

SIMULTANEOUS FLOW INJECTION DETERMINATION OF IRON(II) AND VANADIUM(IV) BASED ON THE REDOX REACTION WITH COPPER(II) IN THE PRESENCE OF NEOCUPROINE

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ABSTRACT

A simultaneous determination of iron(II) and vanadium(IV) is presented, which is based on the redox reactions of copper(II) with iron(II) and with vanadium(IV) in the presence of neocuproine. Redox reaction of copper(II) with iron(II), and/or vanadium(IV) occurs completely by the presence of diphosphate together with neocuproine and a copper(I)-neocuproine complex ($\lambda_{\text{max}} = 454 \text{ nm}$) is produced, while the reduction of copper(II) with iron(II) occurs very slowly in the presence of neocuproine alone. The simultaneous FIA method of iron(II) and vanadium(IV) is developed based on these reactions with a single injection. Maximum sampling rate is 30 samples h^{-1} . The proposed method is evaluated by injecting the composite samples of iron(II) and vanadium(IV). The recovery of each ion is satisfactory and the relative standard deviations of $10^{-5} \text{ mol dm}^{-3}$ levels of iron(II) and vanadium(IV) are less than 1 % ($n = 3$).

INTRODUCTION

Flow injection analysis (FIA) provides versatile application for a simultaneous determination of multi constituents.^{1,2)} The simultaneous FIA determination of iron(II) and iron(III) with 1,10-phenanthroline has been proposed by many authors.³⁻⁸⁾ Zagatto *et al.*⁹⁾ have been proposed for the simultaneous determination of aluminum with

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Eriochrome Cyanine R spectrophotometrically and iron by atomic absorption spectrometry. Wada *et al.*¹⁰⁾ have proposed the simultaneous determination of iron and copper with a multichannel photodiode-array detector.

Recently, we showed that the reduction of copper(II) with iron(II) occurred in the presence of neocuproine together with diphosphate, while the reduction of copper(II) with vanadium(IV) occurred easily even in the presence of neocuproine alone.¹¹⁻¹³⁾ Since the reduction of copper(II) with iron(II) proceeds very slowly in the presence of neocuproine alone, the fractional FIA determination of iron(II) and vanadium(IV) would be possible, i. e., the amounts of iron(II) can be obtained by subtracting the amounts of vanadium(IV) from total amounts of these ions. This paper described the simultaneous FIA method of iron(II) and vanadium(IV) based on this principle with a single injection.

EXPERIMENTAL

Reagents

Stock solutions of iron(II), copper(II) and vanadium(IV) (1×10^{-2} mol dm⁻³) were prepared and the concentrations of these metal ions were standardized as described previously.^{11,14)} Working solutions of metal ions were prepared by suitable dilution with 5.0×10^{-2} mol dm⁻³ sulfuric acid. Neocuproine and diphosphate solutions were prepared as described previously¹¹⁾ and was diluted suitably with water before use.

All reagents used were of analytical reagent grade and used without further purification. Water used to prepare the reagent and buffer solutions was obtained from a Milli-Q water purification system (Millipore Co.).

Apparatus

A schematic flow diagram for the simultaneous FIA of iron(II) and vanadium(IV) is shown in Fig. 1. Two double-plunger micro pumps (Sanuki Kogyo, DM2M-1026) were used for propelling the reagent and the carrier solutions. Sample solutions were injected by a double six-way injection valve (Nihon Seimitsu Kagaku, NV-508-12M) into the carrier stream. The flow lines were made of Teflon tubing (0.5 mm i.d.) and connectors. The absorbance was measured at 454 nm with a Soma Kagaku S-3250 spectrophotometer with a 10-mm micro flow cell (8 μ l) and recorded on a Hitachi Model 056 recorder.

Procedure

In the flow system (Fig. 1), a water carrier solution (C), a mixture of $1 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) and $5 \times 10^{-4} \text{ mol dm}^{-3}$ neocuproine ($5 \times 10^{-2} \text{ mol dm}^{-3}$ acetate buffer, pH 5.6) in reservoir R_1 were pumped at a flow rate of $1.0 \text{ cm}^3 \text{ min}^{-1}$. The diphosphate solution ($1 \times 10^{-3} \text{ mol dm}^{-3}$) and water in reservoirs R_2 and R_3 were also pumped at a flow rate of $1.0 \text{ cm}^3 \text{ min}^{-1}$. The flow path of diphosphate solution and water was changed by a valve V_2 . A $200 \mu\text{l}$ aliquot of the sample solution containing iron(II) and vanadium(IV) was injected by a double six-way valve (V_1) into the carrier stream, which was then separated into two streams by a separation coil (SC). The configuration of the double six-way valve (V_1) is shown in Fig. 2. After the separated sample solutions were merged with a mixture of copper(II) and neocuproine (pH 5.6), the valve V_2 was turned so that the first portion of the sample solution merged with water, while the second portion merged with diphosphate solution. The absorbance of the complex formed was monitored continuously at 454 nm.

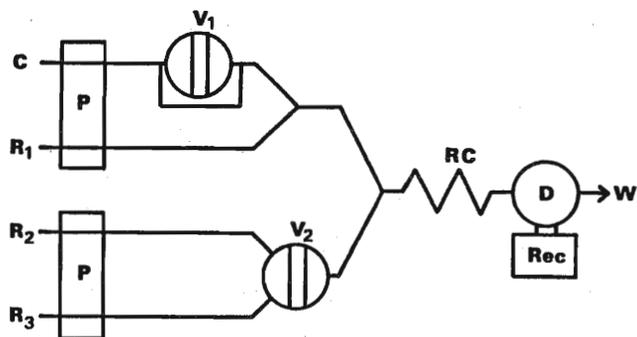


Fig. 1 Flow diagram of FIA for the simultaneous determination of iron(II) and vanadium(IV).

C, water; R_1 , copper(II) ($1 \times 10^{-4} \text{ mol dm}^{-3}$) / neocuproine ($5 \times 10^{-4} \text{ mol dm}^{-3}$) / acetate buffer ($5 \times 10^{-2} \text{ mol dm}^{-3}$); R_2 , diphosphate ($1 \times 10^{-3} \text{ mol dm}^{-3}$); R_3 , water; P_1 and P_2 , pump ($1.0 \text{ cm}^3 \text{ min}^{-1}$); V_1 , double six-way valve; V_2 , six-way valve; RC, reaction coil (2 m long, 0.5 mm i.d.); D, spectrophotometer; Rec, recorder; W, waste.

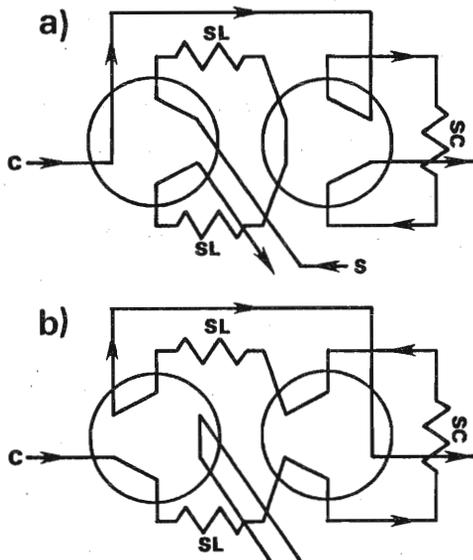


Fig. 2 Double six-way valve (V_1) configuration for sample separation.

a) Load. b) Inject. C, water carrier; S, sample (mixture of iron(II) and vanadium(IV)); SL, sample loop (30 cm long, 0.5 mm i.d.); SC, separation coil (5 m long, 0.5 mm i.d.)

RESULTS AND DISCUSSION

Effect of diphosphate on the reduction rate of copper(II) with iron(II) in the presence of neocuproine

The reduction rate of copper(II) with iron(II) in the presence of neocuproine alone was examined by both batch and FIA methods.

The batch procedure was as follows: a 1×10^{-5} mol dm $^{-3}$ iron(II) solution was added to the mixture of 2.5×10^{-5} mol dm $^{-3}$ copper(II), 1.25×10^{-4} mol dm $^{-3}$ neocuproine and 1.25×10^{-2} mol dm $^{-3}$ acetate buffer (pH 5.6). Then the absorbance of the copper(I)–neocuproine complex formed was measured at definite intervals at 454 nm. The absorbance change at 454 nm with time is shown in Fig. 3. As can be seen from Fig. 3, the reduction rate of copper(II) with iron(II) was very slow under the conditions: it took an hour to complete the reaction.

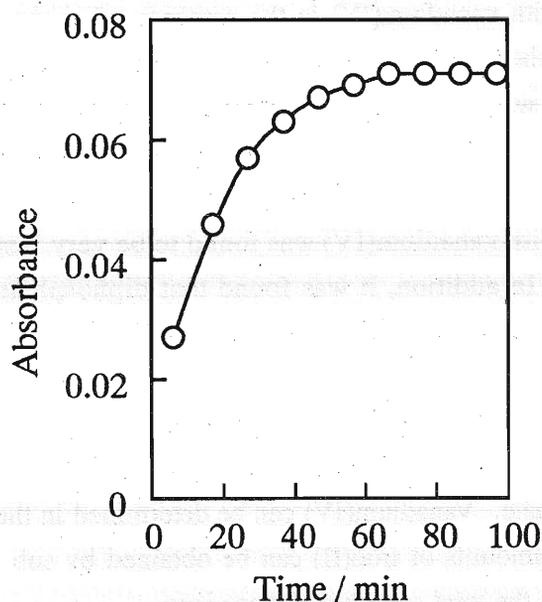


Fig. 3 Formation curve of the copper(I)–neocuproine complex by redox reaction of copper(II) with iron(II) in the presence of neocuproine by batch method. Copper(II), 2.5×10^{-5} mol dm $^{-3}$; iron(II), 1.0×10^{-5} mol dm $^{-3}$; neocuproine, 1.25×10^{-4} mol dm $^{-3}$; acetate buffer, 1.25×10^{-2} mol dm $^{-3}$, pH 5.6.

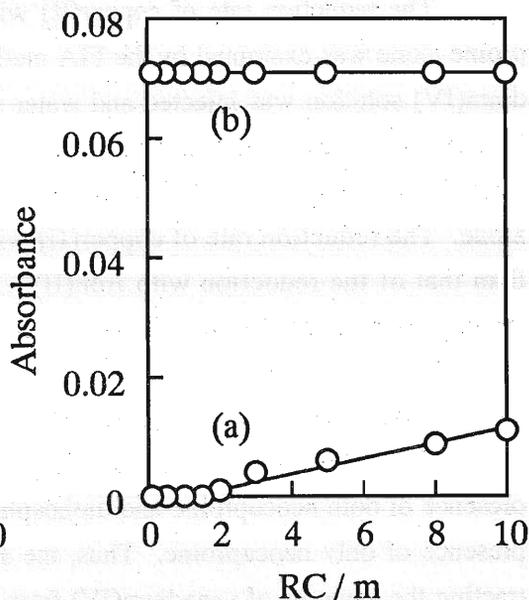


Fig. 4 Reduction reaction of copper(II) with iron(II) in the presence of (a) neocuproine alone and (b) neocuproine and diphosphate by FIA method. Other Conditions as in Fig. 1 and the text.

The effect of reaction coil length (RC) in Fig. 1 was examined by the FIA procedures. To obtain a maximum absorbance of the complex, 2 cm^3 of $2 \times 10^{-5} \text{ mol dm}^{-3}$ iron(II) solution were injected into the carrier stream. In this case, water was propelled from pump 2. Results are shown in Fig. 4 (a). No FIA peaks were observed at shorter reaction coil length less than 2 m. The reduction rate of copper(II) with iron(II) in the presence of diphosphate together with neocuproine was also examined by changing the reaction coil length of RC. In this case, a $1 \times 10^{-3} \text{ mol dm}^{-3}$ diphosphate solution was propelled from pump 2. As shown in Fig. 4 (b), maximum and constant FIA peaks were obtained at the reaction coil length longer than 10 cm. From these results, it was found that the addition of diphosphate accelerated significantly the reduction of copper(II) with iron(II).

Reduction rate of copper(II) with vanadium(IV) in the presence of neocuproine

The reduction rate of copper(II) with vanadium(IV) in the presence of neocuproine alone was examined by the FIA method. A 2 cm^3 of $1.7 \times 10^{-5} \text{ mol dm}^{-3}$ vanadium(IV) solution was injected and water was propelled from pump 2. The height of FIA peaks increased with increasing coil length up to 1 m and showed maximum and constant at a reaction coil length longer than 1 m even in the presence of neocuproine alone. The reduction rate of copper(II) with vanadium(IV) was found to be very fast than that of the reduction with iron(II). In addition, it was found that diphosphate showed no effect on the rate of redox reaction of copper(II) with vanadium(IV).

Simultaneous FIA system for the iron(II) and vanadium(IV) determinations

The total amounts of iron(II) and vanadium(IV) can be determined in the presence of both neocuproine and diphosphate. Vanadium(IV) can be determined in the presence of only neocuproine. Thus, the amounts of iron(II) can be obtained by subtracting the amounts of vanadium(IV) from the total amounts of these ions.

A system for simultaneous FIA of iron(II) and vanadium(IV) was developed (Fig. 1), which was possible to determine both ions with a single injection and a detector. The sample stream was separated into two streams by separation coil (SC) with the valve V_1 . The first portion of the separated sample solution merged with a mixture of copper(II) and neocuproine, and the second portion merged with a mixture of copper(II), neocuproine and diphosphate. The first peak height corresponded to the amounts of vanadium(IV) and the second corresponded to the total amounts of iron(II)

and vanadium(IV).

The reagent concentrations and the reaction pH are the same as previously,^{12,13} and describes in figure caption in Fig. 1. A reaction coil length of 2 m was used for the procedure. All measurements were performed at room temperature.

The effect of the separation coil length (i.d. 0.5 mm) in the valve V_1 was examined by injecting 200 μl of 5×10^{-6} mol dm^{-3} Methyl Orange solution. Water was propelled from pumps 1 and 2. The separation coil of 5 m was needed for complete separation of the sample injected. The height of the second peaks was about a half as low as that of the first one due to the dispersion of the solution in the separation coil.

Calibration graphs

Calibration graph for iron(II) was prepared by propelling the diphosphate solution from pump 2, and the second peaks were used to prepare the calibration graph for iron(II).

Calibration graphs for vanadium(IV) were prepared by propelling the water from pump 2. Typical flow signals for vanadium(IV) are shown in Fig. 5.

In this case, the first and second peaks were used to prepare the calibration graphs for vanadium(IV). Calibration graph obtained from the second peaks was used to subtract the amounts of vanadium(IV) from the total amounts of iron(II) and vanadium(IV).

The features of the calibration graphs for iron(II) and vanadium(IV) are summarized in Table 1. The liner calibration graphs for iron(II) and vanadium(IV) were obtained over the range $2 \times 10^{-5} - 1 \times 10^{-4}$ mol dm^{-3} . The proposed method permits the determination of 30 samples h^{-1} (60 peaks h^{-1}).

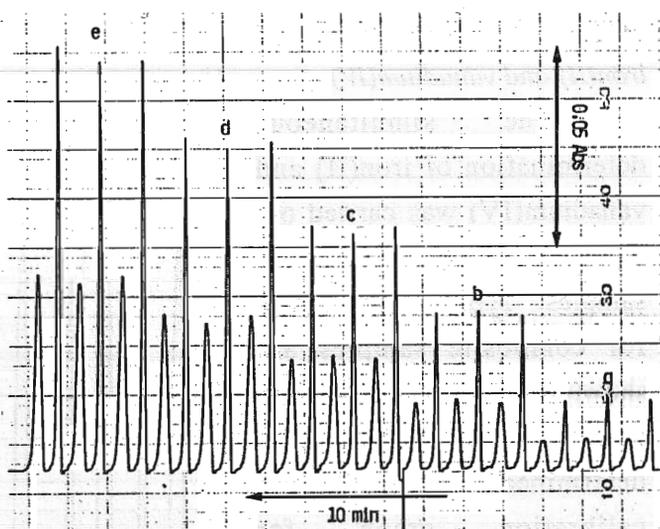


Fig.5 Flow signals for vanadium(IV).

Vanadium(VI) concentrations (mol dm^{-3}): a, 2×10^{-5} ; b, 4×10^{-5} ; c, 6×10^{-5} ; d, 8×10^{-5} ; e, 10×10^{-5} . Conditions as in Fig. 1.

Table 1 Features of the calibration graphs for iron(II) and vanadium(IV)

Sample	Intercept	Slope	Correlation Coefficient
Iron(II)	-0.00094	5.62×10^2	0.999
Vanadium(IV) ^{a)}	-0.00242	11.1×10^2	0.999
Vanadium(IV) ^{b)}	-0.00062	5.25×10^2	0.999

a) The calibration graph obtained from the first peaks.

b) The calibration graph obtained from the second peaks.

Simultaneous determination of iron(II) and vanadium(IV)

The simultaneous determination of iron(II) and vanadium(IV) was carried out by injecting the composite samples. Typical flow signals for composite samples are shown in Fig. 6. From the first peak, vanadium(IV) could be determined by using the first calibration graph for vanadium(IV) in Table 1. Total amounts of iron(II) and vanadium(IV) could be determined from the second peaks in Fig. 6. The absorbance corresponding to the concentration of vanadium(IV) was obtained from the second calibration graph for vanadium(IV) in Table 1. Iron(II) could be determined by

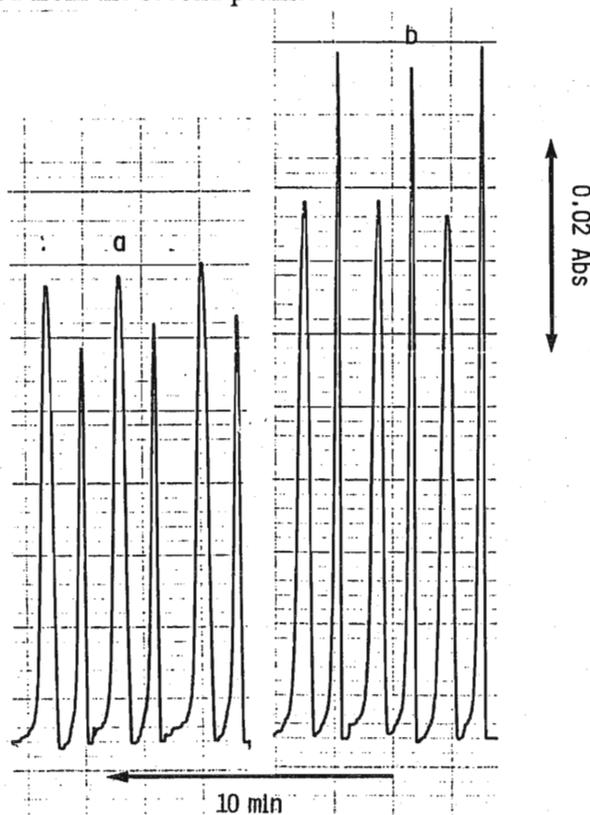


Fig. 6 Flow signals for composite samples of iron(II) and vanadium(IV).

Sample concentrations (mol dm^{-3}): a) iron(II), 5×10^{-5} ; vanadium(IV), 4×10^{-5} . b) iron(II), 4×10^{-5} ; vanadium(IV), 6×10^{-5} . Conditions as in Fig. 1.

subtracting the second peak heights of vanadium(IV) in Fig. 5 from the second peaks in Fig. 6. The results of the fractional determination of iron(II) and vanadium(IV) in the composite samples are presented in Table 2. The relative standard deviations of these ions are less than 1 % ($n = 3$). The recovery of each ion is found to be satisfactory with good precision.

Table 2 Analytical results for simultaneous determination of vanadium(IV) and iron(II) with different $[V(IV)]/[Fe(II)]$ ratios

[V]/[Fe]	added ($\times 10^{-5}$ mol dm $^{-3}$)		found ^{a)} ($\times 10^{-5}$ mol dm $^{-3}$)		rel. error (%)	
	V(IV)	Fe(II)	V(IV)	Fe(II)	V(IV)	Fe(II)
1/1	2.00	2.00	1.93	2.01	-3.5	0.5
1/2	2.00	4.00	2.04	4.05	2.0	1.3
1/3	2.00	6.00	1.96	6.09	-2.0	1.5
1/1	4.00	4.00	3.96	4.00	-1.0	0.0
2/1	4.00	2.00	3.99	2.08	-0.3	4.0
4/5	4.00	5.00	3.91	5.22	-2.3	4.4
3/2	6.00	4.00	6.30	3.79	5.0	-5.3

a) The values are the average of three replicates.

REFERENCES

- 1) M. D. Luque de Castro and M. Valcarcel, *Analyst* [London], **109**, 413 (1984).
- 2) M. D. Luque de Castro, *Talanta*, **33**, 45 (1986).
- 3) S. Kozuka, K. Saito, K. Oguma and R. Kuroda, *Analyst* [London], **115**, 431 (1990).
- 4) T. Yamane and E. Goto, *Anal. Sci.*, **5**, 221 (1989).
- 5) *Idem.*, *ibid.*, **5**, 783 (1989).
- 6) A. T. Faizullah and A. Townshend, *Anal. Chim. Acta*, **167**, 225 (1985).
- 7) T. P. Lynch, N. J. Kernoghan and J. N. Wilson, *Analyst* [London], **109**, 839 (1984).
- 8) *Idem.*, *ibid.*, **109**, 843 (1984).
- 9) E. A. G. Zagatto, A. O. Jacintho, L. C. R. Pessenda, F. J. Krug, B. F. Reis and H.

- Bergamin, *Anal. Chim. Acta*, **125**, 37 (1981).
- 10) H. Wada, T. Murakawa and G. Nakagawa, *ibid.*, **200**, 515 (1987).
 - 11) H. Itabashi, K. Umetsu, K. Satoh and T. Kawashima, *Anal. Sci.*, **6**, 721 (1990).
 - 12) *Idem.*, *ibid.*, **7**, 163 (1991).
 - 13) *Idem.*, *Anal. Lett.*, **24**, 1219 (1991).
 - 14) K. Umetsu, H. Itabashi, K. Satoh and T. Kawashima, *Anal. Sci.*, **7**, 115 (1991).

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