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Simultaneous Flow Injection Determination of Vanadium(IV) and (V) Based on Redox Reactions of Vanadium(IV) with Iron(III) and Vanadium(V) with Iron(II) in the Presence of 1,10-Phenanthroline and Diphosphate

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A new flow injection analysis (FIA) method is presented for simultaneous determinations of vanadium (IV) and vanadium(V) with photometric detection. It is based on redox reactions of vanadium(IV) with iron(III) and vanadium(V) with iron(II) in the presence of 1,10-phenanthroline (phen) and diphosphate (pyrophosphate), respectively. The proposed method makes it possible to appear both positive and negative FIA peaks corresponding to the concentrations of vanadium(IV) and vanadium(V) alternatively.

In a redox reaction of metal ions, the presence of complexing agent modifies the potential of a redox system.1) By using this phenomenon, we have developed new methods for the potentiometric determination of chromium(VI) with iron(II),2) copper(II) with iron(II)2) and vanadium(V) with iron(II)3) in the presence of appropriate complexing agents. The flow injection analysis (FIA) methods for the determination of iron(II)4) and vanadium(IV)5) were also presented with photometric detection and were also developed for the determination of complexing agents such as ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA), diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid (DTPA), nitrilotriacetic acid (NTA), diphosphate, etc. by means of ligand effects.6,7) On the basis of this ligand effect, the present paper describes a new simultaneous FIA method for vanadium(IV) and vanadium(V) using redox reactions of vanadium(IV) with iron(III) and vanadium(V) with iron(II). In the presence of 1,10-phenanthroline (phen), iron(III) is reduced easily by vanadium(IV) to iron(II) and this ion reacts with phen to produce a red iron(II)-phen complex (λ_{max} = 510 nm) because the presence of phen causes an increase in the formal potential of the iron(III)/iron(II) system. By measuring the absorbance of the complex at 510 nm, vanadium(IV) can be determined. On the other hand, the potential of the iron(III)/iron(II) system becomes lower than that of the vanadium(V)/vanadium(IV) system in the presence of diphosphate.3) Hence, the oxidation of iron(II) with vanadium(V) takes place easily and the determination of vanadium(V) is possible by using this oxidation reaction. A simultaneous determination of vanadium(IV) and vanadium(V) is developed by using both reactions.

A schematic flow diagram for the determination of V(IV) and V(V) is shown in Fig. 1. Two double-plunger micro pumps (Sanuki Kogyo, DM2M-1026) and a double six-way injection valve (Nihon Seimitsu Kagaku, NV-508-12M) were used to assemble the system. The flow lines were made from Teflon tubing (0.5 mm i.d.). The absorbance change was measured at 510 nm with a spectrophotometer

(Soma Kogaku, S-3250) equipped with a 10-mm micro flow cell (8 μl) and recorded on a recorder (Chino, EB 22005). The pH of waste solution was monitored with a Corning Model 12 pH/mV meter.

In the flow system (Fig. 1 (a)), a water carrier solution (C), an acetate buffer solution in reservoir R_1, an equimolar mixture of Fe(II) and Fe(III) in reservoir R_2 and a phen solution in reservoir R_3 are pumped at a flow rate of 1.0 $cm^3\ min^{-1}$. The configuration of the double six-way injection valve (V) is shown in Fig. 1 (b). Before the measurement, a mixed sample solution of 400 μl and a mixture of diphosphate and acetate buffer solution of 100 μl are loaded into SL and RL, respectively. In the absence of V(IV) and/or V(V), the absorbance is kept constant as a result of the complex formation of Fe(II)-phen in the reaction coil RC_2 (2 m long). When a mixed sample solution and a mixture of diphosphate and buffer solution are injected into two separate streams, the former is passed through the coil (C_1, 0.1 m long), while the latter is

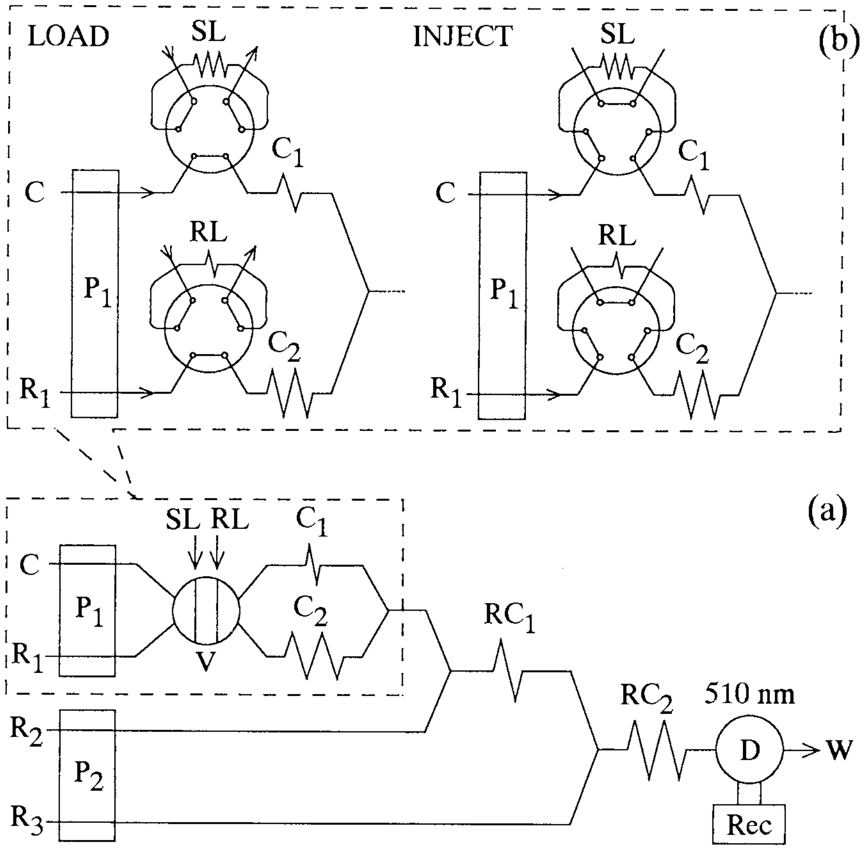

Fig. 1. Flow diagram of FIA for the simultaneous determination of V(IV) and V(V) (a) and configuration of double six-way injection valve (b). C, water; R_1, acetate buffer (5×10^{-2} mol dm^{-3}, pH 5.0); R_2, equimolar mixture of Fe(II) and Fe(III) (5×10^{-5} mol dm^{-3}, respectively); R_3 phen (2×10^{-3} mol dm^{-3}); RL, mixed solution of acetate buffer (5×10^{-2} mol dm^{-3}, pH 5.0) and diphosphate (2×10^{-3} mol dm^{-3}); SL, mixed sample solution (V(IV) and V(V)). The symbols P, V, C_1, C_2, RC, D, Rec and W denote pump, double six-way injection valve , 0.1 m coil, 1.5 m coil, reaction coil, spectrophotometer, recorder and waste, respectively.

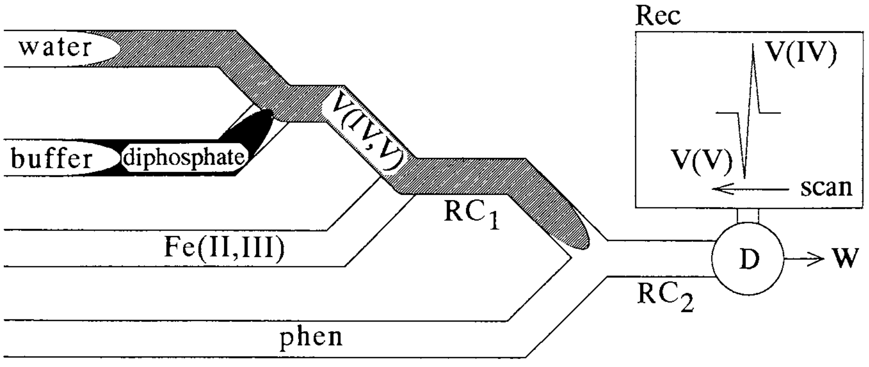

Fig. 2. The situation for zone of mixed sample solution (V(IV,V)) and that of diphosphate solution involving acetate buffer. The symbols RC, D, Rec and W as in Fig. 1.

passed through the coil (C_2, 1.5 m long). The phen stream merges into the front of a mixed sample zone as shown in Fig. 2, and the reduction of Fe(III) with V(IV) proceeds in RC_2. The diphosphate zone merges into the rear of the sample zone, and the oxidation of Fe(II) with V(V) proceeds in RC_1. Both positive FIA peak corresponding to V(IV) and negative one corresponding to V(V) are thus obtained from a single injected sample zone.

To optimize the conditions for simultaneous FIA determination of V(IV) and V(V), individual determinations of V(IV) and V(V) were carried out by using a six-way injection valve (Sanuki Kogyo, SVM-6M2) instead of a double six-way injection valve in Fig 1. In the determination of V(IV), an Fe(III) solution in reservoir R_2 was pumped. In the determination of V(V), a mixture of diphosphate and buffer solution in reservoir R_1 and an Fe(II) solution in reservoir R_2 were pumped. The absorbance at 510 nm showed maximum at pH around 5 for V(IV), while the height of negative peak for V(V) increased with increasing pH up to 2.8, and then decreased gradually in the pH range 2.8 – 5.3, decreasing rapidly beyond pH 5.3. Thus the reaction was carried out in the pH range 4.9–5.1. The FIA peak for V(IV) increased with increasing Fe(III) concentration up to 1.5×10^{-4} mol dm^{-3}, and remained constant in the range 1.5×10^{-4} – 5×10^{-4} mol dm^{-3}. The negative FIA peak for V(V) was maximum and constant over the Fe(II) concentration range 3×10^{-5} – 4×10^{-4} mol dm^{-3}. The baseline, however, became unstable at the Fe(II) concentration range higher than 5×10^{-5} mol dm^{-3} because the absorbance of the reagent blank increased with increasing the concentration of Fe(II) to form intensely colored complex with phen. Hence, a 5×10^{-5} mol dm^{-3} equimolar mixture of Fe(III) and Fe(II) (total concentration of Fe is 1×10^{-4} mol dm^{-3}) was used for the procedure. Maximum and constant FIA peak for V(IV) was obtained over the phen concentration range 2×10^{-4} – 5×10^{-3} mol dm^{-3}. In the determination of V(V), phen used to monitor the decrease in amounts of Fe(II) had no effect on the negative FIA peak over the phen concentration range 1.5×10^{-4} – 5×10^{-3} mol dm^{-3}. A 2×10^{-3} mol dm^{-3} phen concentration was chosen for the procedure. The effect of diphosphate concentration was examined over the concentration range 1×10^{-4} – 5×10^{-3} mol dm^{-3}. The FIA peak for V(V) increased gradually with increasing the concentration of diphosphate up to 2×10^{-3} mol dm^{-3}, and remained constant over the concentration range 2×10^{-3} – 5×10^{-3} mol dm^{-3}. A 2×10^{-3} mol dm^{-3} diphosphate concentration was selected. Using a double six-way injection valve as shown in Fig. 1, the optimum lengths of reaction coils (RC_1 and RC_2) were determined by injecting a mixed sample solution containing V(IV) and V(V) of 2×10^{-5} mol dm^{-3}, respectively, and/or a mixture of diphosphate and buffer solution in FIA system. The effect of length of RC_1 examined by varying coil length. Maximum and constant positive FIA peak for V(IV) was obtained in the coil length range 0.1 – 2 m. The blank peak increased with increasing the coil length of RC_1 and a 0.2 m length of RC_1 was selected for the procedure in considering the small peak height. Maximum and constant positive FIA peak was obtained in the coil length range (RC_2) 0.8 – 2 m, while negative peak decreased gradually with increasing the coil length. A 2 m length of RC_2 was selected for the procedure since more than 2 m length was needed to get a stable baseline. Peak heights decreased gradually when both the coil lengths of RC_1 and RC_2 were further increased, because of increasing dispersion of the sample.

According to the conditions established, equimolar mixed sample solutions of V(IV) and V(V) were prepared and injected to obtain calibration graphs. Typical flow signals are shown in Fig. 3. The linear calibration graphs were obtained over the range 2×10^{-6} – 2×10^{-5} mol dm^{-3} V(IV) and V(V), respectively. The reproducibility of the proposed method is satisfactory with low relative standard deviations (r.s.d.) for ten determinations. The r.s.d. (%) and features of the calibration graphs for V(IV) and V(V) are summarized in Table 1. A sample frequency of 30 h^{-1} was attained for V(IV) and V(V), respectively.

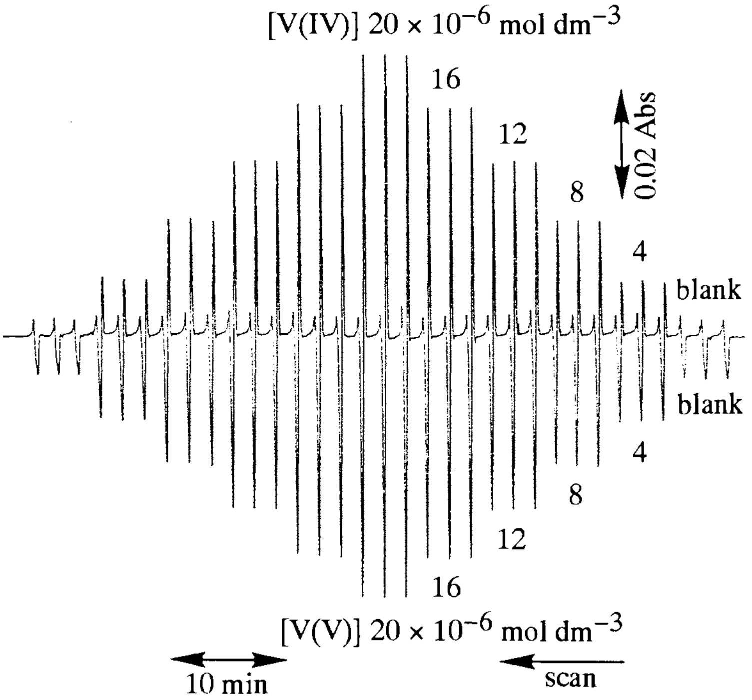

Fig. 3. Flow signals for the simultaneous determination of V(IV) and V(V). Conditions as in Fig. 1.

Table 1. Features of the calibration graphs

Sample	Intercept	Slope	Correlation coefficient	r.s.d./% (n = 10)
Vanadium(IV)	0.000443	2.62×10^3	0.999	1.7,[a] 0.95[b]
Vanadium(V)	-0.000031	2.03×10^3	0.999	2.5,[a] 1.1[b]

a) Concentration of sample was 4 x 10^{-6} mol dm^{-3}.
b) Concentration of sample was 8 x 10^{-6} mol dm^{-3}.

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