Investigations on simultaneous determination of silver and mercury in catalytic - ligand substitution reaction with stopped - flow technique calibrated by synergistic effect

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Abstract—The synergistic catalytic effect of silver(I) and mercury(II) on the ligand substitution reaction between hexacyanoferrous (II) $[Fe(CN)_6]^{4-}$ and α, α'- bipyridyl was studied, and a concept of synergistic catalytic coefficient was defined. A kinetic method for simultaneous determination of silver(I) and mercury (II) was proposed based on their catalytic effect and by introducing the synergistic catalytic coefficient into the previously established procedures for the determination of multi - components with stopped flow technique. The linear concentration ranges were enlarged, which are 0—210 ng/ml for Hg(II) and 0—195 ng/ml for Ag (I) in this method with respect to 0—75 ng/ml for Hg(II) and 0—64 ng/ml for Ag(I) in the previous procedure. The detection limits are 0. 4 ng/ml Hg(II) and 0. 75 ng/ml Ag(I), which are also improved with respect to the former procedure. Mercury and silver content in environmental samples were determined, and the results are satisfactory.

Keywords: kinetic stopped FIA; synergistic catalytic coefficient; simultaneous determination; mercury(II); silver(I).

1   Introduction

The determination of trace silver and mercury is more and more important in environmental analytical chemistry. The kinetic procedures had successfully been applied for determining them (Rao, 1988; Velasco, 1990; Chang, 1987; Jiang, 1991; Wu, 1992) but there are serious interferences and the reproducibilities were poor in most cases. Therefore, in the previous papers, we had proposed a stopped FIA kinetic method for simultaneous determination of a ternary mixture without pre - separation based on the principles of inductive or catalytic reactions (Wang, 1993a; 1993b), but the absorbances arising from the catalyzed reaction deviated from additive principles remarkably within certain concentration ranges, owing to the synergistic catalytic effect, the method can only be used within a very narrow concentration range.

In the present paper, we studied the silver(I) and mercury(II) catalyzed hexacyanoferrous (II)- α, α' —bipyridyl ligand substitution kinetic reactions, in which Hg(II) and Ag(I) interfered seriously each other, with thiourea as an activator, by a stopped flow FIA method spectrophotometrically at 536 nm. The concept of synergistic catalytic coefficient (D) was defined, and a

method for simultaneous determination of a binary mixture in kinetic reactions with synergistic effect was proposed, by introducing the coefficient D into the reaction systems. The deviation of absorbance from additive principles was effectively eliminated , the linear ranges of concentration were enlarged, and the sensitivities were improved.

2 Experimental

2.1 Reagents

Mercury(II) stock solution (5 μg/ml): Dissolve 0.0416 g 2Hg(NO$_3$)$_2$·H$_2$O in 250 ml water to obtain a stock solution of 100 μg/ml. Working solutions of different concentration were prepared by appropriate dilution with water of pH 3.2.

Silver (I) stock solution: Dissolve 0.0787 g of AgNO$_3$ in 100 ml water to give a 500 μg/ml stock solution. Working solutions of 5 μg/ml was prepared by dilution with water of pH 3.2. The solution was stored in brown flask.

Hexacyanoferrous(II) solution: Dissolve 4.220 g of K$_4$[Fe(CN)$_6$]. 3H$_2$O in 250 ml water, and a stock solution of 4.0 x 10^{-2} mol/L was obtained. Working solutions were prepared by appropriate dilution with distilled water of pH 3.2.

α,α'- bipyridyl solution (5.0 $\times$ 10^{-3} mol/L): 0.1953 g of α,α'- bipyridyl was dissolved in 5 ml of alcohol, diluted to 250 ml with water and adjusted to pH 3.2.

Thiourea solution: 3.0 $\times$ 10^{-2} mol/L , pH 3.2.

Buffer solution: pH 3.2.

All solution were prepared with AR grade chemicals and redistilled water.

2.2 Apparatus

The reaction rate was followed at 536 nm on a 721 spectrophotometer (The Third Analytical Instrument Factory, Shanghai), which was equipped with a 10 μl flow cell, connected to a Syntone FIA -2400 analyzer (Syntone Scientific Instrument LTD, Beijing) with two peristaltic pumps of 10 channels and controlled by a computer. The sample solutions were introduced via a 16- ways injection valve with a sample loop of 30 μl. The temperature was controlled with a Syntone FIA - T01 and a JY -501B type thermostat, and pH was measured on a PXS -5 type pH
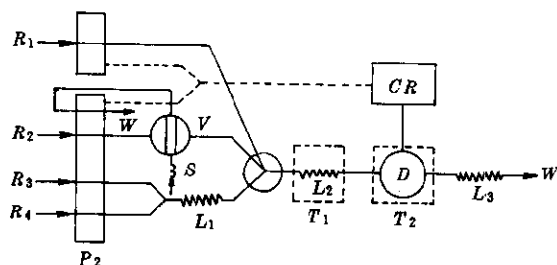

Fig. 1   The sketch of manifold used in the determinations

meter. The sketch of manifold used is shown in Fig. 1. The inner diameter of the used Teflon tube was 0.5 mm, and that of back pressure coil is 0.25 mm. The length of mixing coils L_1, L_2 and the back pressure coil L_3 are 150, 200 and 3000 mm, respectively. The flow rate of buffer solution was 2.4 ml/min, and those of α,α'-bipyridyl, hexacyanoferrous(II) and thiourea solutions were both 2.0 ml/min.

2.3 Principles of simultaneous determination

Given a kinetically prohibited reaction, $O_x + Red \longrightarrow P$, and suppose that M_1, M_2 are the catalysts for this reaction. If the interactions or synergistic effects between M_1 and M_2 were not taken into consideration, and with regards to the additive principle at a certain wavelength, the absorbance after time t_1 and t_2, arising from the product or the combination of it with a color reagent, should, according to the previous papers (Wang, 1993a, 1993b, 1994), be represented as:

$$A_{t1} = A_{1M1} + A_{1M2} = k_{11}[M_1]_0 + k_{21}[M_2]_0 + C_1, \tag{1}$$

$$A_{t2} = A_{2M1} + A_{2M2} = k_{12}[M_1]_0 + k_{22}[M_2]_0 + C_2, \tag{2}$$

where $[M_1]_0$ and $[M_2]_0$ are the analytical concentrations of catalysts M_1 and M_2, which remain unchanged during the determinations, C_1 and C_2 are the surplus items due to the intercept of calibration graphs in most actual determinations. The conditional parameters, k_{11}, k_{12}, k_{21} and k_{22} could be determined with the aid of absorbance-concentration curves, in the reaction systems catalyzed by a single catalyst M_1 or M_2.

In most actual determinations, synergistic effects between catalysts result in the deviation of absorbance from additive principles, that is to say, the total absorbance after time t is not equal to the sum of A_{M1} and A_{M2}, i.e. $A_t \neq A_{M1} + A_{M2}$.

Define $D_{1-2} = (A_t - A_2)/A_1$ is the synergistic catalytic coefficient of M_2 upon M_1, and that $D_{2-1} = (A_t - A_1)/A_2$ the synergistic coefficient of M_1 upon M_2, i.e.

$$D_{2-1} A_1 = A_t - A_2 \tag{3}$$

$$D_{1-2} A_2 = A_t - A_1 \tag{4}$$

With $(3) \times D_{1-2}$, we have:

$$D_{1-2} D_{2-1} A_1 = D_{1-2} A_t - D_{1-2} A_2 \tag{5}$$

From $(5) - (4)$, we will receive:

$$D_{1-2}D_{2-1}A_1 = D_{1-2}A_t - A_t + A_1, \text{ i.e. } A_1 = A_t(D_{1-2} - 1)/(D_{1-2}D_{2-1} - 1) \tag{6}$$

By introducing (6) to (4), there is:

$$D_{1-2}A_2 = A_t - A_t(D_{1-2} - 1)/(D_{1-2}D_{2-1} - 1), \text{ i.e. } A_2$$
$$= A_t(D_{2-1} - 1)/(D_{1-2}D_{2-1} - 1) \tag{7}$$

The relationship between total absorbance by considering the synergistic effect (A_t) and the absorbance arriving from the catalyzed reactions of M_1 and M_2 singly $(A_1$ and $A_2)$ could then be expressed as:

$$A_1 + A_2 = A_t(D_{1-2} + D_{2-1} - 2)/(D_{1-2}D_{2-1} - 1) \tag{8}$$

By dealing with the total absorbance with (8), the procedures previously established could be used for any type of kinetic reactions with synergistic effect or any other similar interactions.

The mechanism of hexacyanoferrous (II) - α,α' bipyridyl reaction at the presence of Hg(II) or Ag(I) (represented by M^{n+}) was proposed to be (Jiang, 1991):

$$[Fe(CN)_6]^{4-} + M^{n+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_6 \ldots\ldots M]^{n-4} \leftrightarrow [(CN)_4Fe-(CN)_2-M]^{n-4} \overset{k_2}{\underset{bipy}{\rightarrow \cdots \rightarrow}}$$

$$[Fe(CN)_4 bipy]^{2-} + [M(CN)_2]^{n-2}, [M(CN)_2]^{n-2} + 2H^+ \longrightarrow M^{n+} + 2HCN.$$
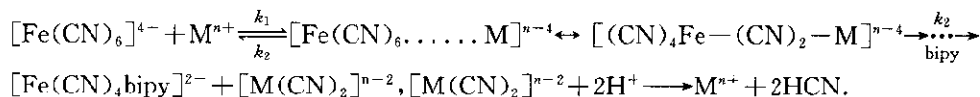
Obviously, Hg(II) or Ag(I) catalyzed the ligand substitutions between hexacyanoferrous (II) and α,α'-bipyridyl, and it is true for these reactions to use the principles of simultaneous determination described above.

3   Results and discussion

3.1   The conditions of determination

Determinations were made in different acidic media, it indicated that HCl will precipitate Ag (I), and HNO_3 or H_2SO_4 are acceptable. In this work, H_2SO_4 is used, and pH 3.2 is chosed in the consideration of enhancing the sensitivities as far as possible for both Hg(II) and Ag(I) determinations.

It has been shown that both the catalyzed and uncatalyzed reactions were accelerated significantly with temperature, and sensitivities were improved. But higher back pressure must be provided in order to prevent the formation of bubbles in the tube, which are difficult to control. So the reaction was carried out at 90°C.

Table 1   The influence of reagent concentrations (50 ng/ml Hg(II); 60 ng/ml Ag(I))

(Concentrations of reagent were multiplied by 10^2)

No.	$Fe(CN)_6^{4-}$, mol/L	Bi-py, mol/L	Thiourea, mol/L	$\sum A_{tj}$ Hg(II) <Ag(I)>	No.	$Fe(CN)_6^{4-}$, mol/L	Bi-py, mol/L	Thiourea, mol/L	$\sum A_{tj}$ Hg(II) <Ag(I)>
1	0.25	0.50	2.00	0.176 <0.0915>	9	0.75	0.50	6.00	0.185 <0.100>
2	0.25	0.75	4.00	0.219 <0.096>	10	0.75	0.75	8.00	0.254 <0.105>
3	0.25	1.00	6.00	0.220 <0.098>	11	0.75	1.00	2.00	0.185 <0.098>
4	0.25	1.25	8.00	0.210 <0.098>	12	0.75	1.25	4.00	0.285 <0.202>
5	0.50	0.50	4.00	0.203 <0.128>	13	1.00	0.50	8.00	0.087 <0.038>
6	0.50	0.75	6.00	0.235 <0.182>	14	1.00	0.75	2.00	0.100 <0.102>
7	0.50	1.00	8.00	0.257 <0.174>	15	1.00	1.00	4.00	0.152 <0.128>
8	0.50	1.25	2.00	0.227 <0.146>	16	1.00	1.25	6.00	0.205 <0.131>

The sensitivities were also improved with stopped time. The flow was stopped 200 s from

the injection of sample solution, with the consideration of only increasing the sampling rate, and the sensitivities were high enough under the conditions established.

In order to determine the optimal concentrations of reagents, a series of experiments were made under fixed temperature (90°C), stopped time (200 s) and pH 3. 2, from which the optimal concentration ranges of α, α'- bipyridyl, hexacyanoferrous (II) and thiourea were obtained. An orthogonal squares experiment was then carried out within the above ranges, and the results are summarized in Table 1. It is obvious that higher sensitivities for both mercury (II) and silver (I) determinations will be obtained under the experimental conditions of number 6, 7 and 12. It had also shown that the blank of number 12 was too high to give good reproducibilities. The conditions of number 6 were then chosen for determinations, i. e. $[Fe(CN)_6]^{4-} = 5. 0 \times 10^{-4}$ mol/L, $[bi - py] = 7. 5 \times 10^{-4}$ mol/L, and $[thiourea] = 6. 0 \times 10^{-3}$ mol/L.

3. 2   Investigations on the synergistic effect between Hg(II) and Ag(I)

The synergistic catalytic effect between mercury (II) and silver (I) on the α, α'- bipyridyl - hexacyanoferrous (II) ligand substitution reaction was studied within different concentration ranges at the optimal conditions established above. The coefficients of 100 s are listed in Table 2 and Table 3.

Table 2   Synergistic coefficient at $t = 100$ s, with Hg^{2+} concentration fixed

$$(D_1 = (A - A_{Hg}/A_{Ag}); D_2 = (A - A_{Ag})/A_{Hg})$$

Ag(I) concentration,	50 ng/ml Hg(II)		100 ng/ml Hg(II)		150 ng/ml Hg(II)		200 ng/ml Hg(II)	
ng/ml	D_1	D_2	D_1	D_2	D_1	D_2	D_1	D_2
10	1. 463	1. 567	1. 256	1. 373	1. 128	1. 262	1. 068	1. 164
30	1. 297	1. 346	1. 131	1. 154	1. 086	1. 148	0. 969	1. 021
50	1. 209	1. 168	1. 087	1. 104	1. 007	1. 063	0. 955	0. 980
70	1. 108	1. 045	1. 003	0. 994	0. 987	0. 972	0. 938	0. 906
90	1. 067	0. 971	0. 969	0. 964	0. 943	0. 916	0. 894	0. 863
110 .	0. 984	0. 967	0. 958	0. 956	0. 925	0. 909	0. 892	0. 855
130	0. 973	0. 962	0. 951	0. 950	0. 913	0. 896	0. 879	0. 845
150	0. 967	0. 953	0. 944	0. 938	0. 895	0. 872	0. 864	0. 832
170	0. 938	0. 927	0. 924	0. 916	0. 859	0. 848	0. 825	0. 814
190	0. 929	0. 916	0. 917	0. 908	0. 847	0. 836	0. 813	0. 792
210	0. 893	0. 887	0. 888	0. 875	0. 819	0. 825	0. 800	0. 778
230	0. 878	0. 873	0. 867	0. 856	0. 861	0. 812	0. 786	0. 761
250	0. 852	0. 857	0. 833	0. 825	0. 785	0. 778	0. 745	0. 733

It is obvious that under certain concentration ranges, the mutual inhibit effect between Hg (II) and Ag(I) was enhanced with the increase of their concentration and consequently, the synergistic catalytic coefficient was decreased. The coefficient, D, is greater than 1 with low concentrations of Hg(II) and Ag(I), and smaller than 1 with higher concentrations of them. D is only close to unity within a quite narrow concentration ranges, and only within this limited ranges, the additive principle of absorbance could be used directly.

On the other hand, the results listed in Table 2 and Table 3 also show that within certain

Table 3   Synergistic coefficient at $t=100$ s, with Ag^+ concentration fixed

$$[D_1 = (A-A_{Hg})/A_{Ag}; \quad D_2 = (A-A_{Ag})/A_{Hg}]$$

Hg(II) concentration,	50 ng/ml Ag(I)		100 ng/ml Ag(I)		150 ng/ml Ag(I)	
ng/ml	D_1	D_2	D_1	D_2	D_1	D_2
20	1.385	1.402	1.214	1.108	1.045	0.987
40	1.254	1.208	1.106	0.991	0.972	0.958
60	1.158	1.134	1.034	0.980	0.964	0.950
80	1.131	1.116	1.001	0.968	0.956	0.944
100	1.092	1.108	0.968	0.962	0.940	0.937
120	1.070	1.081	0.951	0.934	0.922	0.905
140	1.051	1.058	0.938	0.915	0.901	0.881
160	0.992	0.987	0.923	0.906	0.889	0.866
180	0.980	0.964	0.910	0.885	0.880	0.855
200	0.961	0.938	0.887	0.856	0.860	0.841
220	0.945	0.912	0.867	0.835	0.842	0.810
240	0.920	0.898	0.836	0.807	0.812	0.785

ranges of different concentration scopes (rather limited), the variations of synergistic coefficient D is small, so the total absorbance of a given kinetic reaction systems with two catalysts (or a binary mixture) could be calibrated with Formula(8), by introducing coefficient D into the specific kinetic reaction. The additive principle of absorbance could then be applied within a larger concentration ranges, the binary mixture could be determined directly within the same scope, and the sensitivities might also be improved.

3.3   The calibrations and interferences

The linear relationships between absorbance (with respect to the blank) and Hg(II) or Ag(I) concentrations, after 100 s and 200 s from the injection of sample solutions, are obtained as follows:

$$A_t^0(100) = 3.488\, C_{Hg}(\mu g/ml) + 1.211\, C_{Ag}(\mu g/ml) + 0.0010, \tag{9}$$

$$A_t^0(200) = 5.502\, C_{Hg}(\mu g/ml) + 1.722\, C_{Ag}(\mu g/ml) + 0.0003. \tag{10}$$

Where $A_t^0(100)$ and $A_t^0(200)$ represent the absorbance in the systems without synergistic effect. i.e. in the cases that there is no deviation from additive principle of absorbance. The conditional parameters were determined in the reaction systems catalyzed by Hg(II) or Ag(I) only, within the ranges of $0-210$ ng/ml Hg(II) and $0-195$ ng/ml Ag(I).

In the actual determinations, the determined total absorbance, $A_t(100)$ and $A_t(200)$ were calibrated according to Formula (8), before it replace $A_t^0(100)$ and $A_t^0(200)$ in Formula (9) and (10) for calculation. Obviously, in most actual cases, the concentration of analytes (mercury and silver) are not known in advance, and the coefficient D is not a constant between time interval of $100\ s-200\ s$ or within different concentration ranges. We can first use equations (1) and (2) to obtain the approximate concentration of analytes, and according to which the appropriate value of D was chosen from Table 2 and Table 3 for further calculations. In more accurate determinations, the value of D could be chose again according to the secondly calculated concentrations of analytes.

The results of interfering experiments are listed in Table 4, showing that all species that

form a stable coordinating compound or a precipitate with reagents of reaction systems might influence the determinations, but most are tolerated with concentrations higher than that in environmental samples, only Fe^{2+}, Fe^{3+}, Co^{2+} and Zn^{2+} have small tolerance ratios, and pre - separation procedures are necessary when they are in great excess. The influence of Fe^{2+}, Fe^{3+} and Co^{2+} were eliminated by extracting with 0.1% 8- hydroxyl - quinoline in chloroform, by pre - oxidizing Fe^{2+} to Fe^{3+} with potassium permanganate.

Table 4   The influence of foreign ions on the determination of 50 ng/ml Hg(II) and 60 ng/ml Ag(I)

Ion	Tolerance concentration*	Ion	Tolerance concentration*	Ion	Tolerance concentration*
Al(III)	50	Fe(II)	1	Zn(II)	5
As(III)	500	Mg(II)	150	F^-	100
Ca(II)	100	Mo(VI)	50	Br^-	100
Cd(II)	50	Ni(II)	100	I^-	50
Co(II)	2.5	Pb(II)	25	CO_4^{2-}	200
Cr(III)	100	Mn(II)	20	NO^{s-}	500
Cr(VI)	75	Sn(II)	500	PO_4^{3-}	300
Cu(II)	65	V(V)	100		
Fe(III)	4.2	W(VI)	25		

* : Concentration: μg/ml, within ±5% error

3.4   **Applications of the method**

A synthetic solution was prepared by dissolving known amount of $AgNO_3$ and $2Hg(NO_3)_2 \cdot H_2O$ in appropriate volume of water, and adjusted to pH 3.2. 25 ml wastewater was transferred into a 200 ml flask with 5 ml $H_2SO_4(1+1)$ and 1.5 ml saturated potassium permanganate, the solution was heated to boil for about 2 h, adjusted to pH 4−6 after cooling, and was then extracted with 20 ml 0.1% 8- hydroxyl - quinoline in chloroform for two times to separate the coexisting iron and cobalt. 5% ascorbic acid was dropped until the solution decoloured completely. It was adjusted to pH 3.2, and diluted to 200 ml.

200 ml tap water was concentrated to about 50 ml, and was then treated similarly with wastewater. The solution was diluted to 100 ml.

The contents of mercury(II) and silver(I) in the above samples were then determined with the proposed method, the results are summarized in Table 5.

Table 5   Determination of mercury(II) and silver(I) in wastewater and synthetic sample

Samples	Mercury(II) content*, ng/ml				Silver(I) content*, ng/ml			
	Known	Found	Recoveries,%	R.S.D,%	Known	Found	Recoveries,%	R.S.D,%
Tap water		29.74	104.3/40**	4.6		45.86	97.1/40**	5.0
Wastewater		0.253***	96.7/200**	4.3		0.442***	104.1/200**	3.5
Synthetic sample	40.0	41.54	98.5/40**	3.8	40.0	38.67	102.8/40**	4.1

* : Mean of 11 determinations   ** : The amount added, ng/ml   *** : Concentrations in wastewater, μg/ml

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