

Spectrophotometric Determination of Cadmium and Copper with Ammonium Pyrrolidinedithiocarbamate in Nonionic Tween 80 Micellar Media

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The determination of Cd^{2+} and Cu^{2+} with ammonium pyrrolidinedithiocarbamate (APDC) in Tween 80 micellar media has been studied. The UV-visible spectrum of $\text{Cd}(\text{PDC})_2$ complex in Tween 80 media had more sensitivity than in chloroform. Although the UV-visible spectrum of the $\text{Cu}(\text{PDC})_2$ complex in Tween 80 media had somewhat less sensitivity than that in chloroform, absorbance data of Cu^{2+} were more reproducible in Tween 80 media. The $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ complexes were very stable at pH 7.0 for up to 100 minutes and could be quantitatively chelated if APDC were added to the sample solution more than 30 times the moles of Cd^{2+} and Cu^{2+} . The optimum concentration of Tween 80 was 0.1%. The calibration curves of $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ complexes with good linearity were obtained in 0.1% Tween 80 media. The detection limits of Cd^{2+} and Cu^{2+} were $0.0493 \mu\text{g mL}^{-1}$ and $0.0393 \mu\text{g mL}^{-1}$, respectively. Recovery yields of Cd^{2+} and Cu^{2+} ions in the spiked real samples were almost 100%. Based on experimental results, this proposed method could be applied to the rapid and simple determination of Cd^{2+} and Cu^{2+} in real samples.

Keywords : Micellar media, Tween 80, Ammonium pyrrolidinedithiocarbamate, Stream water, Diluted brass sample.

Introduction

The determination of trace amounts of cadmium and copper has received considerable attention in the battle against environmental pollution. In the determination of cadmium and copper, various methods, including ICP-MS,¹ ion chromatography,² anodic stripping analysis,³ and electrothermal atomic absorption spectrometry,⁴ have been used. Many of these methods either are time-consuming or require complicated and expensive instruments. Therefore, methods that could determine low concentrations of cadmium and copper rapidly and conveniently in real sample were researched.

Although ammonium pyrrolidinedithiocarbamate (APDC) has been used recently in various preconcentration and separation techniques,⁵⁻¹⁰ APDC is most widely used to determine the metal ions, such as Cd^{2+} , Pb^{2+} , Ni^{2+} , Co^{2+} , etc that form slightly soluble complexes in an aqueous solution.¹¹ Usually, metal-APDC complexes are measured by UV-Visible spectrophotometry¹² and flame atomic absorption spectrometry,¹³ after extraction with nonpolar organic solvent.¹⁴ Solvent extraction techniques are time-consuming, tedious and usually involve harmful solvents. However, micellar systems have been conveniently used in UV-Vis spectrophotometry,¹⁵⁻¹⁸ because they are stable in aqueous solution and transparent optically, enhance sensitivity, and readily available.¹⁹



When the concentration of surfactant exceeds the critical micelle concentration, micelles are formed in aqueous solu-

tion. Micelles appear to be homogeneous in aqueous solution.²⁰ In the nonpolar core of micellar media, nonpolar compounds, such as organic molecules or nonionic complexes, are very soluble. Cationic surfactants have been used rather than anionic or nonionic surfactants to determine metal ions by UV-Vis spectrophotometry.²¹⁻²⁵ Because a metal ion is a cation, the electrostatic attractive interaction between a metal ion and cationic surfactant is not present, and the complex-forming process is not affected.

However, a nonionic surfactant with a polyoxyethylene (POE) chain is more soluble in aqueous solution than other nonionic surfactants, and nonionic complexes are easily incorporated in nonionic POE micelle.²⁶ Particularly, with polyoxyethylene (20) sorbitan monooleate (Tween 80) having 20 oxyethylene units, which is more than any other Tween series surfactants, it has a property that causes metal complexes to stabilize.²⁷

In the present study, the determination of cadmium and copper was spectrophotometrically performed with their APDC complexes in Tween 80 media.

Experimental Section

Apparatus. A Hewlett-Packard 8453 UV-Vis spectrophotometer was used to measure the absorbances of $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ complexes. To adjust the pHs and prepare the buffer solution, a Bantex model 300A digital pH meter equipped with a combined glass and calomel electrode was used. To determine Cd^{2+} and Cu^{2+} in real samples, a GBC model 903 flame atomic absorption spectrometer and a HP 4500 ICP-MS spectrometer were used.

Reagents and solution. All chemicals such as $\text{Cd}(\text{NO}_3)_2$ (Aldrich Co.), $\text{Cu}(\text{NO}_3)_2$ (Aldrich Co.), APDC (Fluka Co.),

chloroform (Tedia Co.) and Tween 80 (Osaka Co.) were of analytical or guaranteed-grade reagents. Standard Cd^{2+} and Cu^{2+} solutions were made from $1000 \mu\text{g mL}^{-1}$ stock solutions. A 1.0% (w/v) Tween 80 solution was prepared by dissolving 1.0 g of Tween 80 in a 100 mL volumetric flask with stirring. Phosphate buffer (pH = 7.0) was prepared by appropriately mixing 0.1 M KH_2PO_4 and 0.1 M NaOH. Because APDC slowly decomposes in aqueous solution, 0.1% APDC solution was made whenever needed. Deionized water prepared by a Barnstead cartridge deionization system (Barnstead Co.) was used throughout all experimental procedures.

Absorption spectra of $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ in Tween 80 media and in chloroform. After 1.0 mL of $10.0 \mu\text{g mL}^{-1}$ Cd^{2+} solution, 1.0 mL of 1.0% Tween 80 and 0.5 mL of 0.1% APDC solution were transferred to a 10 mL volumetric flask and diluted to the mark with phosphate buffer (pH = 7.0), the absorption spectrum of this complex was obtained.

1.0 mL of $10.0 \mu\text{g mL}^{-1}$ Cd^{2+} solution and 0.5 mL of 0.1% APDC solution were added to another 10 mL volumetric flask and diluted with phosphate buffer. This solution and 10 mL of chloroform were transferred to a 100 mL separatory funnel, and the metal complex was extracted. The absorption spectrum of $\text{Cd}(\text{PDC})_2$ complex was then obtained.

For Cu^{2+} , the experimental procedures were the same as those of Cd^{2+} .

Application to real samples. Standard Cd^{2+} and Cu^{2+} solutions were prepared in the range of 0.5 – $2.5 \mu\text{g mL}^{-1}$ in 10 mL volumetric flasks. 0.1% APDC and 1.0% Tween 80 were added to each standard solution of Cd^{2+} and Cu^{2+} in the amount of 0.5 mL and 1.0 mL, respectively. The solutions were then filled with phosphate buffer. After standing for 20 minutes, calibration curves of Cd^{2+} and Cu^{2+} were constructed by a UV-Vis spectrophotometer.

The brass sample was cleaned with acetone and deionized water and dried off. The brass sample weighing 1.0000 g was taken to a 250 mL beaker, and 15 mL of c- HNO_3 and 25 mL of deionized water were added. After it was dissolved completely by a short heating, the sample solution was carefully transferred to a 1000 mL volumetric flask and diluted to the mark with deionized water. A 1.0 mL of aliquot of brass solution was diluted further to 1000 mL in a volumetric flask with deionized water. This diluted brass sample was used as a real sample.

Water from a stream in Suwon, Korea was taken after suspended matter or particles were filtered out with a glass filter (I-G-4). To investigate the recovery yield of Cu^{2+} in the stream water, 5.0 mL of the water was transferred to each of three 10 mL volumetric flasks, 0.0 mL, 0.5 mL, 1.0 mL of $10 \mu\text{g mL}^{-1}$ Cu^{2+} standard solutions was added to each flask. The other procedures followed the absorption spectra procedures in Tween 80 media. For Cd^{2+} in stream water and Cu^{2+} in diluted brass sample, the experimental procedures were the same as those for stream water.

Results and Discussion

Absorption spectra of $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ in Tween

80 media and in chloroform. The micelle of Tween 80 with the polyoxyethylene group comprises two parts. One part is the hydrocarbon tail directed to the interior core of the micelle and the other is the hydrated polyoxyethylene group located at the outer sphere. Organic compounds and metal chelates that have a large affinity for the polyoxyethylene group may be incorporated into this area.²⁶ $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ complexes could be dissolved by this phenomenon.

The absorption spectra of $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ complexes in 0.1% Tween 80 and in chloroform are shown in Figure 1. The maximum wavelength of Cd^{2+} complex appeared at 323 nm in 0.1% Tween 80, and 308 nm in chloroform. The absorbance measured in 0.1% Tween 80 was about three times the absorbance in chloroform. The maximum wavelength of the Cu^{2+} complex in Tween 80 media appeared at 299 nm, but owing to narrow peak width, the absorbance could not be reproducibly measured. The absorbance of the second peak at 445 nm in Tween 80 media was somewhat less than it was in chloroform, but it was more reproducibly measurable than in chloroform. Thus, the sensitivity enhancement in Tween 80 could be a result of the very strong association of complex to micelles by both electrostatic and hydrophobic interaction.²⁸

pH. The effect of pH on the absorbances of $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ in 0.1% Tween 80 media was investigated and is shown in Figure 2. For both Cd^{2+} and Cu^{2+} , there was little difference in pHs ranging from 1.0 to 10.0. It is known that $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ complexes are well formed in wide pH ranges and well dissolved in 0.1% Tween 80. But, as APDC decomposes in acidic solutions²⁹ and is likely to form metal hydroxide precipitate in basic solutions, pH 7.0 was chosen for the present experiment.

Amount of APDC. It is known that Cd^{2+} and Cu^{2+} are stoichiometrically combined with APDC to form 1 : 2 complexes.¹² For metal complexes to be formed quantitatively, however, one must add more chelating agent to the sample solution. Figure 3 shows how the absorbances of $\text{Cd}(\text{PDC})_2$

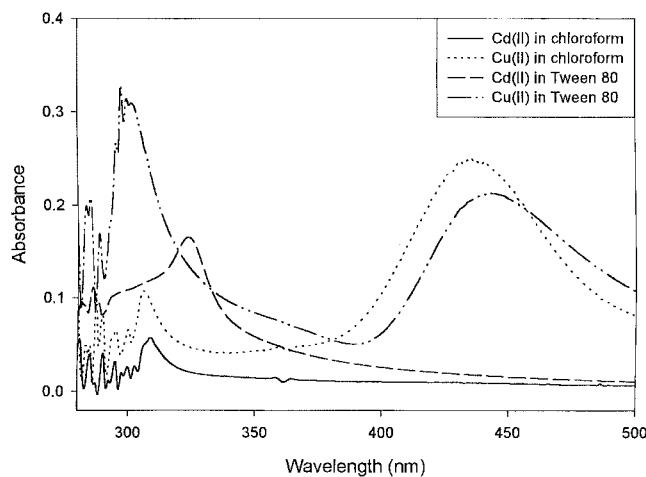


Figure 1. Absorption spectra of $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ ($1.0 \mu\text{g mL}^{-1}$) complexes in chloroform and Tween 80 media.

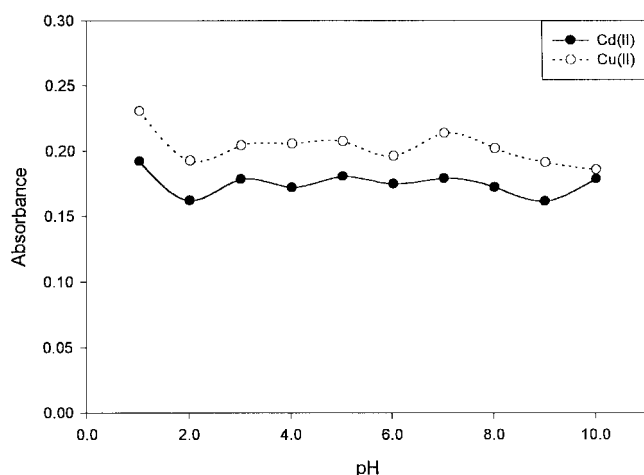


Figure 2. Effect of pH on the determination of Cd^{2+} and Cu^{2+} ($1.0 \mu\text{g mL}^{-1}$) in Tween 80 media.

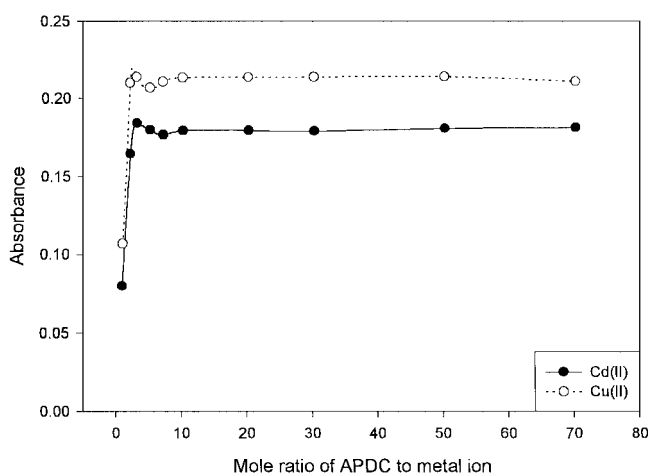


Figure 3. Effect of amount of APDC on the absorbance of its Cd^{2+} and Cu^{2+} ($1.0 \mu\text{g mL}^{-1}$) complexes in Tween 80 media.

and $\text{Cu}(\text{PDC})_2$ complexes changes with the amount of APDC. APDC could be quantitatively chelated with the addition of three times the amount of Cd^{2+} or Cu^{2+} . Since the absorbances of APDC complexes fluctuated to some degree with the addition of less than 10 times Cd^{2+} or Cu^{2+} , APDC was added at 30 times the metal ions in the present experiment.

Concentration of Tween 80. When the concentration of Tween 80 surfactant exceeds its critical micelle concentration, the homogeneous micelle solution is formed at a point where the $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ complexes can be well dissolved. As the concentration of surfactant increases, more micelles are formed, and more nonpolar complexes will be contained in the micelles. Due to high viscosity, the concentrated Tween 80 media was hard to handle, whereas those with low viscosity under diluted conditions could not form a micelle. With the concentration of Tween 80 varying from 0.01% to 2.0%, the absorbances of Cd^{2+} and Cu^{2+} complexes were investigated and are shown in Figure 4. In this concentration range, the absorbances of APDC complexes were almost constant. It also appears that the micelle in solution

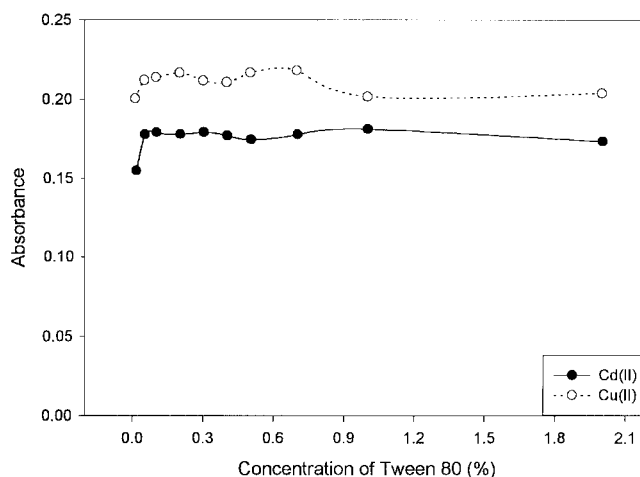


Figure 4. Effect of concentration of Tween 80 on the determination of Cd^{2+} and Cu^{2+} ($1.0 \mu\text{g mL}^{-1}$).

was formed because these concentrations of Tween 80 were above critical micelle concentration ($0.0013\% \text{ w/v}$)³⁰ and the $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ complexes were well incorporated in the polyoxyethylene region. Here, 0.1% Tween 80 was used as a suitable concentration.

Stability of $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$. The decomposition rate of the metal-APDC complexes as well as APDC depends upon pH and time.³¹ These compounds were unstable especially in an acidic solution. The stability of the $\text{Cd}(\text{PDC})_2$ and $\text{Cu}(\text{PDC})_2$ complexes by time was investigated at $\text{pH} = 7.0$. Cd complex was observed stable in Tween 80 media for up to 100 minutes. But, the Cu complex was formed in 20 minutes and remained stable for up to 100 minutes. The expected formation mechanism of the APDC complex could be explained by the fact that the dissolution process is dynamic. It seems that APDC combines with metal ion to form a nonpolar complex, and the complex is extracted instantaneously into the local nonpolar environment of micelle. This is the advantage of this method over liquid-liquid extraction, which requires more time.

Interferences. When Cd^{2+} and Cu^{2+} are determined with APDC, the other metal ions in real samples might interfere with Cd and Cu complex-forming. The interfering effects on the determination of Cd^{2+} and Cu^{2+} were investigated under the optimum conditions given above and are shown in Table

Table 1. Effect of foreign ions on the determination of $1.0 \mu\text{g mL}^{-1}$ Cd^{2+} and Cu^{2+}

Tolerance limit ($\mu\text{g mL}^{-1}$) ^a	Cd^{2+}	Cu^{2+}
100	Na^+	K^+ , Mn^{2+} , Na^+ ,
50	Mn^{2+}	Cr^{3+} , Zn^{2+} , Co^{2+}
30	K^+ , Cr^{3+} , Zn^{2+}	Sn^{2+}
10	Cu^{2+} , Sn^{2+}	Al^{3+}
5	Co^{2+} , Fe^{3+} , Pb^{2+}	Fe^{3+} , Pb^{2+}
1	Ni^{2+}	Ni^{2+} , Cd^{2+}

^atolerance limit is the maximum concentration in which there is less than 3% effect on absorbance.

Table 2. Figures of merit for calibration curves of Cd²⁺ and Cu²⁺ in Tween 80 media

	Cd ²⁺	Cu ²⁺
Linear range ($\mu\text{g mL}^{-1}$)	0.30-10.0	0.05-8.0
Regression equation	0.1508x+0.0083	0.2006x+0.0077
Correlation coefficient (R ²)	0.9997	0.9982
Detection limits ($\mu\text{g mL}^{-1}$)	0.0493	0.0393

Table 3. Analytical data of Cd²⁺ and Cu²⁺ in real samples

Real sample	Analyte ion	Spiked ($\mu\text{g mL}^{-1}$)	Measured ($\mu\text{g mL}^{-1}$)			Recovery (%)
			Other method ^a	This method ^b	CV	
Stream water	Cu ²⁺	0.000	0.107	0.112	7.1	
		0.500		0.626	2.6	103
		1.000		1.131	2.4	102
	Cd ²⁺	0.000	8.6×10^{-5}	0.000	—	
		0.500		0.510	2.0	102
		1.000		1.040	2.2	104
Diluted brass sample	Cu ²⁺	0.000	0.664	0.655	3.9	
		0.500		1.147	3.5	98
		1.000		1.624	3.2	97

^aICP-MS data on stream water and flame AAS data on diluted brass sample. ^bthe average values were obtained from seven samples.

1. As for Cd²⁺, Ni²⁺ interfered more seriously than any other ions, and this interference could be completely eliminated by adding 2 mL of 0.1 M EDTA. As for Cu²⁺, Cd²⁺ and Ni²⁺ interfered seriously. This interfering effect was also eliminated by adding 1.0 mL of 0.01 M NaCN.

Applications to brass sample and stream water. The calibration curves of Cd²⁺ and Cu²⁺ were constructed at optimum conditions, according to the procedures described in the experimental section, and their figures of merit are listed in Table 2. The calibration curves showed good linearity. The detection limits³² of Cd²⁺ and Cu²⁺ were 0.0493 $\mu\text{g mL}^{-1}$ and 0.0393 $\mu\text{g mL}^{-1}$, respectively. After a given amount of Cd²⁺ and Cu²⁺ was spiked in the diluted brass sample and stream water, recovery yields were determined using these calibration curves and were found to be nearly 100%. They are listed in Table 3. Cd²⁺ and Cu²⁺ in stream water and Cu²⁺ in diluted brass sample were also determined by ICP-MS and flame AAS, respectively. The results from these techniques are in Table 3, and all data were nearly equal. Therefore, we have concluded that this proposed method could be applied to the determination of Cd²⁺ and Cu²⁺ in real samples.

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