin] was 1.67%, which further indicates the appreciable reproducibility of the present electrode. The calculated detection limit, (D_L, S/N = 3) is 0.125 ppm (5 μL sample loop), which is very close to a D_L value of 0.44 ppm (i.e., 0.18 μM) at a clay-modified electrode by SWV using 10 mL as the working volume.[10] Figure 2 is the FIA response for a real sample (skin-lightening cream) by the standard-addition method. Table 1 summarizes real sample data for the arbutin in the cosmetic products (gel and cream). The calculated [arbutin] values (2nd column in the Table 1) are close to the FIA results. Meanwhile, the obtained recovery values falling in the window near to 100% indicate the excellent applicability of Cu_{PCB}/SPE to practical assays.

In conclusion, we have for the first time demonstrate an useful recycling procedure for printed-circuit board waste into a chemically modified screen-printed electrode and to a sensor application using a cosmetic skin-lightening sample arbutin, as a standard model. Since the approach is environmentally friendly, low cost, and moss-producible, the procedures can be expand to a wide variety of chemical sensor applications.

Experimental

The standard samples of arbutin and all supporting electrolytes in this study were purchased from Merck (Darmstadt, Germany). Copper-containing printed circuit board (PCB) waste material (Cu_{PCB}) was obtained from a local PCB manufacturing company, Hsin-chu. Electrochemistry was performed on a CHI 620A electrochemical workstation (Austin, TX, USA) with a SPE or Cu_{PCB}/SPE (working), Ag/AgCl (reference) and Pt (counter) electrode system. Disposable carbon SPE strips (0.196 cm^2) were purchased from Zensor R&D Taichung, Taiwan. Arbutin containing cosmetic products were obtained from a local shop. Weights of about 0.1–0.2 g of gel or cream with a dilution factor of 1000 were uniformly used in this study. Real samples were prepared by dissolving the products directly in the base electrolyte and for FIA analysis. The Cu_{PCB}/SPE was prepared as a follows: a mixture containing 0.09 g of carbon-ink + 0.01 g of Cu_{PCB} + 0.5 g of CH_2Cl_2 + 0.5 g of acetonitrile was first sonicated for about 30 min and then 4 μL of the mixture was dip-coated on a cleaned SPE. Finally, the electrode was dried at 70 °C for about 15 min in an oven.

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