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Determination of the Toxic Lead Level in Cosmetic-Hair Dye Formulations Using a Screen-Printed Silver Electrode

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A disposable-type screen-printed non-single crystal silver electrode (AgSPE) surface has been demonstrated for the sensitive and selective quantification of lead in cosmetic hair-dye formulations using its underpotential deposition (UPD-Pb) process.

Heavy metal lead (Pb) has a long history of use in cosmetic-hair dyes as a color additive. Studies have demonstrated that when human volunteers used a cosmetic-hair dye, lead-ion (as ~2% lead(II) acetate) was absorbed into the body and expected to cause adverse effects.[1–3] As instructed by the 21st US code of federal regulations, the Pb level should not exceed 0.6% (weight to volume) in cosmetic products. Hence, controlling and easy identification methods for the toxic heavy metal Pb in cosmetic products is of practical importance. Even though conventional Hg-based stripping voltammetric analysis has been promising,[4] the inherent health hazards of Hg poisoning restrict its use for further analytical assays. Zen et al. recently reported on disposable screen-printed silver electrodes (AgSPE) for the Pb under-potential deposition (UPD-Pb) process,[5] where a metal monolayer is plated onto a foreign substrate at a potential (E_{UPD}) more positive than the standard redox potential (E^{o}) of the bulk material (i.e., $E_{\mathrm{UPD}} - E^{\mathrm{o}} > 0$). It is noteworthy that most of the UPD-Pb process was operated with highly ordered single crystal surfaces, like Ag(100) and Ag(111),[6–8] that require a tedious and expensive preparation job. Alternatively, we have demonstrated an easy and a less-expensive AgSPE system for Pb(II) assays in cosmetic hair-dye samples by using a square-wave anodic stripping voltammetry (SWASV) method.

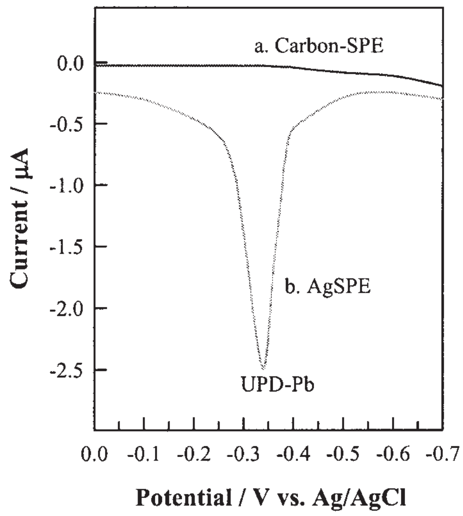

Fig. 1. SWV responses of 0.5 μM standard lead(II) acetate on (a) carbon-SPE and (b) AgSPE in pH 2, 0.05 M Na_2SO_4 solution. SWV parameters (optimal): SW frequency, 30 Hz; SW amplitude, 15 mV; step height, 5 mV. Preconcentration potential = −0.6 V vs Ag/AgCl at 60 s.

Figure 1 shows the SWASV (optimized) of 0.5 μM standard Pb(II) in pH 2, 0.05 M Na_2SO_4 solution at bare and Ag modified SPE surfaces after a pre-concentration process (−0.6 V vs Ag/AgCl for 60 s, were Pb(II) → Pb^0). As can be seen, no signal was observed on a bare carbon-SPE (Fig. 1a) whereas, a sharp increase was observed in the anodic stripping peak current at −0.34 V vs Ag/AgCl due to the selective UPD-Pb ($Pb^0 \rightarrow Pb(II)$) when the AgSPE modified system was used (Fig. 1b).[5] Note that the bulk deposition of Pb was normally stripped at >−0.45 V vs Ag/AgCl due to high over-potential problems.[6–8] Following is the possible mechanism:

$$\mathrm{AgSPE} + \mathrm{Pb(II)_{aq}} + 2e^- \rightarrow \mathrm{Pb^0}_{\mathrm{UPD}} - \mathrm{AgSPE}$$
$$\text{(deposition at } -0.6 \text{ V/60 s)}, \tag{1}$$

$$\mathrm{Pb^0}_{\mathrm{UPD}}\text{-}\mathrm{AgSPE} \rightarrow \mathrm{AgSPE} + \mathrm{Pb(II)_{aq}} + 2e^-$$
$$\text{(SWASV at } -0.34 \text{ V)}. \tag{2}$$

Investigated medium effects with different electrolytes and pH values (2–5) from the combinations of Na_2SO_4/H_2SO_4 and KNO_3/HNO_3 systems resulted in an optimal value for a pH 2 Na_2SO_4/H_2SO_4 solution (Fig. 2). It is obvious that Pb(II) salts derived from acetate and nitrate anions having higher soluble

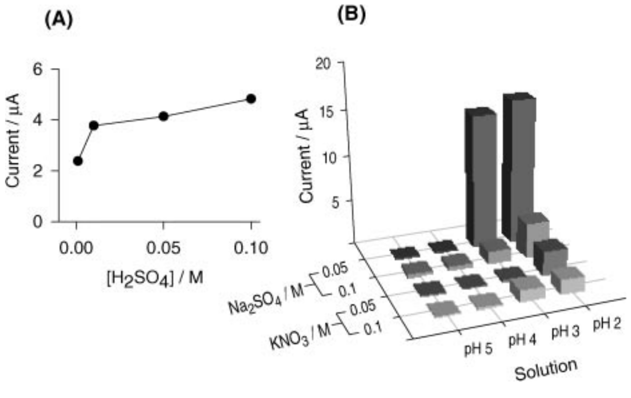

Fig. 2. Effects of base electrolytes using pure [H_2SO_4] (A) or different pH solutions from Na_2SO_4/H_2SO_4 and KNO_3/HNO_3 (B) systems for the detection of 0.5 μM Pb(II) acetate by SWV. Other conditions are the same as in Fig. 1.

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Table 1. Pb(II) Acetate Assays for the Different Cosmetic-Hair Dye Real Samples[a)] Using AgSPE

	Original value /nM[c)]	Spike /nM	Detected value after spike/nM	Recovery /%
Sample #1[b)]	102.06 ± 0.70	100	198.49 ± 0.82	96.43 ± 1.08
		200	300.74 ± 1.45	99.34 ± 0.81
Sample #2[b)]	101.83 ± 1.86	100	197.36 ± 0.52	95.53 ± 1.93
		200	298.11 ± 0.32	98.14 ± 0.94

a) 100 nM labeled (after dilution). b) Dilution factor of 1/264000. c) Determined from the UPD-Pb stripping current value at −0.34 V without any standard Pb(II) spike.

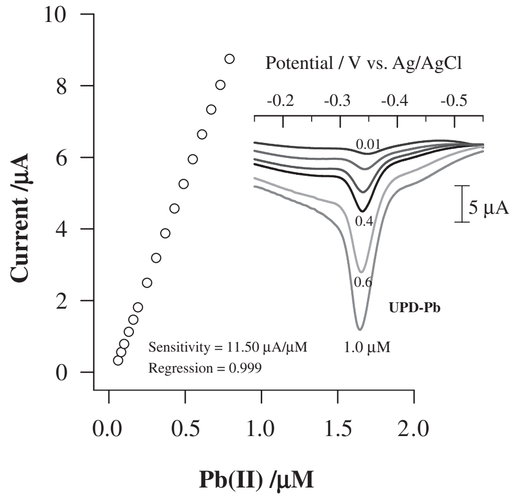

Fig. 3. Typical calibration plot for increasing concentrations of standard lead(II) acetate in pH 2, 0.05 M Na_2SO_4. SWV conditions are the same as in Fig. 1.

characteristic values of 60 g/100 g and 50 g/100 g in water respectively, while the Pb(II) sulphate shows poor solubility function ($K_{sp} = 1.6 \times 10^{-8}$ M),[9] beside the latter one yielded with a highly adhered film. The exact reason for the current maximum in pH 2/0.05 M solutions is presently unknown.

Under the optimal conditions, the Pb(II) calibration graph is linear from 0.06 to 0.79 μM with a slope (μA/μM), intercept (μA), and correlation coefficient of 11.50, −0.37, and 0.999, respectively (Fig. 3). The detection limit (3σ) is 0.31 nM, which is improved by 10 times compared to that given in recent reports based on organic systems modified by a carbon paste electrode for the determination of lead in water.[10,11] The interference effect was studied in the detection of 50 ppb of the standard Pb(II) with twice-excess concentration of Ti(IV), Mn(II), Ni(II), Cd(II), Cu(II), Zn(II), Hg(II), Tl(II), and Sn(IV), resulting in % alteration of 5, 4, 1, −4, −13, −6, −3, 1, and 9, respectively. Repetitive measurement-regeneration cycles ($n = 15$) for the 0.01, 0.08, and 0.4 μM lead(II) acetate resulted in coefficient variation of only 1.67%, 0.68%, and 0.33%, respectively.

The Pb(II) acetate in commercial hair dyes has been demonstrated as given in Table 1. Obvious and selective UPD-Pb signals were noted at −0.34 V for real hair-dye samples. Real diluted samples were spiked with standard lead(II) acetate solutions (100 and 200 nM) resulting in Pb(II) values of 102.06 and 101.83 nM. This is in agreement with the labeled values of 100 nM (calculated after dilution). The recoveries of lead acetate in the hair dyes were satisfactory with values ranging from 95.53% to 99.34% confirming that quantitative results can be obtained with this method. Finally, because of its stability, precision, and low cost, AgSPE is convenient for the routine analysis of Pb(II) in commercially available cosmetic hair dyes, and may also be possible with other real samples.

Experimental

The standard solution of lead(II) acetate and all supporting electrolytes in this study were obtained from Merck (Darmstadt, Germany). Electrochemistry was performed on a CHI 620A electrochemical workstation (Austin, TX, USA) with AgSPE (working), Ag/AgCl (reference), and Pt (counter) electrode system. Disposable AgSPE strips (0.196 cm^2, 0.47 ± 0.05 $\Omega\,cm^{-1}$) were purchased from Zensor R&D Taichung, Taiwan. 1% of lead(II) ion containing (as lead(II) acetate form) cosmetic products (Sample #1 and #2) were purchased from a local shop, which were additionally formulated with a skin moisturizing agent (lanoline), surfactant and other ingredients.

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References

1 A. B. G. Lansdown, *Int. J. Cosmet. Sci.*, **22**, 169 (2000).

2 F. N. Marzulli, P. M. Watlington, and H. I. Maibach, *Curr. Probl. Dermatol.*, **7**, 196 (1978).

3 "Lead Poisoning," ed by J. Breen and C. Stroup, Lewis Publishers, CRC Press, Boca, Raton, FL (1995).

4 G. Gillain, G. Duyckaerts, and A. Disteche, *Anal. Chim. Acta*, **106**, 23 (1979).

5 J.-M. Zen, C.-C. Yang, and A. Senthil Kumar, *Electrochim. Acta*, **47**, 899 (2001).

6 W. J. Lorenz, H. D. Hermann, N. Wuthrich, and F. Hilbert, *J. Electrochem. Soc.*, **121**, 1167 (1974).

7 R. R. Adzic, J. Wang, C. M. Vitus, and B. M. Ocko, *Surf. Sci.*, **293**, L876 (1993).

8 E. Herrero, L. J. Buller, and H. D. Abruña, *Chem. Rev.*, **101**, 1897 (2001).

9 D. Skoog, D. M. West and F. J. Holler, "Fundamentals of Analytical Chemistry," 7th edition, Saunders College Publishes, New York (1996).

10 M. F. Mousavi, A. Rahmani, S. M. Golabi, M. Shamsipur, and H. Sharghi, *Talanta*, **55**, 305 (2001).

11 T. H. Degefa, B. S. Chandravanshi, and H. Alemu, *Electroanalysis*, **11**, 1305 (1999).