

시차펄스 음극벗김 전압전류법에 의한 시안이온 측정의 감도향상

羅紋鮮 · 權英順 · 蔡命俊*

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Increased Sensitivity in Cyanide Measurement by Differential-Pulse Cathodic Stripping Voltammetry

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요 약. 수은방울전극에서 바로 시안이온을 시차펄스음극벗김 전압전류 법으로 측정한 결과 검출한계를 낮출수가 있었다. 가장 알맞는 실험조건은 다음과 같다 : 0.1 M KCl-0.01 M 인산염 지지 전해질, pH 7, 석출전위 0.00V, 그리고 석출시간 3분이었다. 이 조건에서 검출한계는 $3 \times 10^{-7} M$ (8ppb) CN^- 이다.

ABSTRACT. Direct differential-pulse cathodic stripping voltammetry on mercury electrode (HMDE) provides a sensitive technique for low level cyanide measurement in distilled and sulfide free solution. Cyclic voltammetry revealed the forming and redissolution reactions were reversible at pH7 in 0.1M KCl-0.01 M phosphate supporting electrolyte. The analytical conditions have been optimized. With deposition time of 3 min at deposition potential 0.00V (vs. Ag/AgCl) in this medium of pH7, quite reproducible and linear calibration curve was obtained down to $3 \times 10^{-7} M$ (8ppb) CN^- which was the detection limit.

INTRODUCTION

The toxic effect of even low concentrations of cyanide on aquatic life, man and on the biota of wastewater treatment is well established¹. The increasing need for the determination of trace amount cyanide therefore is associated with many practical applications.

Because cyanide is vulnerable to various interfering substances, it is common practice that actual measurement is carried out in the alkaline distillate subsequent to preliminary treatment including distillation, in which step

the loss of cyanide is inevitable^{2,3}. As a result, the detection limit becomes an important factor, especially when its concentration in the original sample is very low. Detection limits of all methods available that will determine low levels of cyanide in solution are no less than $10^{-6} M$. For example, $1.3 \times 10^{-6} M$ in spectrophotometric method (pyridine-pyrazoline) that recommended in "Standard Methods"^{2,4}, $10^{-5} M$ in ion-selective electrode^{5,6}, $5 \times 10^{-6} M$ and $4 \times 10^{-6} M$ in dc⁷ and differential pulse⁸ polarography respectively.

Cathodic stripping voltammetry (CSV) is used to determine a wide range of organic and

inorganic compounds that form insoluble salts with the electrode material⁹. Anions such as halide, sulfide, and oxyanions, can be determined by CSV¹⁰. These determinations are based on the reactions of the anions with the electro-generated mercurous ion to form a partially insoluble mercurous film that can be preconcentrated on the mercury electrode surface. The sensitivity of the method is largely defined by the film solubility. The minimum detectable concentration (which can be determined with error not exceeding 20%) of Cl^- ($\text{p}K_{\text{sp, Hg}_2\text{Cl}_2} = 17.88$) is $5 \times 10^{-6} M$, and that of Br^- ($\text{p}K_{\text{sp, Hg}_2\text{Br}_2} = 22.24$) is $1 \times 10^{-6} M$ (the deposition time was 10 to 20 min)¹⁰. Perchard et al¹¹ and Propst¹² used CSV to measure I^- ($\text{p}K_{\text{sp}} = 28.35$) at the ppb concentration level. The low solubility of mercurous cyanide, $\text{Hg}_2(\text{CN})_2$ ($\text{p}K_{\text{sp}} = 39.3$) suggests that CSV of CN^- on mercury electrode would provide a very sensitive alternative to the existing methods.

This paper discusses a new CSV method to measure cyanide at the ppb concentration level after the distillation step. It is based on the formation of an insoluble mercury cyanide salt during the preconcentration step, and the deposit is stripped off and measured during a cathodic (negative-going) potential scan.

EXPERIMENTAL

All purchased reagent-grade chemicals were used without further purification. KCN, KCl, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, and borax were obtained from E. Merck AG. (Germany). All other reagents were obtained from Shinyo Pure Chem. Co. (Japan). The water used for dilution and for the standards was deionized and double distilled in quartz material. Oxygen was removed from the electrochemical cell by purging with pre-purified nitrogen saturated with water vapor. Mercury used in the hanging mercury drop

electrode (HMDE) was triply distilled.

An EG&G Princeton Applied Research Polarographic Analyzer (Model 264) and a Scanning Potentiostat (Model 362), equipped with a PAR Model 303 static mercury drop electrode and a PAR Model 305 stirrer were used to record all voltammograms on a Model RE 0088 X-Y recorder.

Deposition was achieved by using a slow (AUTO) stirring rate and a medium size drop with a surface area of 0.00156 cm^2 . Having a rest period of 30 sec after deposition, the cathodic redissolution procedure was initiated. The scan rate was 10 mV/sec in DP (differential pulse) mode, the pulse amplitude was 50 mV , and drop time was 0.5 sec . Ambient temperature of $(20 \pm 2^\circ \text{C})$ was used throughout.

RESULTS AND DISCUSSION

Cyclic Voltammetry. Cyclic voltammetry as a preliminary experiment was carried out at various pHs and buffer media to determine the optimal conditions for analytical purposes. Fig. 1 shows typical cyclic voltammograms of cyanide in $0.1 M \text{ KCl} - 0.01 M$ phosphate buffer at two pHs. This result indicates that both, cathodic and anodic, peak potentials shifted in the negative directions as the pH increased (46 mV/pH unit). It was found that the ratio of peak currents ($i_{\text{pc}}/i_{\text{pa}}$) equaled to nearly unity (1.1 at pH 7; 0.91 at pH 10), whereas the separations of peak potentials, $\Delta E_p (= E_{\text{pa}} - E_{\text{pc}})$ are 60 mV at pH 7 and 70 mV at pH 10. Cathodic (reduction) peak current decreased by 13% as the pH was changed from 7 to 10. These results of diagnostic test show that the electrochemical reaction in which cyanide is involved is a Nernstian reaction at pH 7, but the reversibility decreases as the pH increases¹³. Therefore, it is evident that the cathodic peak current, which is obtained when the potential of a HMDE, having a ins-

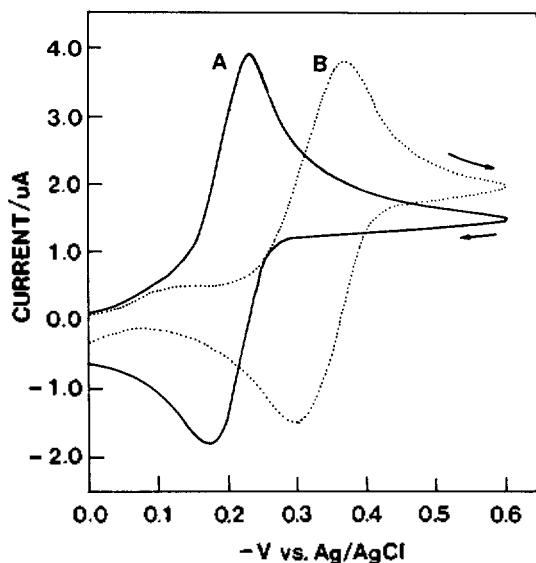


Fig. 1. Cyclic voltammograms of cyanide ion ($3 \times 10^{-4} M$) in $0.1 M$ KCl- $0.01 M$ phosphate electrolyte at: A, pH=7.0; B, pH=10.0.

oluble mercury film is scanned by CSV, will be significantly improved in sensitivity by application of the differential modulation. Thus sensitivity of a method would be increased by differential pulse CSV (DPCSV) at relatively lower pH, 7, with compared to conventional one, where the pHs are commonly above 9.

Effects of Buffer Media and pH on DPCSV. DPCSV measurements were made at various pHs of two supporting electrolyte-buffer media. To ensure that loss of cyanide as volatile HCN be minimized during any running, the measurement at pH below 7 was avoided. It was found that at pH above 10 the cyanide peak was seriously hampered by the hydroxide peak. Fig. 2 shows that phosphate buffer media is superior to borate at lower pH, but the sensitivity is reversed at pH higher than 8.5, where the conventional anodic polarographic measurements have been made⁷. With KCl-phosphate supporting electrolyte, the greatest peak current was obtained at pH 7 as suggested in the cyclic voltammetric test ($0.29 \mu A / \mu M CN^-$). The peak potential

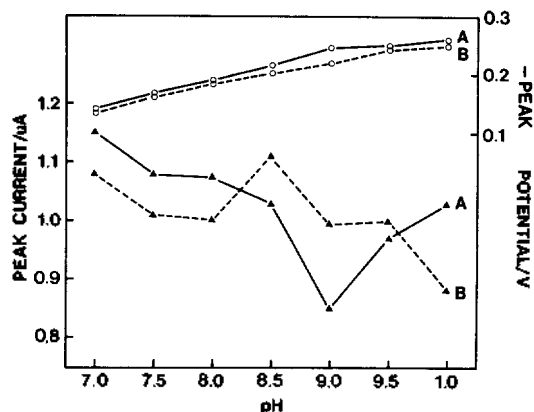


Fig. 2. Peak current (Δ) and peak potential (\circ) of DPCSV of CN^- ($4 \times 10^{-6} M$) as a function of the pH in A (—), KCl-phosphate; B (---), KCl-borate. The deposition time was 3 min at 0.00V.

shifted strongly (more than 50mV/pH unit) in a more negative direction as the pH increased up to 9. Above pH 9, however, the potential shift slows down and the peak current tends to increase again (see curves A's in Fig. 2). The behavior of this peak potential (E_p) dependence on pH can be easily derived from the expressions

$$\begin{aligned}
 E_p &= E_{1/2} - \frac{\Delta E}{2} = \pi + \frac{RT}{2\beta} \ln(Hg_2^{2+})_0 \\
 &= \pi + \frac{RT}{2\beta} \ln \frac{K_{sp, Hg_2(CN)_2}}{[CN]_0^2} \\
 &= \pi' - \frac{RT}{\beta} \ln [CN]_0 \\
 &= \pi'' - \frac{RT}{\beta} \ln \left(\frac{K_a}{K_a + [H^+]_0} \right) \quad (1)
 \end{aligned}$$

in which the subscript zero denotes the concentration at the interface of mercury and solution, and K_a is the acid dissociation constant of hydrocyanic acid (5.0×10^{-10}). The peak potentials at total concentration of cyanide $4.0 \times 10^{-6} M$ calculated with the aid of equation (1) agreed well with the observed values as shown by the following data: at pH 7, $E_{p \text{ obsd.}} = -0.140$, (calcd. -0.137); at pH 8, $E_{p \text{ obsd.}} = -0.192$, (calcd. -0.195); at pH 9, $E_{p \text{ obsd.}} = -0.245$,

(calcd. -0.245); at pH 10, $E_{p, \text{obs.}} = -0.260$, (calcd. -0.268).

All the results obtained so far indicate that the involved reaction is given by $\text{Hg}_2(\text{CN})_2 + 2e = 2\text{Hg} + 2\text{CN}^-$ at smaller cyanide concentrations and lower pH, in contrast with the electrode process in dilute NaOH (0.01 to 0.1M) and $5 \times 10^{-4} \text{M CN}^-$ where $\text{Hg}(\text{CN})_2$ is involved¹⁴.

Effects of deposition time and potential.

The reduction current was measured as a function of the deposition potential (E_d) and deposition time (t_d) at pH 7 in 0.1M KCl-0.01M KCl-0.01M phosphate media. The optimal deposition potential, after deposition for 3min, is found to be 0.00V as shown in Fig. 3. At more positive potential, current due to dissolution of mercury electrode itself interfered. With other deposition time the results were the same.

Fig. 4 shows the effect of various deposition times at $E_d = 0.00\text{V}$. The maximum peak current was obtained after three min deposition with $4 \times 10^{-6} \text{M CN}^-$. Sharp decreases in the peak current with short or longer than 3 min indicates that this factor is very critical. With more dilute cyanide solution ($5 \times 10^{-7} \text{M}$), it was found that the peak current did not proportional to t_d , but gave also maximum current after a deposition period of 3 min. This kind of nonlinearity in deposition efficiency (charge Q in μCoul vs. $C t_d$, where C is concentration), probably caused by the interfacial complications due to a variety of the insoluble-film forming species, is not unusual phenomena described elsewhere¹⁰. Neglecting the formation of $\text{Hg}(\text{CN})_2$ and $\text{Hg}(\text{CN})_4^{2-}$ ¹⁵ the formations of $\text{Hg}(\text{OH})_2$, $\text{Hg}_2(\text{OH})_2$ and Hg_2HPO_4 may be considered as such competitors when the activity of cyanide ion is very low. Fig. 5 suggests that these competing species can not be reduced at the potential where the main species is reduced.

An abrupt drop to a blank level of the peak

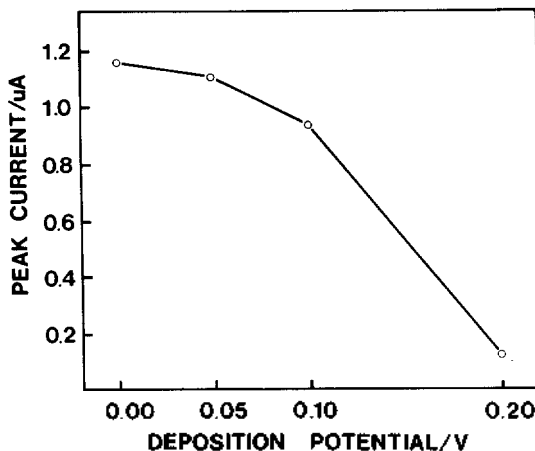


Fig. 3. Effect of deposition potential on the peak current of $4 \times 10^{-6} \text{M}$ cyanide ion in 0.1M KCl-0.01M phosphate medium of pH 7. The deposition time was 3 min.

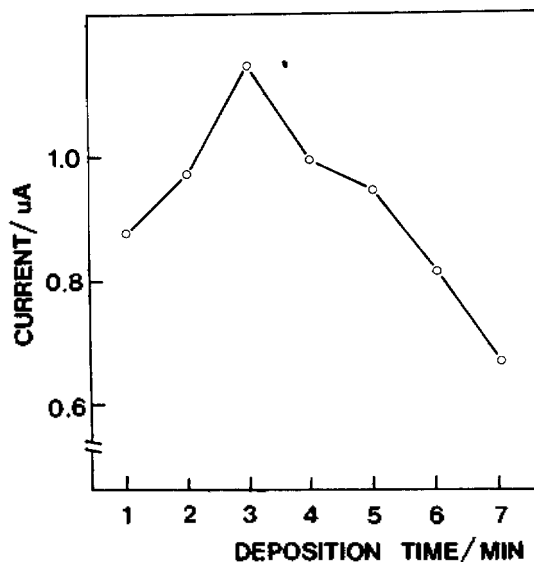


Fig. 4. Effect of the deposition time on the stripping peak current of CN^- . The deposition potential was 0.00V. Other conditions as in Fig. 3.

current (see Fig. 5) at concentration under $3 \times 10^{-7} \text{M CN}^-$ verifies this account.

CONCLUSION

Nevertheless these interfacial complications, low level cyanide can be determined by direct

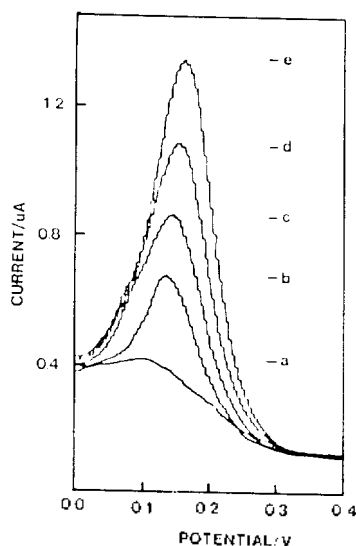


Fig. 5. DPCSV-grams of cyanide with varying concentrations(M): a, 1.5×10^{-7} ; b, 3.0×10^{-7} ; c, 7.0×10^{-7} ; d, 9.0×10^{-7} ; e, 1.9×10^{-6} . Other conditions as in Fig. 3. Noticeable current drop from (b) to (a) at half concentration indicates 3×10^{-7} (b) is not detection limit, strictly speaking.

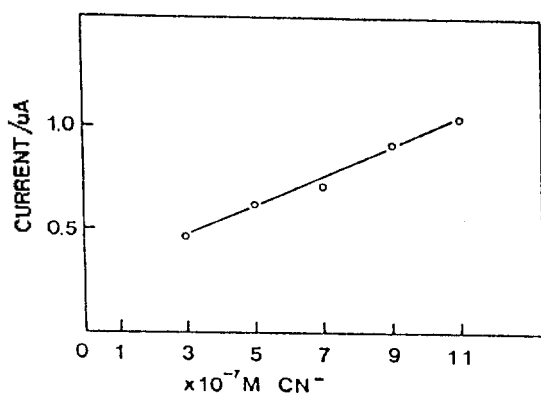


Fig. 6. Calibration graph by DPCSV peak current measurement. Other condition as in Fig. 3 and 4.

CSV on HMDE under the proper conditions. Fig. 6 shows a reproducible and linear calibration curve which can be used with confidence for concentration level down to $10^{-7} M CN^{-}$ or lower if a standard addition method is employed. The

optimal conditions are: $E_d = 0.00V$, $t_d = 3min$ in $0.1M KCl - 0.01M$ phosphate supporting electrolyte of pH 7.

With this direct DPCSV, the detection limit was $3 \times 10^{-7} M$ (8ppb) CN^{-} , an order of magnitude lower than any of the existing electroanalytical techniques. It is remarkable that this overall detection limit is not described by signal-to-noise ratio parlance but is governed by the deposited quantity of involved species in the collecting step.

REFERENCES

1. P. Doudoroff and M. Kat, *Sewage Ind. Wastes*, **22**, 1432 (1950).
2. APHA, "Standard Methods", 16th Ed., P. 327, 1985.
3. P. D. Goulden, B. K. Afghan, and P. Brooksbank, *Anal. Chem.*, **44**, 1485 (1972).
4. J. Epstein, *Anal. Chem.*, **19**, 272 (1947).
5. J. Vesely, O. J. Jensen, and B. Nicolaisen, *Anal. Chim. Acta*, **62**, 1 (1972).
6. M. S. Frant, J. W. Ross, Jr., and J. H. Riseman, *Anal. Chem.*, **44**, 2227 (1972).
7. D. R. Canterford, *Anal. Chem.*, **47**, 88 (1975).
8. Application Short, Cyanide, Princeton Applied Research Corp., Princeton, N. J., 1976.
9. J. Wang, "Stripping Analysis", P. 54, VCH Publishers, Inc., Deerfield Beach, U. S. A., 1985.
10. Kh. Z. Brainina, "Stripping Voltammetry in Chemical Analysis", Chap. IV, John Wiley & Sons, New York, 1974.
11. J. Perchard, M. Buvet, and R. Molina, *J. Electroanal. Chem.*, **14**, 57 (1967).
12. R. C. Propst, *Anal. Chem.*, **49**, 1199 (1977).
13. A. J. Bard and L. R. Faulkner, "Electrochemical Methods", Chap. 6, John Wiley & Sons, New York, 1980.
14. I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, **63**, 1045 (1941).
15. N. Tanaka and T. Murayama, *Z. Physik. Chem.*, **11**, 366 (1957).