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흡착 벗김 전압전류법에 의한 해수중 미량 철의 정량

蔡命俊* · 金 敬† · 權英順‡
漢陽大學校 化學科
†金星電線(株) 研究所
‡가톨릭大學校 化學科
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Determination of Iron in Seawater by Adsorptive Stripping Voltammetry

Myung-Zoon Czae*, Kyung Kim†, and Young-Soon Kwon‡
Department of Chemistry, Hanyang University, Seoul 133-791, Korea
†Research Lab, Goldstar Cable Co., Anyang 430-080, Korea
‡Department of Chemistry, Catholic University, Puchon, Kyonggi-Do 422-743, Korea
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요 약. 바닷물 중의 미량 철을 별도의 사전 농축이나 분리절차 없이 바로 정량할 수 있을 만큼 예민하면서 비용이 절감되는 손쉬운 흡착 벗김 분석 방법을 제안한다. 용액의 pH가 8.0인 붕산염 완충액에서 철/카테콜 착물을 수은 방울전극에 흡착시켜 수집한 후 음극 벗김과정을 수행하면서 펄스차이 방식 전류를 측정한다. 최적조건은 2.5 mM 붕산염, pH 8.0, 2 mM 카테콜, 수집전위 −0.25 V, 수집시간 1~3분이었다. 이 조건에서의 검출한계는 1.5 nM Fe였다. 붕산염 완충용액(높은 pH)의 사용은 기존의 지지전해질에서 문제되던 구리의 방해를 피할 수 있음은 물론 바탕선의 기울기가 완만해져 바탕선 잡기가 매우 좋았으므로 정밀성의 향상을 기대할 수 있다. 표준물 첨가법에 의해 실제시료에 적용해 본 결과 기대에 잘 부합하였다.

ABSTRACT. A simple procedure, readily available at low cost with a sensitivity sufficient to determine trace levels of iron in seawater is proposed, which utilizes adsorptive accumulation of the iron/catechol complex on the mercury drop electrode in a borate medium of pH 8.0. Optimal conditions include a solution concentration of 2 mM catechol, 2.5 mM borate and a pH of 8.0, an accumulation potential of −0.25 V is applied for 1~3 min, and the potential scan is in the differential pulse mode. The limit of detection is 1.5 nM Fe using a preconcentration time of 3 min. The interference from copper can be eliminated and baseline slope is greatly improved, because its peak is well separated from that of iron in the proposed medium.

INTRODUCTION

Adsorptive stripping voltammetry provides a highly sensitive route to the measurement of numerous important analytes (particularly trace metals) that are not accessible to conventional stripping measurements due to the electrolytic nature (faradaic process) of the preconcentration step.[1] Trace iron is one of the typical metals that cannot be quantified by conventional stripping voltammetric scheme due to its extreme redox potential, low solubility in mercury, and formation of intermetallic compounds with zinc and manganese.[2]

C.M.G. van den Berg *et al.* have developed a highly sensitive adsorptive stripping scheme for iron using catechol[2] with the limit of detection (LOD) of 0.6 nM, and using 1-nitroso-2-naphthol[3,4]

with LOD of 0.2 nM as the chelating agents. These procedures have sufficient sensitivity for direct measurement of trace levels of iron in seawater. They, however, used novel and expensive buffers such as PIPES (piperazine-*N,N'*-bis-2-ethane sulphonic acid) for pH 6.9 and HEPES (*N*-2-hydroxyethyl-piperazine-*N'*-2-ethane sulphonic acid) for pH 7.0 in all their schemes. The scheme using catechol, moreover, is subject to interferences (stripping peaks overlapping) from other reducible complexes since the iron/catechol complex is not formed selectively. For example, copper and lead, the ubiquitous metals, interferences must be eliminated by prior addition of EDTA (masking). Accordingly a procedure with improved selectivity and easy availability at low cost is desirable for many practical measurements.

As in most cases, utilizing a suitable supporting electrolytes is the proper solution to the resolution problem.[5] In the course of the present work, it was found that adsorptive stripping measurement of iron-catechol complex in a borate medium of pH 8.0, a very common buffer, eliminates the interferences and offers an improved baseline slope, as suggested in the earlier work.[6]

The results of the parametric evaluation for the optimal analytical conditions of the procedure are presented in this paper.

EXPERIMENTAL

Apparatus and reagents. Polarographic equipment was from Princeton Applied Research: a PAR 174A Polarographic Analyzer connected to a PAR 303A hanging mercury drop electrode (HMDE). Solutions were stirred using a teflon-coated stirring bar propelled by a PAR 305 magnetic stirrer set to "slow". The drop size used was "medium", which gave a drop with a weight of 2.5 mg and a surface area of 1.56 mm^2. Timings (accumulation periods, quiscence and stirring times) were controlled manually using a home-built control timer.

Stock solutions of Fe(III) were prepared by dilutions of an atomic absorption spectrophotometric standard solution (1000 ppm, Junsei Chem.). Sodium borate and catechol were GR grade which contained Fe less than 0.0002%, obtained from Kokusan Chemical Works and used without further purifications. A stock aqeous 0.1 M catechol solution was prepared freshly every 10 hours.

Atomic absorption spectrophotometry was perfomed by using a GBC Model 900 A A spectrophotometer.

Seawater (surface) samples were collected from Seochon located in the west coast, immediately acidified to pH 2, filtered through a 0.45 um membrane filter and next stored frozen (−20 ℃) in an acid-soaked polyethylene container.

All the glasswares and containers were cleaned by soaking in 6 M nitric acid more than 24 hrs prior to use.

Procedure. A 10-mL volume of the sample or the supporting electrolyte solution was added to the voltammetric cell, sodium borate solution (0.05 M) was added, and degassed with purified nitrogen for 4 minutes. The pH was adjusted to 8.0 after addition of catechol and the solution was purged for 8 min more. The accumulation potential was applied at the electrode for a selected time. The stirring was then stopped and after 15 seconds the voltammogram was recorded by applying a differential pulse scan in the negative direction. A scan rate of 10 mV/s, a modulation amplitude of 25 mV, and a drop time of 0.5 sec were used. Stripping peak currents were measured in the usual way.

RESULTS AND DISCUSSION

Effects of the accumulation potential and time. Catechol is known to form highly stable complex ions with several metal ions that adsorb onto HMDE and give reduction peaks, but the sensitivities are greatly variable.[2]

Fig. 1 shows typical differential pulse adsorptive stripping voltammetric responses obtained in a seawater sample containing 2.0 mM catechol and 2.5 mM borate buffer of pH 8.0 with different accumulation potentials (E_a: a, −0.05 V and b, −0.25 V). As was in PIPES of pH 6.92, only copper gives a significant peak (at about −0.22 V) by which the iron peak is preceded with $E_a = -0.05$ V (*Fig.* 1(a)).

But now in borate of pH 8.0, the peak potential (E_p) of iron-catechol complex shifted to more (0.07 V) negative with compared to that in PIPES of pH 6.9 (second column in *Table* 1). *Fig.* 2(a) shows the effect of E_a variation on the iron peak current (I_p). The differences in effects in two buffer media at their respective optimal conditions are summarized in *Table* 1. The measurements in borate medium of pH 8.0 by applying E_a other than -0.05 V produced somewhat (12%) reduced but constant (over the range varied) I_p (0.212 A), contrasting with the decrease in a large amount in the PIPES buffer. This independance of the I_p on E_a variation up to -0.3 V, together with the shift of the iron-catechol peak potential only (while that of copper unchanged), enables the E_a to be set at -0.25 V or more negative. With $E_a=-0.25$ V (*Fig.* 1(b)), the preceding copper peak disappeared and the baseline slope was significantly improved as a result of the elimination of the copper interference. Thus the use of borate buffer of pH 8.0 in place

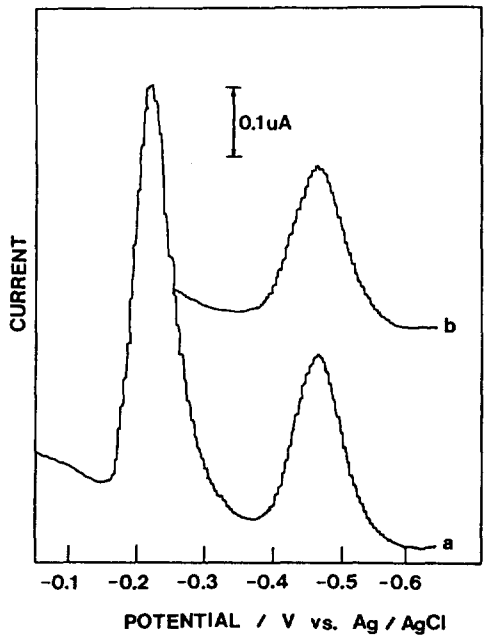

Fig. 1. Typical DPAdSV responses of the catechol complexes of metals in seawater containing 6.6×10^{-8} M Fe(III), 2 mM catechol, and 2.5 mM borate (pH 8.0). The accumulation time was 1 min at an accumulation potential of -0.05 V (a), and of -0.25 V (b).

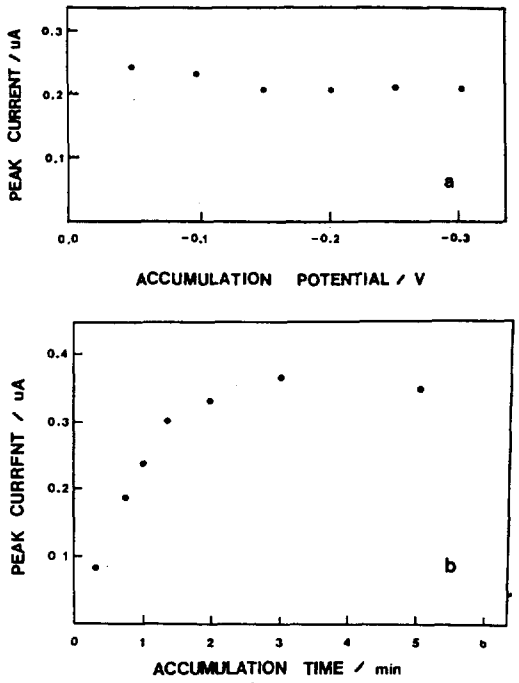

Fig. 2. Effect of the accumulation potential (a) and accumulation time (b) on the peak current. Experimental conditions were the same as in *Fig.* 1.

Table 1. Comparison of peak potential (E_p) and effect of accumulation potential (E_a) on peak current (I_p) of Fe(III) in different buffers[a]

Peak value / Buffer medium	E_p		Effect of E_a (decrease in I_p/%)					Choice of E_a
	Cu(II)	Fe(III)	E_a/V					
			−0.05	−0.15	−0.20	−0.25	−0.30	
					$-\Delta I_p$/%			
PIPES[b] (pH 6.9)	−0.22	−0.40	−	−	6	20	50	−0.10
Borate[c] (pH 8.0)	−0.22	−0.47	−	12	12	12	12	−0.25

[a]At the optimal conditions, [b]Based on reference 2, [c]Present method.

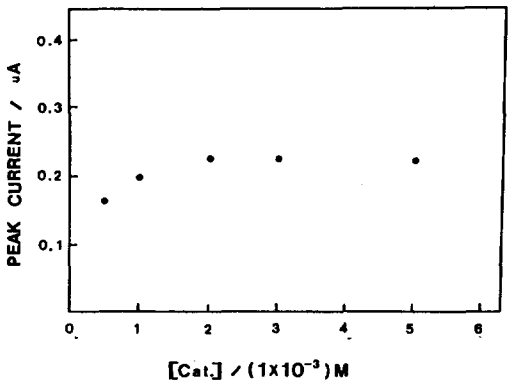

Fig. 3. The peak current as a function of the catechol concentration at an accumulation potential −0.25 V. Other conditions, same as in *Fig.* 1.

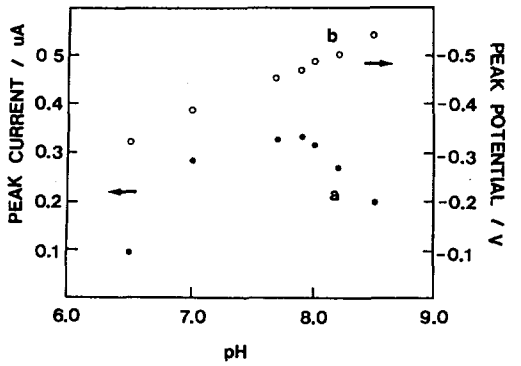

Fig. 4. Effect of the pH on the peak current (a) and peak potential (b). The accumulation time was 1 min at −0.25 V. Other conditions were same as specified in *Fig.* 1.

of PIPES of pH 6.9 has the distinct advantage that minimizing copper interference and improving the baseline slope without sacrificing the sensitivity of iron.

The dependence of the current on the accumulation time (t_a) was examined at 6.6×10^{-8} M Fe (III) in seawater. The peak current with this iron concentration was found to increase gradually with increasing t_a to a maximum of ca. 370 nA at 3 min after which it decreased (Fig. 2b). This maximum sensitivity (5.6 nA/nM) in a borate buffer is much (×4.5) greater than in a PIPES buffer[2] (50 nA for 4×10^{-8} M gives 1.25 nA/nM). The decrease in peak current which occurs with longer t_a is probably caused by the adsorption of other complex ions of competing metals in combination with dissociation or desorption of Fe-catechol complex.[2]

Effects of catechol concentration and pH. Measurements were made on seawater containing 6.6×10^{-8} M Fe(III), buffered to pH 8.0 with 2.5 mM borate, in the presence of catechol concentrations over 0.5 to 5 mM. Preconcentration was carried out for 1 min at −0.25 V. The peak current attains maximum at 2 mM catechol and remains nearly constant at higher concentrations (*Fig.* 3). The peak potential dependence behaves similarly (not shown by figure), constant within 0.005 V, over 2 mM catechol contrary to the case in the PIPES buffer.

The dependences of the current and peak potential upon the pH were examined by measurements at a fixed concentration of 2 mM catechol. Peak height and potential were strongly affected by the pH as shown in *Fig.* 4. The greatest peak height was obtained at pH 7.9. The peak potential shifted 0.14 V per pH in a more negative direction as the pH increased as a consequence of the greater stability of the Fe-catechol complex ions at higher pH values, for the catechol is a weak diprotic acid. All these results including *Table* 1 illustrate the superiority of borate buffer of pH 8.0 over PIPES of pH 6.9 as a proper buffer medium for the iron-catechol scheme.

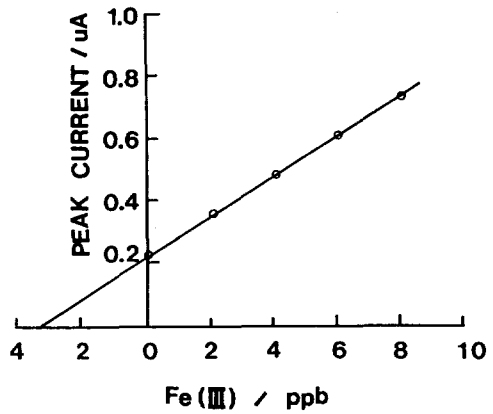

Fig. 5. Determination of the iron level in a seawater sample by standard addition method.

Determination of iron in real samples. The dissolved iron concentrations in the seawater samples

Table 2. Determination of iron in seawater samples

Sample	Iron found (ppb)	
	Present method[a]	A A S[b]
4C-3H	22.2	22.9
4C-5L	32.8	33.7
4C-6L	30.6	31.4
4C-9L	24.6	25.6
4C-10L	37.3	38.8

[a]With a relative standard deviation less than 5% over four measurements ($n=4$). [b]With a relative deviation less than 10% from the mean over two measurements.

were determined by standard additions as illustrated in *Fig.* 5. The sample contained 2 mM catechol and 2.5 mM borate buffer (pH 8.0). The accumulation time was 1 min at a potential of −0.25 V. The peak height increased linearly with Fe concentration until 8 ppb (1.5×110^{-7} M). The limit of detection (3σ) in these conditions was 0.3 ppb (1.5×10^{-9} M) determinable without any difficulty in baseline interpretation, which could be brought lower value by extending the accumulation periods up to 3 min. The results agreed well with the atomic absorption spectrophotometric method[8] (*Table* 2).

REFERENCES

1. Wang, J. In *Electroanalytical Chemistry*; Bard, A.J., Ed.; Marcel Dekker: New York, 1989; Vol. 16, p 1.
2. van den Berg, C. M. G.; Huang, Z. Q. *J. Electroanal. Chem.* **1984**, *177*, 269.
3. van den Berg, C. M. G.; Nimmo, M.; Abollino, O.; Mentasti, E. *Electroanalysis* **1991**, *3*, 477.
4. Yokoi, K.; van den Berg, C. M. G. *Electroanalysis* **1992**, *4*, 65.
5. Wang, J. *Stripping Analysis: Principles, Instrumentation, and Application*; VCH Publishers: Deerfield Beach, 1985; p 99.
6. Hong, T.-K.; Czae, M.-Z. *Bull. Korean Chem. Soc.* **1988**, *9*, 77.
7. van den Berg, C. M. G. *Anal. Chim. Acta* **1984**, *264*, 195.
8. Brooks, R. P.: Presley, B. J.; Kaplan, I. S. *Talanta* **1967**, *14*, 809.