Studies on a New Water-Soluble Sulfur-Containing Cellulose Derivative

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SYNOPSIS

A new sulfur-containing cellulose derivative, carboxymethyl cellulose (CMC) xanthate (CMCX), has been prepared by the reaction of CMC with CS_2 in 10–15% NaOH solution for 1 h. Degree of esterification (DE) of the product, determined by UV, may reach 3.3% by mole (or about 1.1% by weight). The product was water soluble. The stability of CMCX has been studied by UV, DSC, and TGA, and it was found that CMCX was more stable in the solid state than in solution. The precipitation of gold ion in dilute solution (10 μg Au · mL^{-1}) by CMCX was very rapid, and the recovery efficiency of gold could reach 96% or higher. The optimum dosage was about 0.1 g CMCX for 10 mL 10 μg Au · mL^{-1} solution. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Since the 1980s, cellulose derivatives with functional groups, such as cotton cellulose xanthate,[1] sulfhydryl cotton[2,3] and chelating cellulose filter,[4,5] and some other functional resins[6-8] have been utilized as ion-exchange materials for separation and concentration of trace precious metal ions or heavy metal ions in analytical chemistry. However, all these cellulose derivatives or other functional resins cannot dissolve in water and can only react with metal ions in heterogeneous systems. These methods are not adequate to treat large amounts of aqueous solution. There are no reports in the literature on the synthesis of water-soluble cellulose derivatives with functional groups, and their applications in separation, concentration, and recovery of precious metal from dilute solution. In this article, a new water-soluble sulfur-containing carboxymethyl cellulose (CMC) derivative, carboxymethyl cellulose xanthate (CMCX), has been prepared by the reaction of CMC with CS_2 in aqueous solution. CMCX can form a complex with gold ion in dilute $AuCl_4^-$ solution. With $CaCl_2$ as a coagulant aid, the complex will precipitate rapidly, and the recovery efficiency of gold can reach 96%. The properties of CMCX, as well as the relationship between preparation condition of CMCX and the recovery efficiency of gold, are also discussed.

EXPERIMENTAL

Preparation of CMCX

Carboxymethyl cellulose (CMC) used in this study was a commercial product obtained from Guangzhou Hong-Guang Chemical Factory. Its degree of substitution (DS, the number of carboxymethyl groups in one glucopyranose unit) was 0.44 determined by conductometric titration.[9] Three grams of CMC was weighed into a 100 mL beaker, and 20 mL of NaOH solution was added. The mixture was stirred for 1 h, and 20 mL CS_2 was added, and stirring was continued. The reaction mixture became two layers after the stirring was stopped. The upper layer liquid was decanted (most of it was CS_2), and the yellowish viscose substance (mainly CMCX and H_2O) was washed several times using 100 mL isopropanol containing 15% distilled water, and dried in vacuum at 50°C.

Characterization of CMCX

Degree of esterification (DE, the number of ~ CSSNa groups in one glucopyranose unit) was

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Table I Molar Absorptivity and Maximum Absorption Wavelength of Some Concerned Compounds[11]

Compounds	Max. Absorption Wavelength (nm)					
	336	303	272	250	226	206.2
CMCX	3,600[a]	17,750			8,920	
Na_2CS_3	18,200	3,440			12,230	
Na_2COS_2		600	10,500	3,250		
Na_2S					7,730	
CS_2						58,624

[a] Determined in this text.

determined by UV spectrum with the use of a Beckman Co. DU-8B UV spectrophotometer.

The stability of CMCX was determined by UV spectrum analysis, by elemental analysis using a 240-C apparatus, by DSC using DSC-2 and by TGA using TGS-2, all purchased from Perkin Elmer Co.
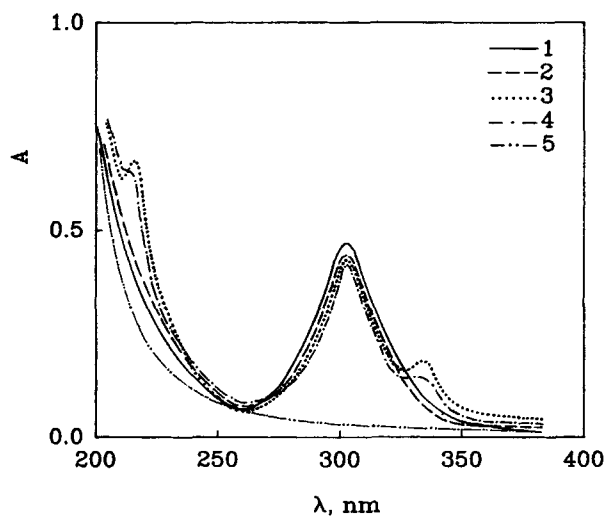
Determination of Gold Concentration and Recovery Efficiency of Gold

Gold concentration was determined by the crystal-violet butyl acetate extraction-photometric method (CV method)[10] as follows: 1 mL of gold-containing solution ($AuCl_4^-$) was measured into a 25 mL color comparison tube along with 5 drops of 30% H_2O_2 and put into a boiling water bath for about 10 min. The solution was diluted to the 10 mL scale with

Figure 1 UV spectra of CMCX and CMC. 1, 2, 3, 4—CMCX samples 1, 2, 3, 4 (see Table II); 5—CMC.

distilled water after cooling to room temperature. Then 5 mL butyl acetate, 2 mL 0.02% crystal violet aqueous solution, and 0.5 mL anhydrous ethyl alcohol were added in sequence, and shaken about 50 times by hand. The tube was left standing until two layers separated clearly and 1 mL of the upper liquid was taken out to determine the absorbance at 600 nm. The gold concentration was obtained from the absorbance according to the calibration curve.

The recovery efficiency of gold was determined as follows: 10 mL of CMCX aqueous solution was measured, the pH was adjusted to about 11 by adding 10% NaOH aqueous solution, and 1 mL of Au(III) aqueous solution ($AuCl_4^-$, 5 ~ 10 μg Au mL^{-1}) and 1 mL of 10% $CaCl_2$ aqueous solution were added. After the mixture was stirred for ca. 1 min, the precipitate was centrifuged. 5 mL of the upper solution was measured, and the pH was adjusted to 1.0 by adding 1N HCl. 1 mL of the solution was taken to detect the gold concentration by the CV method. The recovery efficiency of gold was calculated from the original concentration of gold and that after treatment with CMCX:

$$\text{Recovery}(\%) = \frac{C_0 - C_1}{C_0} \times 100$$

Table II Preparation Condition for CMCX Samples

Sample	[NaOH][a] Wt. %	Reaction Time, Hr.
1	10.0	1
2	10.0	2
3	15.0	2
4	10.0	5

[a] Concentration of NaOH used.

Table III   DE of CMCX and Content of Byproducts

Sample	Total Sulfur[a] S (Wt %)	~ CSSNa		Na$_2$CS$_3$		Na$_2$S[b]	
		DE (mol %)	S (Wt %)	mol %	S (Wt %)	mol %	S (Wt %)
1	2.7	3.3	1.1			3.9	1.6
2	2.4	3.1	1.0			3.4	1.4
3	4.3	3.0	1.0	1.5	0.9	5.8	2.4
4	4.0	3.3	1.1	1.8	1.0	4.7	1.9

[a] Determined by elementary analysis.
[b] Calculated by substrating DE and Na$_2$CS$_3$ from total sulfur.

Where

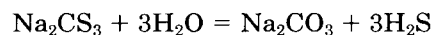C_0—Original gold concentration (μgAu $\cdot$ mL^{-1});

C_1—Gold concentration after treatment with CMCX, the volume variation due to adjusting pH has been taken into consideration, (μg Au $\cdot$ mL^{-1}).

RESULTS AND DISCUSSION

Determination of the Degree of Esterification(DE) in CMCX

It is difficult to determine DE of CMCX accurately, because the reaction between CMC and CS$_2$ is reversible and there are several side reactions as follows:

$$3CS_2 + 6NaOH = Na_2CO_3 + 2Na_2CS_3 + 3H_2O$$

$$Na_2CS_3 + 3H_2O = Na_2CO_3 + 3H_2S$$

$$H_2S + 2NaOH = Na_2S + 2H_2O$$
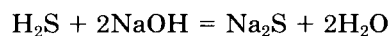
DE of CMCX cannot be determined by iodimetry[11] or by elementary analysis, because it is not easy to extract all sulfur-containing byproducts completely. Since CMCX has strong absorption at 303 nm due to the presence of ~ CSSNa group resulting from the esterification of CMC (Fig. 1), we tried to determine DE with UV spectrum. The molar absorptivity (ε) and maximum absorption wavelength of all concerned compounds are listed in Table I.

Ultraviolet spectra of all samples prepared under different conditions were determined (see Table II), and it was found that the UV spectra could be clas-
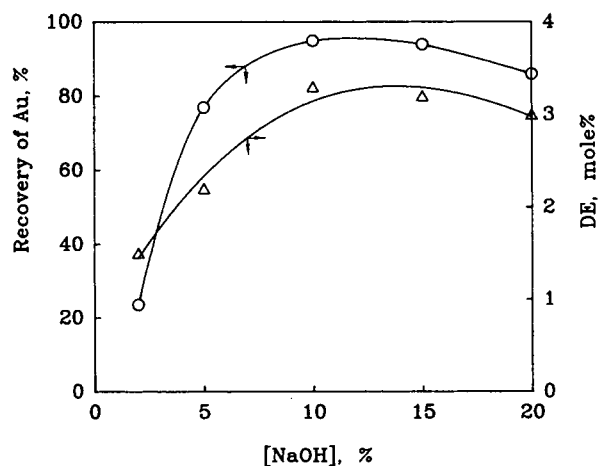
Figure 2   Effect of [NaOH] on DE and the recovery of gold. Time: 1 h, Temp.: 25°C.
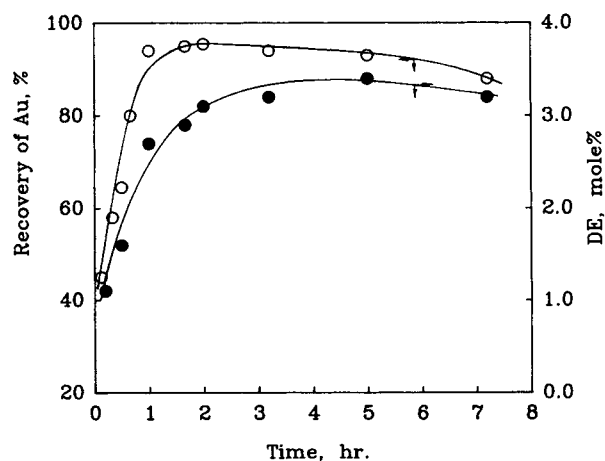
Figure 3   Effect of reaction time on DE and the recovery of gold. [NaOH]: 10 wt %, Temp: 25°C.

Table IV Storage Stability of CMCX^{a,b}

| Time (Days)	Solution		Solid	
	Recovery, %	DE, %	Recovery, %	DE, %
0	96.5	3.3	94.7	3.0
1	80.0	2.5	94.0	—
3	53.0	1.8	93.2	—
5	32.0	1.0	94.0	3.0

[a] Solution sample is stored in aqueous solution, while solid sample is stored in solid state until it is used to determine the recovery of gold and DE.
[b] The dosage of CMCX is 0.1 g for 10 mL 10 μg Au·mL^{-1} gold solution.

sified as two types. Type I (curve 1 and 2 in Fig. 1) has no absorbance peak at 336 nm, indicating that the byproduct Na_2CS_3 in these samples can be neglected. Type II (curve 3 and 4 in Fig. 1) has weak absorbance at 336 nm in addition to the strong absorbance at 303 nm indicating that some Na_2CS_3 may exist. In all curves, no absorbance appears at 272 and 250 nm, indicating that the impurity Na_2COS_2 can be ignored. For type I CMCX, the concentration of the $\sim$ CSSNa group (Cs–s, expressed in mol·mL^{-1}) can be found through the experimental value of the absorbance at 303 nm (A_{303}):

$$\text{Cs–s} = A_{303}/((\varepsilon_{s-s})_{303} \cdot b)$$

where $(\varepsilon_{s-s})_{303} = 17750$ (from Table I) and $b = 1$ cm (thickness of sample cell).
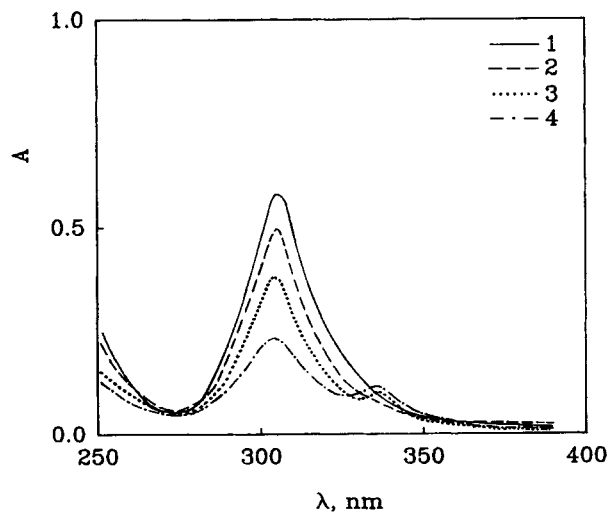
**Figure 4** UV spectra of CMCX solution. 1 = 0 day; 2 = 1 day; 3 = 3 days; 4 = 5 days.
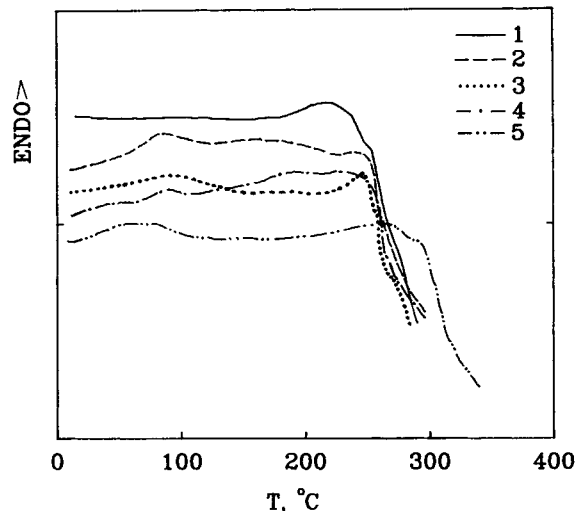
Figure 5 DSC thermograms of CMCX and CMC. 1, 2, 3, 4—CMCX samples 1, 2, 3, 4; 5—CMC.

Also with the known value of Cs–s and the known absorbance at 336 nm (A_{336}), $(\varepsilon_{s-s})_{336}$ can be calculated:

$$(\varepsilon_{s-s})_{336} = A_{336}/(\text{Cs–s} \cdot b)$$

The calculated value of $(\varepsilon_{s-s})_{336}$ is 3600, as shown in Table I.

For type II CMCX, the absorbances at 303 nm and 336 nm are caused by a combination of $\sim$ CSSNa and $\sim$ CS$_3$ groups, from which the corresponding concentrations Cs–s and C_{CS_3} can be found by solving the following simultaneous equations:
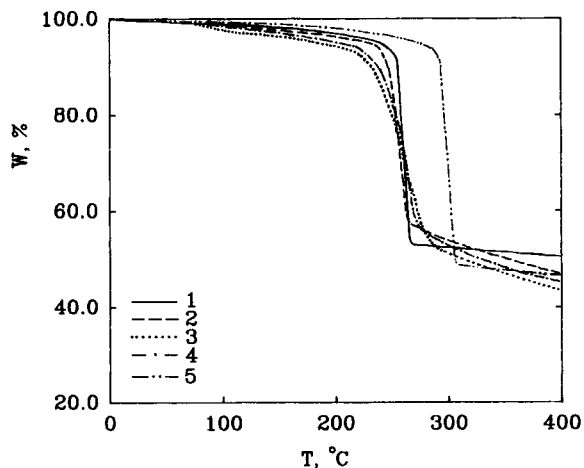
Figure 6 TGA thermograms of CMCX and CMC. 1, 2, 3, 4—CMCX samples 1, 2, 3, 4; 5—CMC.

Table V   Effect of CMC and CaCl$_2$ on the Recovery of Gold by CMCX

Reagent	CMCX	CMCX + CaCl$_2$	CMC	CaCl$_2$	CMC + CaCl$_2$
[Au]^a (μg·mL^{-1})	6.0	1.26	10.0	10.0	9.7
Recovery of Au^b (%)	40.0	87.4	0	0	3.0

Note: (a) [Au] in this table is the residual concentration of gold, and the original concentraiton is 10 μg·mL^{-1}. (b) The reaction time between reagent and AuCl$_4^-$ is about 1 minute.

$$A_{303} = (\varepsilon_{s-s})_{303} \cdot b \cdot \text{Cs-s} + (\varepsilon cs_3)_{303} \cdot b \cdot \text{Ccs}_3$$

$$A_{336} = (\varepsilon_{s-s})_{336} \cdot b \cdot \text{Cs-s} + (\varepsilon cs_3)_{336} \cdot b \cdot \text{Ccs}_3$$

For both types of CMCX, the DE can be obtained by:

$$\text{DE(mole\%)} = \frac{\text{Cs-s}}{W/(Mo \cdot V)} \times 100$$

or expressed in S content (wt %):

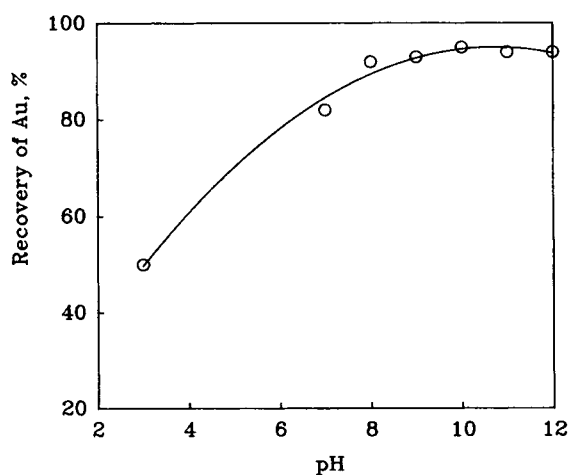$$S(\text{wt \%}) = \frac{\text{Cs-s} \cdot Ms\text{-s}}{W/V} \times 100$$

Where

W is the weight of sample

V is the volume of water used to dissolve the sample

Mo is the average molecular weight of one repeating unit of CMCX, which is nearly the same as that of CMC ($=197.34$)

Ms-s is the molecular weight of s-s ($=64.12$) (in $\sim$ CSSNa)

The content of Na$_2$CS$_3$ can be calculated by:

$$\text{Na}_2\text{CS}_3(\text{mole \%}) = \frac{\text{Ccs}_3}{W/(Mo \cdot V)} \times 100$$

or expressed in S content (Wt %):

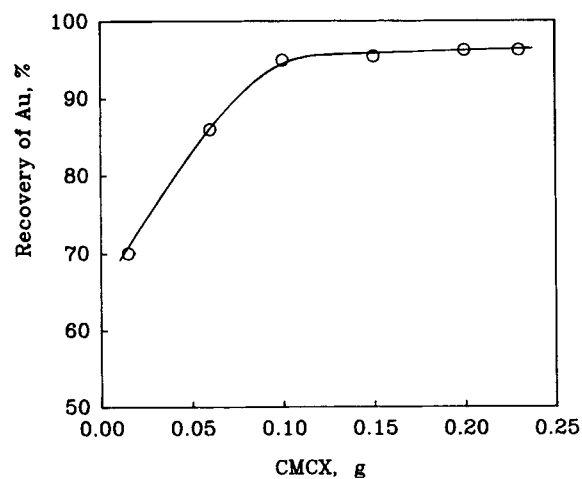$$S(\text{Wt \%}) = \frac{\text{Ccs}_3 \cdot Ms_3}{W/V} \times 100$$

Where Ms_3 is the molecular weight of S_3 in Na$_2$CS$_3$ ($=96.18$).

The results are listed in Table III.

From the above results, it is apparent that increasing the concentration of NaOH from 10 to 15% or increasing the reaction time from 1 to 5 h has little effect on DE, but acts mainly to increase the amount of byproduct Na$_2$CS$_3$.

Effect of Preparation Conditions of CMCX on DE and Recovery Efficiency of Gold

From Figure 2 it can be seen that the optimum concentration of NaOH is about 10–15%, where the

Figure 7   Relationship between pH and recovery of gold. AuCl$_4^-$: 10 μgAu·mL^{-1}, 10 mL; CMCX : 0.1 g; CaCl$_2$: 0.02 g.

Figure 8   Relationship between amount of CMCX added and recovery of gold. AuCl$_4^-$: 10 μgAu·mL^{-1}, 10 mL; CaCl$_2$: 0.02 g.
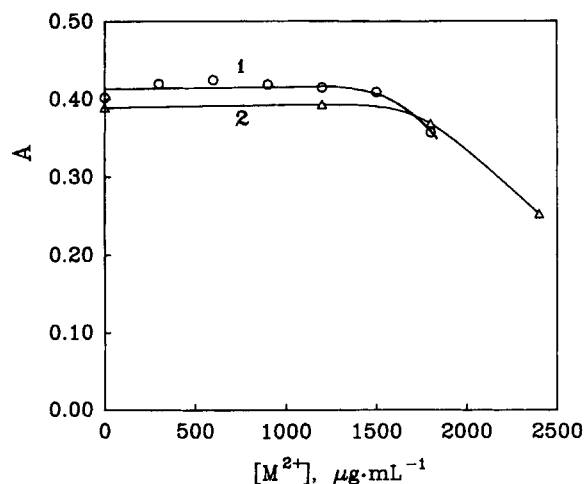
Figure 9 Effect of Cu^{2+} and Zn^{2+} on determining gold by CV method. 1—[Cu^{2+}], 2—[Zn^{2+}], [Au] : 0.5 $\mu gAu \cdot mL^{-1}$.

corresponding recovery of gold can reach 96% or higher. When the concentration of NaOH is too low, fewer —OH groups in CMC are transformed into —ONa, which is unfavorable for the reaction of CMC with CS_2, resulting in the lower DE. If the concentration of NaOH is too high, DE is apparently not affected, but byproduct Na_2CS_3 is increased due to side reactions. As regards the reaction time, the optimum value according to Figure 3 is about 1–2 h.
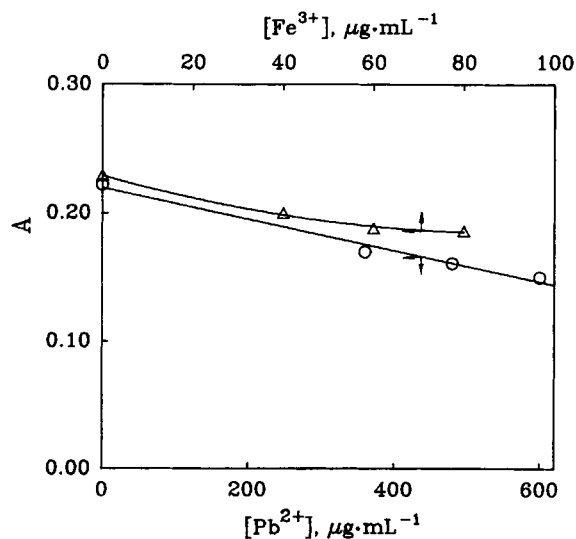
Figure 10 Effect of Fe^{3+} and Pb^{2+} on determining gold by CV method. [Au] : 0.5 $\mu gAu \cdot mL^{-1}$.

Table VI Effect of Other Metal Ions on The Recovery of Gold by CMCX

	None	Cu^{2+}	Zn^{2+}	Fe^{3+}	Pb^{2+}
[M]/[Au][a,b]		3000	3600	40.0	300
Recovery of gold (%)	64.3	85.5	80.7	75.6	75.7

[a] [M] is concentration of other metal ions.
[b] [Au] is 10 $\mu g \cdot mL^{-1}$, and dosage of CMCX is 0.04 g for 10 mL $AuCl_4^-$ solution.

Stability of CMCX

Table IV and Figure 4 show experimental results for the stability of CMCX during storage. It can be seen that CMCX (solid) is more stable than CMCX (solution). For CMCX in aqueous solution, DE and recovery efficiency of gold decrease as the length of time increases. The 303 nm absorbance peak corresponding to the xanthate group is reduced, and a new peak appears at 336 nm corresponding to the byproduct Na_2CS_3 (see Fig. 4). These results indicate that the decrease of DE is attributed to the decomposition of CMCX.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) thermograms of CMCX (solid) are shown in Figures 5 and 6. It is obvious that the thermal stability of CMCX is lower than that of CMC, where the decomposition temperature of the former is about 30°C lower than the latter.

Effect of Coagulation Conditions on the Recovery of Gold

Coagulant Aids

The results listed in Table V show that CMCX can recover Au from solution within 1 min, while CMC or $CaCl_2$ or CMC + $CaCl_2$ cannot. This implies the ~ CSSNa group in CMCX plays a key role in the coagulation of Au. But high efficiency of recovery can be obtained only in the presence of the coagu-

Table VII Adsorption of Gold By Other Metallic Hydroxides

	Cu^{2+}	Zn^{2+}	Fe^{3+}	Pb^{2+}
Recovery of gold (%)	19.9	9.9	11.0	12.0

lation aid $CaCl_2$. In the absence of $CaCl_2$, most of the CMCX-Au complex cannot precipitate due to the low DE of CMCX and the low concentration of Au ions, in the presence of $CaCl_2$, Ca^{2+} can react with $\sim$ COO$^-$ in CMCX to form intermolecular crosslinking,[12] causing rapid precipitation of CMCX-Au complex.

pH Value

The effect of pH on the recovery of gold has been investigated (Fig. 7). When the pH is greater than 9, the recovery of Au is at a maximum and does not change with increasing pH. This is because most — COOH has been transformed into — COO$^-$ and has formed intermolecular crosslinks with Ca^{2+} resulting in nearly complete precipitation of the CMCX-Au complex. In the case of pH < 9, the recovery of Au drops rapidly with decreasing pH owing to the decomposition of CMCX in acid solution.

The Effect of Dosage of CMCX on the Recovery of Gold

From Figure 8, it can be seen that the optimum dosage is 0.1 g CMCX for 10 mL 10 μgAu $\cdot$ mL^{-1} gold solution, wherein the recovery efficiency of gold can reach 96%. When the amount of CMCX added is more than 0.1 g, it does not further increase the recovery efficiency of gold.

Effect of Other Metal Ions

The effect of other metal ions may have two aspects: first is the effect on the accuracy of determining gold based on the CV method, and second is on the recovery efficiency of gold. Four other metal ions, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Fe^{3+}, have been studied. The results indicate that Cu^{2+} up to 1500 μg $\cdot$ mL^{-1} (3000 times [Au]) and Zn^{2+} up to 1800 μg $\cdot$ mL^{-1} (3600 times [Au]) do not show obvious interference in the determining of recovery of gold by the CV method (Fig. 9). For Pb^{2+} up to 150 μg $\cdot$ mL^{-1} (300 times

of [Au]) and Fe^{3+} up to 20 μg $\cdot$ mL^{-1} (40 times of [Au]), the influence is less than 5%. Considering that the gold concentration is low, the result is acceptable (Fig. 10).

It is interesting that the recovery of gold increases in the presence of these four ions as shown in Table VI. Comparison of the data in Table VI and Table VII suggests that the enhancement of gold recovery might be attributed to the adsorption of gold by the precipitates of the metallic hydroxides.

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