

Voltammetric measurements of iron using an infrared photodiode electrode

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적외선 광 다이오드를 사용한 철의 전압전류 정량

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요 약: 사각파형 벗김 전압 전류법과 순환 전압 전류법에서 적외선 광 다이오드의 간단한 전자 회로를 사용한 철의 정량을 연구하였다. 기존에 사용되는 작업 전극과 최적 분석 조건을 비교하였으며, 순환 전압 전류법의 결과는 보다 간단하며 정밀하였으며, 최적 조건에서 농도 범위는 0.1-0.8과 0.85-6.0 mg/L 이었다, 0.4 mg/L의 철 농도에서 15번 반복 측정 한 상대 표준편차는 0.09%였으며, 최소 분석 검출 한계는 $80 \pm 0.6 \mu\text{g/L}$ 였다, 이결과는 폐수중의 철 정량에 응용하였다.

Abstract: A simple electric circuit of an infrared photodiode electrode (IPDE) was utilized to monitor iron using square-wave (SW) anodic stripping voltammetry (SV) and cyclic voltammetry (CV). The optimum analytical conditions were determined and were compared with those of common working electrodes. The comparison showed that CV is more sensitive and convenient to use than the common voltammetry methods. At the optimized conditions, the working ranges of 0.1- to 0.8- and 0.85- to 6.0 mg/L iron was obtained. Relative standard deviation of 15 measurements of iron (0.4 mg/L) was 0.09%. The analytical detection limit was found to be $80 \pm 0.6 \mu\text{g/L}$, which was applied to iron in waste water.

Key words: Iron, voltammetry, infrared, photodiode

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1. Introduction

A number of investigators in the field of analytical science have described the determination of iron and its components through low-level analysis.¹⁻⁵ This type of study is very important in the biological field, and is the type of study used on food and medicines. Advanced methods of analytical study, such as high-performance liquid chromatography with inductively coupled plasma mass spectrometry⁶, ion chromatography,⁷ inductively coupled plasma optical emission spectrometry,⁸ flame atomic absorption spectrometry,⁹ and other conventional analytical methods, were therefore developed. All these methods involve spectroscopic or electrochemical detection systems. More sensitive and simpler methods, however, are currently being required in analytical science.

Electrochemical voltammetry detection systems have long been recognized as powerful techniques for analyzing trace ions and their speciation. Moreover, they make use of relatively low-cost equipment and elicit rapid responses.¹⁰⁻¹² Since systems with very sensitive working electrode techniques are needed, various usable iron detection methods have been developed, such as those using conventional mercury electrodes,^{13,14} glassy carbon electrodes,¹⁵⁻¹⁷ diamond modified electrodes,¹⁸ and metal electrodes.^{19,20} Although pre-treatment modification methods are in demand, the common mercury electrode is toxic. More sensitive and simpler working electrodes are thus needed.

In this study, the infrared photodiode electrode, an inexpensive and easy-to-prepare one-chip electric circuit directly applied to electrode systems, was examined for the first time, and its optimum analytical conditions were determined. Aside from its aforementioned advantages, the IPDE surface is also photosensitive, and its HOMO and LUMO energy levels depend on the cyclic voltammetric P or the N doping process.²¹ (The results of other studies were examined to determine IPDE's cyclic voltammetric specifications with its p or n doping condition.²²) In addition, IPDE's copolymer structure

on a metal surface has strong electron-donating properties.²³ Also, its kinetic effect, electron affinity, and energy levels depend on the cyclic voltammetry redox potential,²⁴ thus, its polymerized surface is usable in electrochemical analysis.

Also in this study, the surfaces of the derivatives of chelate were applied to iron detection, and were compared with other common electrodes. They responded very sensitively to iron, which means that they can be applied to multi-array sensing electrodes and to multi-trace analysis.

2. Experimental

2.1. Apparatus and Reagents

Experimental voltammetric measurements were taken through CV and SWSV with the use of the CHI 660A instruments electrochemical workstation (from CH Instruments, Inc, Cordova, TN, USA). A three-electrode system was used to record the voltammograms, consisting of the IPDE electrode as the working electrode, an Ag/AgCl electrode (saturated KCl) as the reference electrode, and a platinum wire as the auxiliary electrode. All the solutions were prepared using double-distilled water (18M Ohm/cm).

2.2. Procedure of Electrode Preparation

2.2.1. IPDE

The working electrode was prepared using a 430- to 1,050-nm infrared photodiode electrode with a peak sensitivity wavelength of 950 nm and a packing view size of 4.8-5.5 mm (SPI5342-H from the AUK Semiconductor Company). This electrode is commonly used in TV/VCR audio remote control circuits. It was purchased from an electrical circuit shop. First, the colorless and transparent glass lens cover was removed. Then the flat base was extracted. At this state, two bare-type cylinder electrodes (1 mm in diameter and with a 1-cm-long wire) were obtained, and both the forward and backward electrodes were used. (In the experiment, these electrodes produced identical peaks signals in their CV or SW reactions).

2.2.2. Carbon paste electrode

The carbon paste electrode was prepared by mixing 70 % graphite powder (Fisher) with 20 % mineral oil. The mixture was homogenized in a mortar for 30 min. The mixed paste was then inserted in a plastic syringe needle with a 3-mm diameter. A copper wire was used to connect the measurements to the system.^{25,26}

2.2.3. Carbon fiber microelectrode

A carbon fiber microelectrode with a 7- μ m diameter was prepared. A 15-mm-long carbon fiber was attached to a copper wire with the use of silver paint.^{27,28} This fiber was inserted into a polyethylene tube with a 0.3-mm diameter. The electrode was sealed by heating and was cleaned by sonication for 10 min, first in acetone, then in nitric acid (1:1), and finally, in double-distilled water. Other conventional-type electrodes, such as platinum and glassy carbon electrodes, were used. The iron standard stock solution was obtained from Aldrich and was diluted within the required time. The three-electrode system was immersed in a stirred solution of phosphate buffer (pH 4.0) that contained a known amount of Fe. Pre-concentration prior to stripping was carried out at an open circuit. CV and SWSV were then conducted at optimum conditions. The common parameter for CV was a scan rate of 100 mV/sec, and the parameters for the SWSV were as follows: an accumulation potential of -1.1 V (vs. that of the Ag/AgCl reference electrode); an accumulation time of 40 sec; a quiet time of 2 sec; a square-wave amplitude of 40.0 mV; an SW frequency of 80 Hz; and an increment potential of 5 mV.

3. Results and Discussion

First, the electrolyte solutions of acid and base were tested to determine if they could be used as supporting electrolytes. The ammonium phosphoric acid solution was found to have the best peak separation. The various ionic activities of the 0.1- to 0.01-M electrolyte solutions were examined with a fixed concentration of iron, and high peak signals

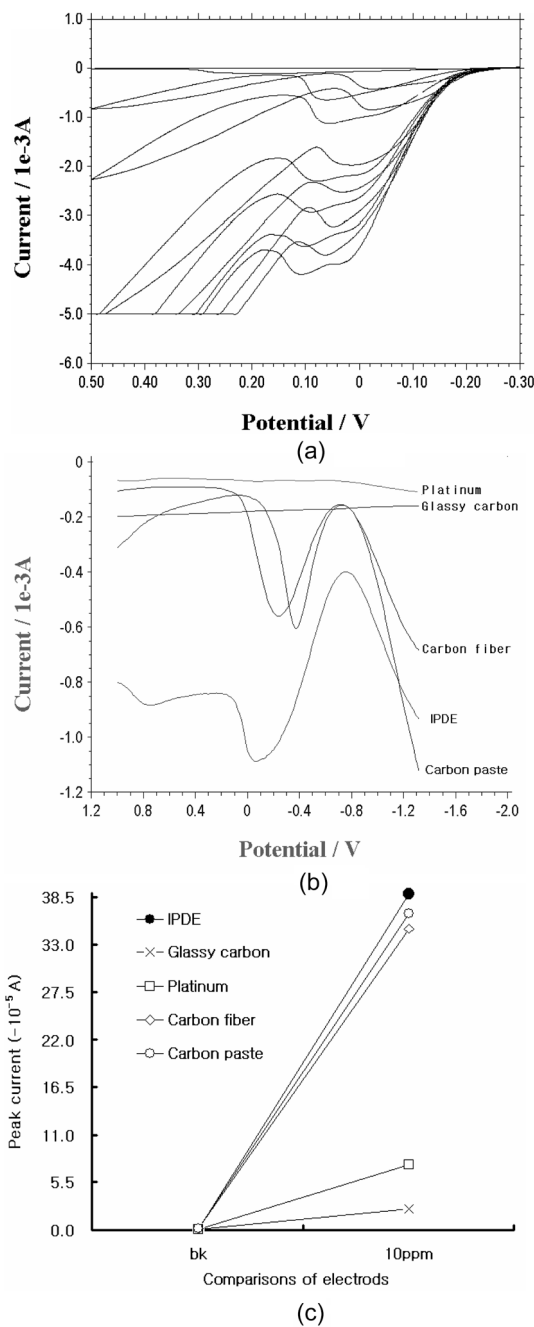


Fig. 1. (a) Cyclic voltammograms of IPDE in 0.1-M $\text{NH}_4\text{H}_2\text{PO}_4$ of pH 4.0 with 0, 10, 30, 50, 70, 85, and 100 mg/L of Fe. (b) Square-wave stripping voltammograms of 10 mg/L Fe spike for the various electrodes, an accumulation potential of -1.7 V, an accumulation time of 40 sec, an increment potential of 50 mV, an SW frequency of 80 Hz, and an SW amplitude of 0.14 V. (c) The peak current is shown in Fig 2(b).

were obtained in the concentration of 0.1-M $\text{NH}_4\text{H}_2\text{PO}_4$. Thus, all the solutions were used with the 0.1-M electrolyte solution. The latter can also be used in analytical applications. Other conventional working electrodes, on the other hand, were compared after they were subjected to identical conditions, and their usable IPDEs were examined.

In this study, a cylinder-type bare electrode with a 1-mm diameter and a 1-cm-long wire was first examined through cyclic voltammetry. The experiment parameters used were an initial potential of 0.3 V, a switching potential of -0.3 V, and a scan rate of 0.03 V/sec. As shown in *Fig. 1(a)*, no signals appeared in the blank electrolyte solution. Thus, more Fe ions were spiked at six points for the 10- to 100 mg/L Fe ions. At the oxidation scan, the -0.1V peak potential continually and linearly increased, while at the reverse scan, no reduction currents were obtained. Thus, the anodic peak current was used in all the other experiments. Then more sensitive reactions were examined using square-wave stripping voltammetry. As shown in *Fig. 1(b)*, various common electrodes were compared with the IPDE. All the electrodes were composed of the same electrolyte solutions, and the same parameters (an increment potential of 50 mV, an SW frequency of 80 Hz, an SW amplitude of 0.14 V, and an accumulation potential of -1.1 V) were used. The anodic peak currents were used as a function of the Fe concentrations of 10 mg. For the raw voltamograms, at these conditions, the IPDE's sharp peak width was obtained in a better way compared to how the same was obtained for the common electrode. The peak high of the IPDE was determined to be 38.92×10^{-5} A; of the glassy carbon electrode, 2.45×10^{-5} A; of the platinum electrode, 7.55×10^{-5} A; of the carbon fiber electrode, 34.9×10^{-5} A; and of the carbon paste electrode, 36.67×10^{-5} A. *Fig. 1(c)* shows the high peak currents. The glassy carbon and platinum electrodes did not respond, whereas the other electrodes produced the same results and the IPDE appeared more sensitively. More optimized experimental conditions were then examined using the SW parameters.

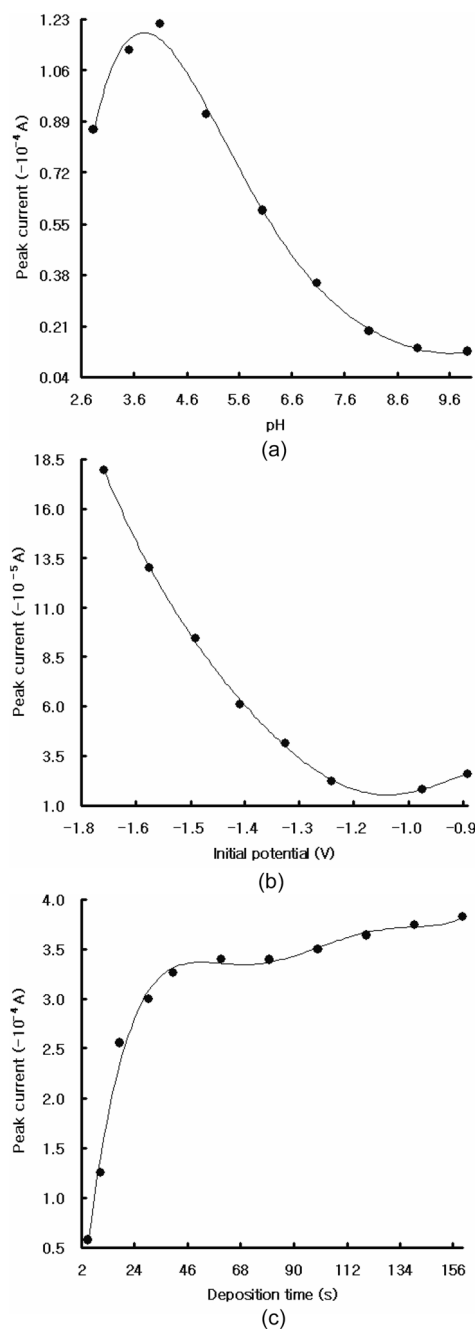


Fig. 2. (a) Square-wave voltammetry peak current at the various pH values of 2.8, 3.5, 4.1, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0. (b) SW accumulation potentials of -1.7, -1.6, -1.5, -1.4, -1.3, -1.0, and -0.9 V. (c) SW accumulation times of 5, 10, 18, 30, 40, 60, 80, 100, 120, 140, and 160 sec for the 5 mg/L Fe spike, with an increment potential of 50 mV, an SW frequency of 80 Hz, and an SW amplitude of 0.14 V. The other conditions were held constant.

3.1. Effects of Square-wave Voltammetry Parameters

Since the stripping voltammetry peak currents were dependent on the various SW parameters, the optimum conditions were investigated. First, anodic and cathodic scanning was conducted using square-wave stripping voltammetry, and the anodic peak current was obtained. Then the electrolyte's hydrogen ionic strength was determined. The results are shown in Fig. 2(a). The pH was changed using a 0.1-M HCl and a 0.1-M NaOH solution. At the acid ranges of 2.83-3.52, the peak widths broadly increased. At the base range of 4.97-9.94, the peak currents quickly decreased and their signals disappeared. At the 4.1 pH level, the peak half-width sharply and sensitively responded and a maximum peak current of 1.216×10^{-4} A was obtained. The accumulation potentials were then examined for the negative range of -1.7 V to -0.9 V. Their peak highs decreased linearly, and a maximum peak current of -1.7 V of 17.94×10^{-5} A was obtained. At this condition, the SW accumulation times of 0-160 sec were determined. The 0- to 40-sec peak currents quickly increased whereas the 60- to 160-sec peak currents did not, and only the peak width sharply responded. Thus, a short accumulation time of 40 sec was used, which produced more sensitive results (32.52×10^{-4} A peak high) than did the pH or accumulation potential results. In this optimized state, the other parameters were determined, and their results affected the iron analysis. The SW amplitude for the 0.04-0.25V range at 11 points was examined (not shown here). Its peak width widely increased and the 0.14V SW amplitude sensitively responded, for which a maximum peak current of 13.52×10^{-5} A was obtained. All other conditions were used. Moreover, various SW frequencies of 30-294 Hz at 12 points were examined (not shown here), and 80 Hz of 19.21×10^{-5} A sensitively appeared. The latter responded more actively than did the SW amplitude or the accumulation time. The range of 5- to 50-mV SW increment potentials at 10 points was determined, and a 5-mV 7.0×10^{-5} A peak high was obtained (not shown here). Their peak sharps sharply appeared and 5 mV was determined

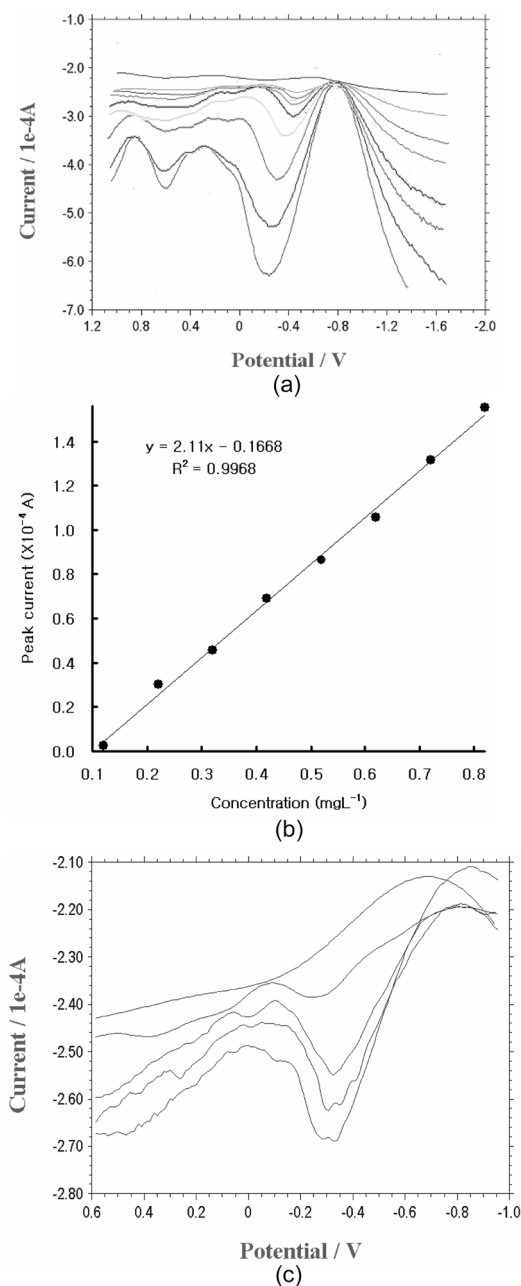


Fig. 3. (a) Square-wave stripping voltammogram of Fe at the concentration range of 0.1- to 0.8 mg/L Fe, and (b) their calibration curve, with the results of regression at optimum conditions, in a 0.1-M $\text{NH}_4\text{H}_2\text{PO}_4$ electrolyte solution. (c) Real waste samples of blank, known samples, and of 1-, 2-, and 3 mg/L Fe spikes.

as the optimum level. All these parameters were used in the analytical application.

3.2. Applications and Statistics

At the optimized conditions, various working ranges were examined. The results for 0.1-, 0.2-, 0.3-, 0.4-, 0.5-, 0.6-, 0.7-, and 0.8 mg/L Fe are shown in *Fig. 3(a)* and *Fig. 3(b)*. High working ranges of 0.85-, 1.5-, 2.2-, 2.6-, 3.3-, 3.8-, 4.3-, 4.8-, 5.4-, and 6.0 mg/L Fe were also examined (not shown here). The high concentration ranges' peak sharps broadly increased, while the low concentration ranges' peak sharps appeared as narrow as they were before and sensitively increased. The working curve can be used to determine the Fe concentrations in various known samples. Finally, real analytical samples were examined at the optimized conditions, as shown in *Fig. 3(c)*, as were laboratory-known waste solutions. First, a blank solution was stripped using optimized parameters; it did not produce any noise signal. Then known waste-contaminated solutions of 0.2 mg/L Fe were spiked, at which time small peak signals were obtained; standard solutions of 1-, 2-, and 3 mg/L Fe were then spiked. Since their signals continually increased, their statistical linear equations were plotted using the standard methods, which resulted in the calculated values for 0.19 mg/L Fe. Moreover, various other real samples were tested, and good results were obtained. The precision for the 15th repeated determinations of the 2- and 4 mg/L Fe standard solutions yielded relative standard deviations of $0.102 \pm 0.06 \%$ and $0.089 \pm 0.07 \%$, respectively. The current voltammetry response was highly reproducible. The developed methods were optimized and the detection limit was calculated to be 80 ± 0.6 ug/L of Fe per concentration based on the signal-to-noise characteristics of the data for the given $S/N = 3$ optimum conditions. The possible analytical interference of the chemical species with Fe determination was then examined; various other metal ions that contained 0.1 mg/L Fe were spiked; and the existence of 10 holds of 1 mg/L Fe in Co(III), Cr(III), Cd(II), Ni(II), Zn(II), Cu(II), Hg(II), and Bi(II) was found to be 115.0 %, 79.2 %, 164.1 %, 96.0 %, 0 %, 0 %, 67.8 %, and 0 %. The 1 mg/L Zn(II), Cu(II) and Bi(II) ions did not show any interference, however other ions strongly interfered in the peak current,

respectively. The presence of other ions was also effectively corrected using standard addition methods.

4. Conclusion

In this study, the optimized conditions for determining iron through voltammetry were found using IPDE as a working electrode. The latter's analytical concentration ranges at microgram levels were arrived at, common voltammetric working electrodes were compared with it, and more sensitive results were obtained compared with those of common electrodes. Thus, the CV and SW methods used with the commercial IPDE-type electrode are viable techniques for carrying out iron analysis. The use of an IPDE electrode is much more economical than the use of a carbon paste electrode or a glassy carbon electrode. Furthermore, the IPDE electrode can be used in multi-array diode systems of multi-trace assays, and directly with any other untreated electric circuit.

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