Successive Flow-injection Determination of Iron(III) and Copper(II) by Means of the Effect of Activators

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A novel flow-injection (FI) photometric method has been proposed for the successive determination of iron(III) and copper(II). It is based on the effect of activators such as 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline (neocuproine) on iron- and copper-catalyzed oxidative coupling of *p*-anisidine with *N*,*N*-dimethylaniline in the presence of hydrogen peroxide. By injecting two activators, alternatively, into the FI system, iron(III) (50 – 200 ng cm^{-3}) and copper(II) (5 – 20 ng cm^{-3}) can be selectively determined.

Kinetic-catalytic methods of analysis based on catalytic reactions have been applied to trace analyses for various elements because of their high sensitivity.[1] One of the possibilities for further increasing the sensitivity of kinetic-catalytic methods is the application of activators on the catalytic effect of metal ion as a catalyst. The use of activators in catalytic methods also permits an improvement in their selectivity.[2] Flow injection analysis (FIA) has been recognized as a suitable device for improving the catalytic methods because the reaction can easily be controlled by fixing the flow rate of solutions and the length of the reaction coil, yielding reproducible mixing.[3]

Iron(III)[4] and copper(II)[5] catalyze the oxidative coupling of *p*-anisidine with *N*,*N*-dimethylaniline (DMA) to form a colored dye (λ_{max} = 735 nm) in the presence of hydrogen peroxide at pH range 3.5 – 4.0. Thus when iron(III) is determined by this indicator reaction, copper(II) causes a serious interference in the absence of suitable masking agent for copper(II), and also iron(III) may cause a positive interference in the determination of copper(II). In the present work, we found that when the Britton-Robinson buffer solution containing acetic, phosphoric and boric acids was used for the pH adjustment, the catalytic action of iron(III) completely disappeared at wide pH range examined (pH 2 – 10), probably because of masking of iron(III) with phosphate. However, the catalytic action of iron(III) appeared again by adding 1,10-phenanthroline (phen) as an activator, *i.e.*, iron(III) showed the catalytic effect on the dye-forming reaction at pH around 2.5 even if the Britton-Robinson buffer was present. Furthermore, we also found that 2,9-dimethyl-1,10-phenanthroline (neocuproine) acted as an effective activator for copper(II) at pH around 2.5, while in the absence of neocuproine copper(II) did not act as a catalyst at this pH. By using these two activators alternatively, iron(III) and copper(II) can selectively be determined. In this paper, a successive flow injection catalytic determination of ng cm^{-3} levels of iron(III) and copper(II) has been developed based on the effect of activators.

A schematic diagram of the flow-injection system used for the determination of iron(III) and copper(II) is shown in Figure 1. Carrier and reagent solutions were propelled by two double-plunger micropumps (Sanuki Kogyo, DMX-2000). All connecting lines and reaction coil were made from 0.5 mm i.d. Teflon tubing. Sample and activator solutions were introduced into the flow-lines by two six-way injection valves (Sanuki Kogyo, SVM-6M2) with loops. The reaction coils of RC_1 and RC_2 were immersed in a circulating thermostated bath (Taiyo Kagaku Kogyo, H-100). A spectrophotometer (Soma Kogaku, S-3250) with a 10-mm micro flow-cell (8 μl) and a recorder (Chino, EB 22005) were used for detecting and recording the absorbance of the reaction product. The pH of the waste solution was measured with a Horiba Model F-8 AT pH/mV meter.

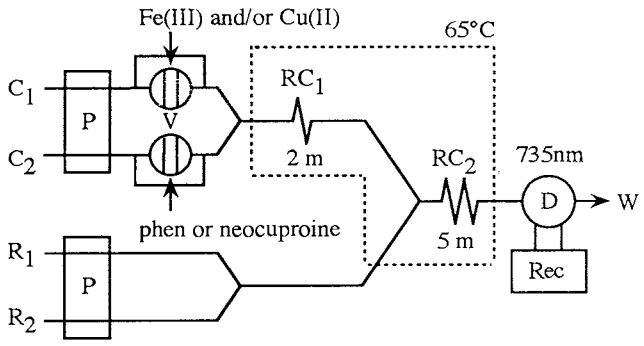

Figure 1. Flow diagram of FIA for the successive determination of iron(III) and copper(II). C_1, 0.01 mol dm^{-3} hydrochloric acid; C_2, water; R_1, mixture of 4×10^{-2} mol dm^{-3} *p*-anisidine and 4×10^{-2} mol dm^{-3} DMA; R_2, mixture of 1 mol dm^{-3} Britton-Robinson buffer and 0.8 mol dm^{-3} hydrogen peroxide; P, micropump; V, loop-valve injector; RC_1 and RC_2, reaction coil; D, spectrophotometer (735 nm); Rec, recorder and W, waste.

As shown in Figure 1, the carrier solutions of C_1 (0.01 mol dm^{-3} hydrochloric acid) and C_2 (water) were pumped into the analytical flow line of RC_1 at a flow rate of 0.43 cm^3 min^{-1}. A mixed solution of *p*-anisidine and DMA in reservoir R_1 and a mixed solution of the Britton-Robinson buffer and hydrogen peroxide in reservoir R_2 were also pumped into the line at the same flow rate. Both mixed solution (370 μl) of iron(III) (0 – 200 ng cm^{-3}) and copper(II) (0 – 20 ng cm^{-3}) and phen solution (5×10^{-3} mol dm^{-3}, 370 μl) were simultaneously introduced into each carrier stream by loop-valve injectors. These two solutions injected were propelled into RC_1 (2 m long); the dye formation catalyzed by iron(III) took place in RC_2 (5 m long) submerged in the thermostated bath at 65.0 ± 0.1 °C. The absorbance of the dye produced was monitored at 735 nm. After the first peak for iron(III) appeared, both the same mixed sample solution and neocuproine solution (2×10^{-3} mol dm^{-3}, 370 μl) were simultaneously introduced: copper(II) catalyzed the dye forming reaction. The absorbance at 735 nm was also monitored. Thus, the concentration of copper(II) can be obtained from the second peak.

The effect of pH of the solution on the dye forming reaction was examined over the pH range 1.7 – 5.7 by injecting a 1 μg cm^{-3} iron(III) and a 1 μg cm^{-3} copper(II) in the presence or absence of phen and neocuproine. The FIA peak for iron(III) was not obtained in the absence of phen and presence of neocuproine over the pH range examined, while in the presence of phen

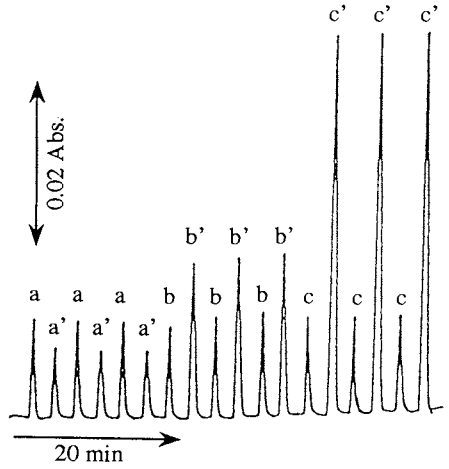

Figure 2. Typical flow signals for iron(III) and copper(II). Concentrations of mixed sample solutions of iron(III)/copper(II) (ng cm^{-3}): (a) and (a'), 100/5; (b) and (b'), 100/10; (c) and (c'), 100/20. Activator: (a), (b), and (c), phen for the catalysis of iron(III); (a'), (b'), and (c'), neocuproine for the catalysis of copper(II). Other conditions as in Figure 1.

maximum peak height was obtained at pH around 2.5. In the absence of any activators the peak for copper(II) was not obtained over the pH range 1.7 – 2.6, while maximum peak height for copper(II) was obtained at pH around 4.9. In the presence of phen copper(II) showed no catalytic effect on the dye forming reaction in the pH range examined. However, in the presence of neocuproine the peak height for copper(II) increased with increasing pH of the solution up to 2.7, and then decreased at higher pH values. Thus at pH around 2.5 iron(III) and copper(II) can be selectively determined by injecting phen or neocuproine solution alternatively.

The effect of phen concentration on the dye forming reaction was examined over the range $5 \times 10^{-4} - 1 \times 10^{-2}$ mol dm^{-3} by injecting a 500 ng cm^{-3} iron(III). The peak height for iron(III) increased with increasing phen concentration up to 5×10^{-3} mol dm^{-3}, gradually decreasing at higher phen concentrations. A 5×10^{-3} mol dm^{-3} phen concentration was selected for the procedure. The effect of neocuproine concentration on the dye forming reaction was also examined over the range $1 \times 10^{-4} - 5 \times 10^{-2}$ mol dm^{-3} by injecting a 10 ng cm^{-3} copper(II). The peak height for copper(II) increased with increasing neocuproine concentration up to 2×10^{-3} mol dm^{-3}, and was almost constant over the range $2 \times 10^{-3} - 5 \times 10^{-3}$ mol dm^{-3}, decreasing at higher neocuproine concentrations. A neocuproine concentration was selected as 2×10^{-3} mol dm^{-3}.

Calibration graphs for iron(III) and copper(II) slightly displayed upward curvature in the ranges 50 – 200 ng cm^{-3} iron(III) and 5 – 20 ng cm^{-3} copper(II), respectively. The repeatability of the method was satisfactory with the relative standard deviations of 2.3 and 1.7 % for ten determinations of 100 ng cm^{-3} iron(III) and 10 ng cm^{-3} copper(II), respectively. Typical flow signals are shown in Figure 2.

The proposed method was applied to the determination of iron and copper in river water as certified reference material (JAC 0032).[6] Before the measurement of the water sample, it was confirmed that foreign ions did not interfere with the determination of iron(III) and copper(II) even when they were present in a 2-fold excess over the individual certified value (Table 1). As shown in Table 2, the analytical results were in good agreement with the certified values of iron and copper.

Table 1. Effect of foreign ions on the determination of 50 ng cm^{-3} iron(III) and 10 ng cm^{-3} copper(II)

Ion added[a] /ng cm^{-3}		Found/ng cm^{-3} Fe	Cu	Ion added[a] /μg cm^{-3}		Found/ng cm^{-3} Fe	Cu
Pb(II)	20	49.2	10.3	K(I)	1	49.9	9.9
Cr(III)	20	47.1	10.1	Na(I)	10	49.9	10.1
Cr(VI)	20	50.6	10.2	Mg(II)	10	50.0	10.0
Cd(II)	2	50.3	10.2	Ca(II)	20	49.1	9.7
Se(IV)	10	50.0	10.1				
As(III)	10	50.6	10.1				
Mn(II)	10	51.8	10.1				
Zn(II)	20	51.2	10.1				
B(III)	100	49.7	10.1				
Al(III)	100	49.7	10.0				
Ni(II)	20	50.0	9.9				

[a]The amount of each ion added to sample solution was about two times excess over the individual certified value.

Table 2. Determination of iron and copper in river water as certified reference material

Fe in sample/ng cm^{-3}		Cu in sample/ng cm^{-3}	
Found[a]	Certified value	Found[a]	Certified value
58.0 ± 1.2	57 ± 2	10.5 ± 0.1	10.5 ± 0.2

[a]Average value for five determinations. The sample solution was diluted 1.1 times before measurement.

References and Notes

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6 The river water sample is issued by the Japan Society for Analytical Chemistry