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Detection of Toxic Heavy Metal, Co(II) Trace via Voltammetry with Semiconductor Microelectrodes

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The cobalt (Co(II)) ion is a main component of alloys and considered to be carcinogenic, especially due to the carcinogenic and toxicological effects in the aquatic environment. The toxic trace of the Co(II) detection was conducted using the infrared photodiode electrode (IPDE) using a working electrode, via the cyclic and square-wave anodic stripping voltammetry. The results indicated a sensitive oxidation peak current of Co(II) on the IPDE. Under the optimal conditions, the common-type glassy carbon, the metal platinum, the carbon paste, and the carbon fiber microelectrode were compared with the IPDE in the electrolyte using the standard Co(II). The IPDE was found to be far superior to the others.

***Key words*:** Infrared, Diode, Electrode, Anodic, Voltammetry, Trace cobalt (Co(II))

INTRODUCTION

In recent years, the intensive researches were directed towards the development of new organic materials for the organic light-emitting diodes (OLEDs), and substantial progress was achieved by using a variety of organic materials, meeting the chemical and physical requirements of the electroluminescent devices (1). Mid-infrared IR diode lasers have been widely used in the absorption experiments, particularly in molecular spectroscopy, the atmospheric measurements, and the kinetics (2), where the chelate-complexing agents of the P- or N-type semiconductor are the electron donors and acceptors. Therefore, the quasi-Fermi-level semiconductor can be used for the voltammetric electrode sensors. It has also been used for the trace gas analysis (3), the methane detection (4,5), the potassium (6), the atmospheric CH_4, H_2O (7), and the copper and cadmium ions (8). In this study, the photodiode was used as a working electrode, with promising results. Moreover, as cobalt ion shows hardness, strength, and abrasion resistance at the elevated temperatures, the automotive, aerospace, and arms industries are the prospective areas for its application. Co(II) is mostly used as a main component of the alloys and considered as a carcinogenic agent, which can be a possible cause of lung cancer (9). The possible human carcinogen (10) and the toxicological effects in the aquatic environment (11), due to its toxicity and utility, are important for the detection of cobalt. Thus, several methods of the cobalt detection have been developed, such as the precipitation method, the stopped-flow techniques, the CCD detection (12), the FT-IR studies (13), the resonance-ionization mass spectrometry (14), the ESI mass spectrometry (15), and the gas chromatography with the mass spectrometric detection (GCMS) (16). These methods are too complicated and time-consuming, whereas the voltammetric methods are simple and less time-consuming. The voltammetric methods have also been developed, such as those involving the use of the plated-lead-film electrode (17), the mercury film electrode (18), the bismuth film microelectrode (19), the platinum disc electrode (20), and the modified electrode with the hybrid hexacyanoferrates (21). These electrodes can detect the low cobalt concentrations. In this study, the IPDE was found to be more sensitive in terms of the cobalt detection and other toxic heavy metals (22,23).

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MATERIALS AND METHODS

Systems, reagents, and the electrode preparation. The IPDE was prepared with the SPI5342-H from the AUK

Semiconductor. A sensing range of 430 nm~1,050 nm with the wavelength of 950 nm and with the packing sizes of 4.8~5.5 mm was used as the audio control circuits. Regarding the photo diode, the forward and backward electrodes responded to the same results of the anodic or cathodic reactions. Electrochemical instruments were used with the new system of Bioelectronics-1, which was first constructed at the authors' institute.

Voltammetric property. Fig. 1A shows the cyclic voltammetry (CV) effect in the blank electrolyte and the 300-mg/L cobalt addition. With regard to the blank solution, the peak current did not have any signal. After the 300-mg/L cobalt was spiked, the peak current of 1.756×10^{-4} A was obtained with the −0.2 V oxidation and the −0.45 V reduction peak. Fig. 1B shows the four types of the common electrodes which were compared with the IPDE, the glassy carbon, the metal platinum, the carbon paste electrode, and the carbon fiber micro electrodes. Here, the peak current of the IPDE was highest and was sharpest among the electrodes. For this reason, the IPDE was chosen as a working electrode. Fig. 1C shows the concentration effects of the 0.5~10 mg/L Co(II) variation. The peak current increased from 0.1 to 0.3619×10^{-3} A, which can be used in the optimal parameters.

The square-wave optimized conditions. Fig. 2A shows the effects of the electrolyte pH variation on the peak current. From pHs of 2.92 to 10.98 the strengths were examined using the 0.1 M HCl and 0.1 M NaOH titrations. The peak current decreased from 3.042 to 1.556×10^{-3} A within the 2.97 pH~8.36 pH range, and it slightly increased to 1.566×10^{-3} A at 9.07 pH. It decreased again from 1.76 to 1.575 within the 10.1~10.98 pH range. As the maximum current was obtained at 2.97 pH, it was chosen as an optimum condition. Under the acidic conditions, the accumulation potentials were searched. Fig. 2B shows the results from the −100 to −800 V potential variation. The peak current decreased from 0.768 to 0.7389×10^{-3} A within the −100 V~−200 V, and increased from 0.7876 to 0.8313 ×

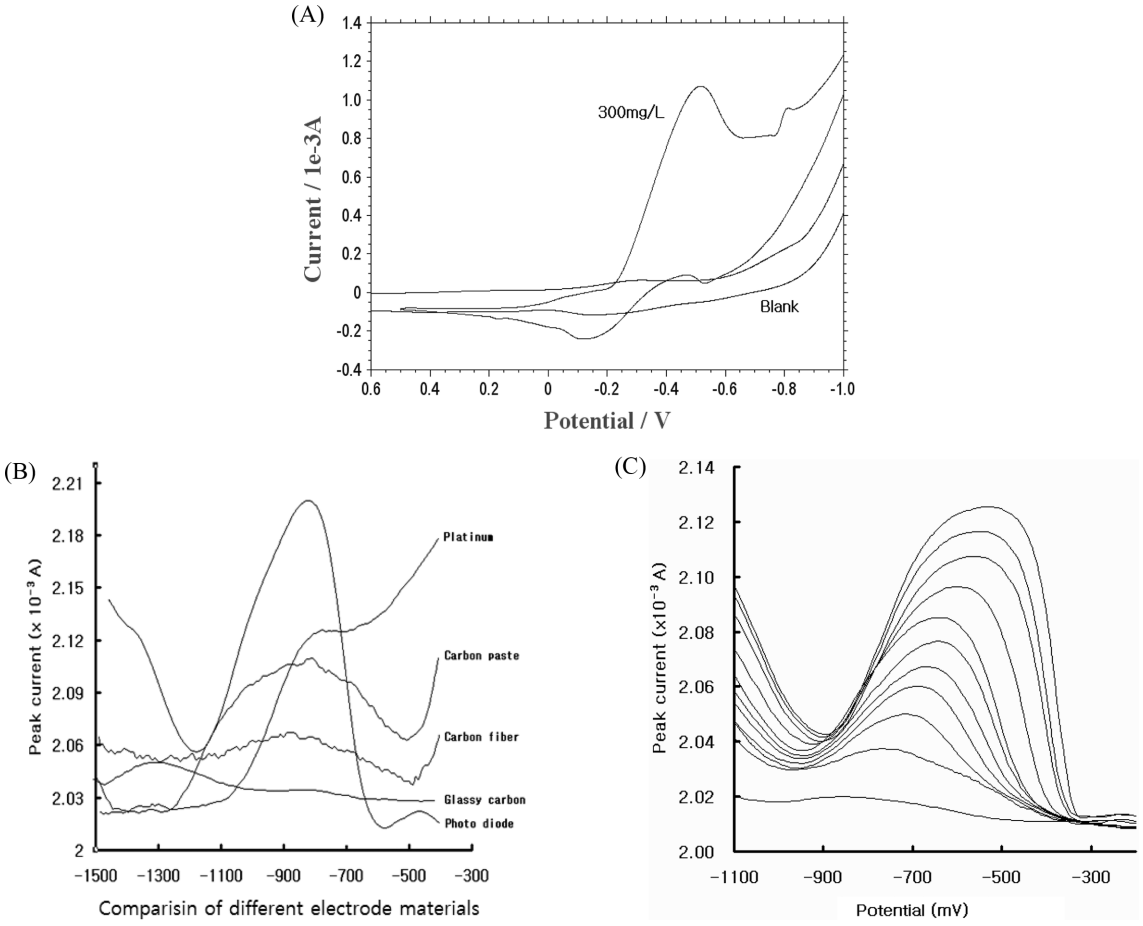

Fig. 1. (A) CV voltammograms of electrolyte blank and 300-mg/L Co(II) add, −1.0 V initial potential, 0.8 V switching potential, 500 mV/S scan rate. (B) Sensor property of IPDE, glassy carbon, metal platinum, carbon paste, and carbon fiber micro electrode. (C) Stripping voltammetric concentration effects of 0.5-, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- and 10-mg/L Co(II) add using IPDE with optimum conditions.

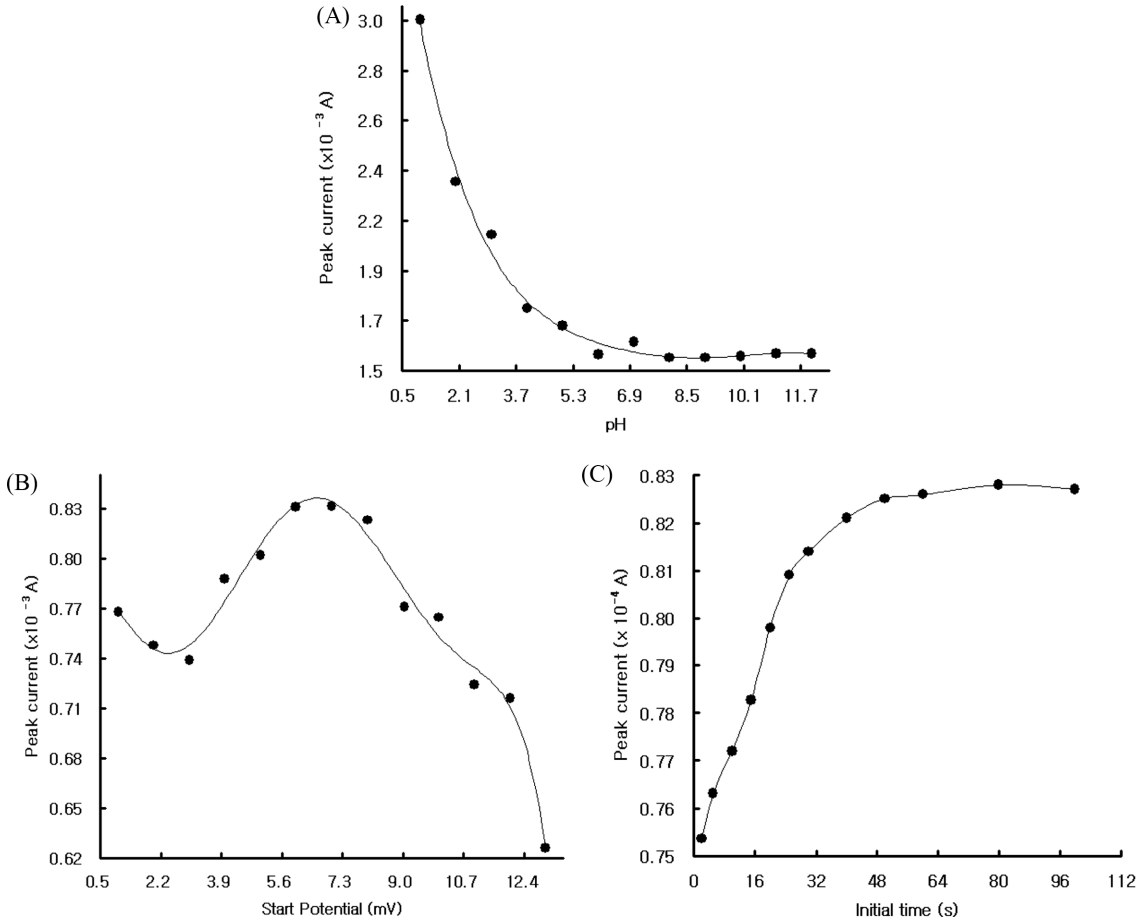

Fig. 2. (A) The square wave stripping voltammetry (SW) pH variation of 2.92, 3.72, 4.31, 4.6, 5.24, 6.07, 6.88, 7.69, 8.36, 9.07, 10.1, and 10.98 strength. (B) Variation of 100, −150, −200, −250, −300, −350, −400, −450, −500, −550, −600, −700, and −800 V accumulation potential. (C) The 1, 5, 10, 15, 20, 25, 30, 40, 50, 60, 80, and 100 sec SW accumulation time variation.

10^{-3} A within the −250 V~ −400 V. At −400 V, the maximum current was obtained. Fig. 2C shows the stripping time effects from the 0 sec to 100 sec variation. The peak current increased from 0.7536 to 0.828 × 10^{-4} A within the 2 sec~80 sec range and decreased slightly to 0.827 × 10^{-4} A at 100 sec. The maximum current was obtained at 80 sec, and the optimal conditions, interferences, statistics, and applications were examined.

RESULTS

Statistics, working ranges and the applications. The analytical interference effects were studied by adding several other ions into the medium containing the 40-mg/L Co(II) analysis. The existence of the 40-mg/L Fe(II), Cd, Hg, Zn(II), Cu(II), Cr(III), and Ni(II) resulted in −74.630, −2.121, 9.317, −5.352, −14.241, 7.937, and the 13.122% changes, respectively (data not shown). On the other hand, Fig. 3A, showing the presence of a three-fold excess of Fe(II), Cd(II), Hg(II), Zn(II), Cu(II), Cr(III), and Ni(II) resulted in the 100, 405.161, 30.204, −80.088, 157.389, −6.603, −59.221, and 1.005% changes, respectively. The interference effects were also calibrated using the standard addition methods. Under these conditions, Fig. 3B, shown results for repeated statistic detection peak currents, only 42.0~15.0 μA width appeared. Fig. 3C shows the analytical working range of the 0.5~18 mg/L Co(II) variations. Three ranges were obtained: The result of the linear equation of $y = 0.030x + 0.094$, with $R^2 = 0.0994$. Their slope sensitivities were sharp. The results show that the IPDE can detect cobalt in low concentrations and can be applied to the fields where the cobalt detection is needed.

The analytical applications were performed on the pharmaceutical-company waste and on the waste of a sewage disposal plant near the city, using the standard addition method based on the optimum conditions. Fig. 4A shows the pharmaceutical waste. The first is the electrolyte blank, and the 1 mL non-treated waste spike, and the peak current of 39.1 were obtained. After that, the 2 mg/L Co(II) standards, the 4 mg/L Co(II) standards, and the 6 mg/L Co(II)

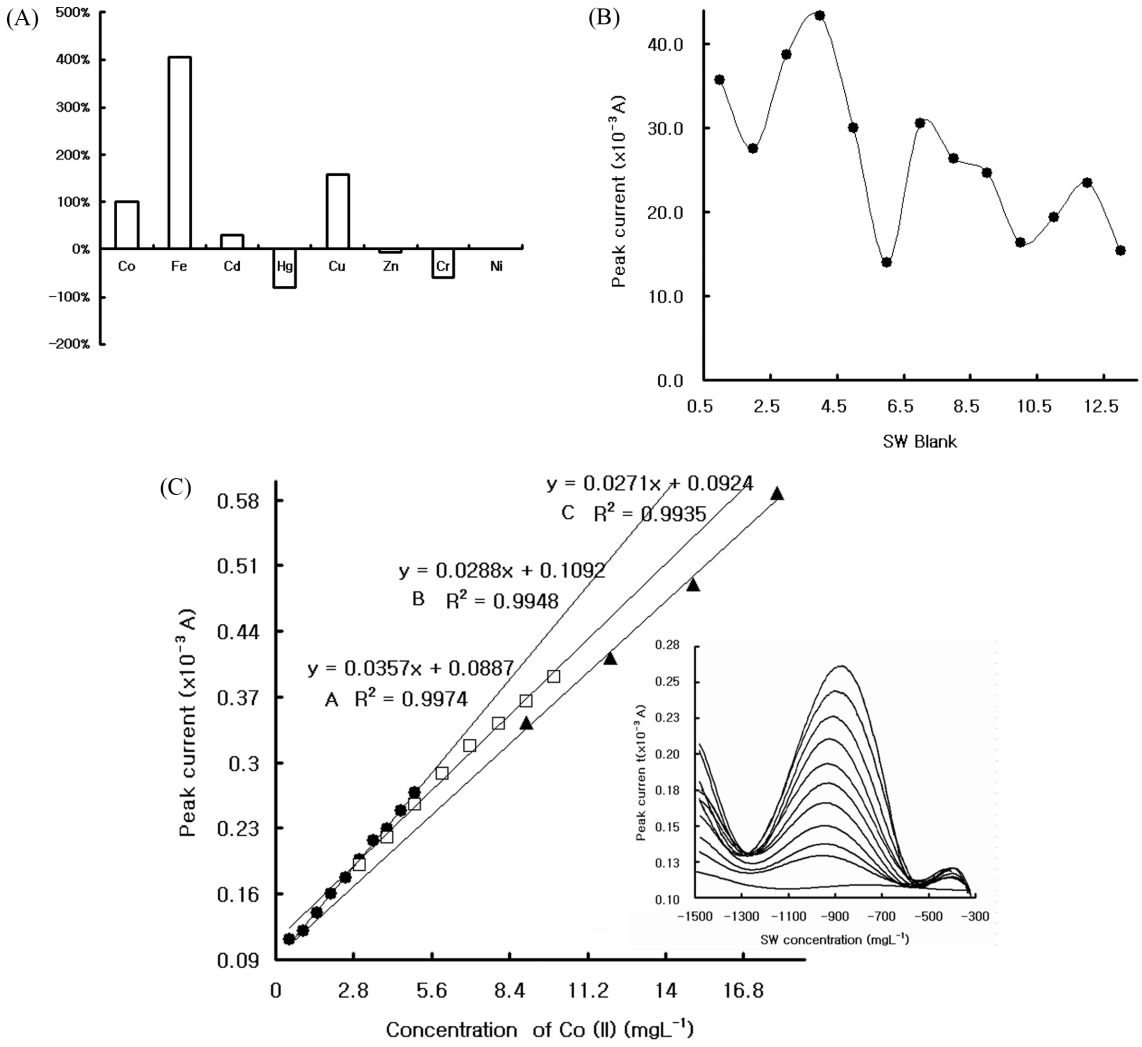

Fig. 3. (A) The results of the interference analogy metal ions. (B) Statistics. (C) The SW concentration effects based on the optimum conditions, with 80 sec accumulation time.

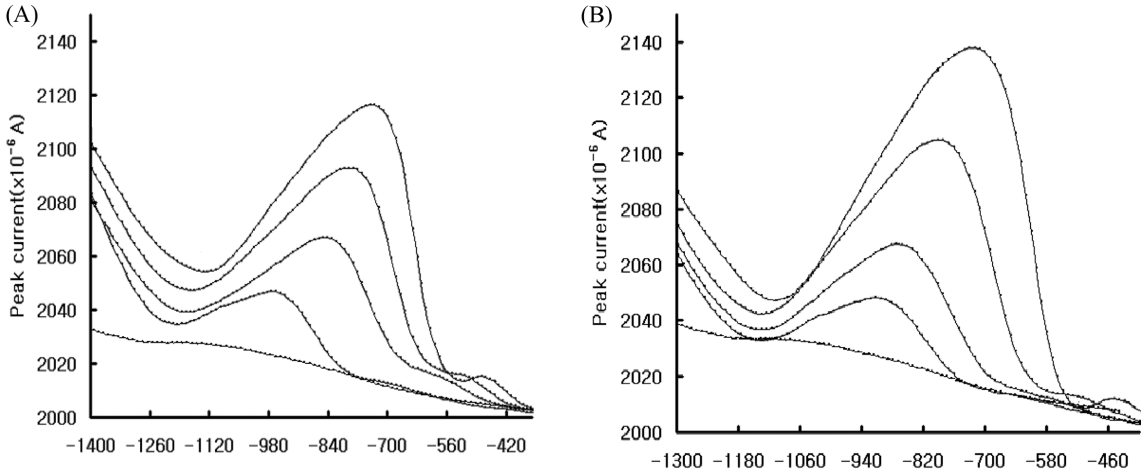

Fig. 4. (A) Analytical application to pharmaceutical-company waste using stripping voltammetry. (B) Application to the waste of a sewage disposal plant near the city, using stripping optimum conditions with 80 sec accumulation time.

standards were spiked, in that order. They increased from 45.87 to 70.4. The result's equation was y = 8.259x + 29.23 with R^2 = 0.985 (not shown here). Fig. 4B shows the application to the waste of a sewage disposal plant near the city, where 1-mL waste was spiked and the peak current of 33.5 was obtained. Then, the 2 mg/L Co(II) standard, the 4 mg/L Co(II) standard, and the 6 mg/L Co(II) standard were spiked, and the 45, 54.32, and 59.39 peak currents were obtained. The peak current increased continuously. These results mean that cobalt exists in the wastes of the pharmaceutical companies and the sewage disposal plants. The square-wave stripping voltammetry method and the IPDE electrode were used to detect the low cobalt concentrations.

DISCUSSION

The analytical optimal conditions were examined, and the results were obtained. The IPDE electrode showed a high sensitivity for the detection of cobalt ions. In this condition, the common-type probe was compared using the IPDE in the same electrolyte with the 10 mg/L Co(II) standard addition, using the stripping optimal parameters for the 30 sec accumulation. Each peak obtained the platinum (0.03×10^{-3} A), the carbon paste (0.07×10^{-3} A), the carbon fiber (0.04×10^{-3} A), the grassy carbon (0.01×10^{-3} A), and the IPDE (0.03×10^{-3} A). The IPDE is ten times more sensitive than the other probes such as the platinum, the carbon paste, the carbon fiber and the grassy carbon. Which of final working range were obtained of the 0.5~5.6 mg/L, 2.9~10.2 mg/L, 8.7~18.5 mg/L Co(II) variations, moreover working equations for Y = 0.0357X + 0.0887, R^2 = 0.9974, y = 0.0288X + 0.1092, R^2 = 0.9948, and y = 0.0271X + 0.0924, R^2 = 0.9935 obtained. Under the optimum conditions, the analytical detection limit was attained at 52 μg/L Co(II). The result was applied to the soil waste and the waste of a sewage disposal plant near the city. The current IPDE results can be useful for the analytical applications to the pharmaceutical-company wastes, the wastes of the sewage disposal plants and can also be used in the other fields that require the detection of cobalt ions.

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