

# Simultaneous determination of copper and cadmium in environmental water and tea samples by adsorptive stripping voltammetry

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A sensitive and selective method for the simultaneous determination of copper and cadmium in seawater, river water, and tea samples is described. The method is based on the adsorptive accumulation of 2,2-dithiosalicylic acid complexes of these elements onto a hanging mercury drop electrode, followed by reduction of adsorbed species by voltammetric scan using differential pulse modulation. Optimal analytical conditions were as follows: ligand concentration of 11 nM, pH of 9.5, and an adsorption potential at -300 mV versus Ag/AgCl, with an accumulation time of 60 s. The peak currents are proportional to the concentration of copper and cadmium over the 1-80 and 1-240 ng mL<sup>-1</sup> ranges with detection limits of 0.5 and 0.3 ng mL<sup>-1</sup>, respectively.

**Key Words:** Copper, cadmium, 2,2-dithiosalicylic acid, stripping voltammetry, seawater, river water, tea

## Introduction

The determination of heavy metals in environmental, biological, and food samples has drawn significant attention due to the toxic and nutritional effects of these elements or their compounds.<sup>1,2</sup> Copper is widely distributed

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in nature and is an essential trace element for humans.<sup>2,3</sup> Copper functions as a cofactor and is required for structural and catalytic properties of a variety of important enzymes, including cytochrome c oxidase, tyrosinase, p-hydroxyphenylpyruvate hydrolase, and dopamine  $\beta$  hydroxylase.<sup>4</sup> Nonetheless, Cu shows some toxicological effects. Food, beverages, and drinking water are potential sources of excess exposure. Daily intake of Cu in adults varies between 0.9 and 2.2 mg. The amount of Cu ingested is relatively low, and most humans are able to control excess amounts of Cu in the body by either decreased absorption or increased excretion.<sup>5</sup> Exposure to elevated concentrations of Cu primarily affects the liver and is typically manifested by the development of liver cirrhosis, episodes of hemolysis, and damage to renal tubules, brain and other organs.<sup>2,6</sup> Cadmium can be accumulated in biological systems, becoming a potential contaminant along the alimentary chain. This element has harmful effects on human health, affecting several organ systems, such as nervous, gastrointestinal, reproductive and skeletal, and biochemical activities.<sup>2,7,8</sup> The need for regular monitoring of trace elements in materials has led to an increasing demand for suitably sensitive and selective analytical methods.<sup>9,10</sup> Recently adsorptive stripping voltammetry has been employed as a powerful technique for determination of ultratrace levels of metals. This method is an extremely sensitive technique that offers low detection limits and is based on adsorptive accumulation of metal ions and suitable complexing agent on the electrode surface while potential is scanned in the negative direction.<sup>11,12</sup> Several organic compounds such as 1-(2-pyridylazo)-2,7-dihydroxynaphthalene,<sup>13</sup> 8-quinolinol,<sup>14</sup> carbamoylphosphonic acid,<sup>15</sup> xylenol orange,<sup>16</sup> and thymolphthaleone<sup>17</sup> have been used as complexing agent for the simultaneous voltammetric determination of copper and cadmium.

The main propose of this work is to describe a sensitive AdCSV procedure for simultaneous determination of copper and cadmium in environmental water and tea samples using dithiosalicylic acid (DTSA) as a complexing agent. This ligand forms a complex with both elements and can be used as an accumulating agent free from interference. This method makes use of a well-defined differential pulse voltammetric reduction peak resulting from stripping of the accumulated Cu and Cd-ligand complex on the mercury drop in the medium. The peak currents were proportional to concentration in  $\text{ng mL}^{-1}$  ranges. This method is reasonably sensitive and therefore has been applied for determination of copper and cadmium in environmental water and tea samples.

## Experimental

### Reagents

All solutions were prepared with deionized water. Nitrogen (99.99%) was used to remove dissolved oxygen. The support electrolyte chosen was a 0.05 M borate buffer solution (pH 9.5) obtained by dissolving adequate quantities of boric acid (analytical-reagent grade, Merck, Darmstadt, Germany) and borax (sodium tetra borate) (analytical-reagent grade, Merck, Darmstadt, Germany) in water. Stock standard solutions of copper ( $1000 \text{ mg L}^{-1}$ ) were prepared by dissolving an adequate amount of  $\text{Cu}(\text{NO}_3)_2$  (reagent grade, Merck, Darmstadt, Germany) in water. Stock standard solutions of cadmium ( $1000 \text{ mg L}^{-1}$ ) were prepared by dissolving an adequate amount of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (reagent grade, Merck, Darmstadt, Germany) in water. Solutions of the chelating agents were prepared by dissolving appropriate quantities of 2,2- dithiosalicylic acid (Merck) in water.

## Apparatus

All polarographic measurements were obtained using a Metrohm multifunction instrument Model 693 VA processor equipped with a 694 VA stand. Measurements were carried out with a hanging mercury drop electrode (HMDE) (drop size 9) in a 3-electrode arrangement. The auxiliary electrode was a wire of platinum with a considerably larger surface area than that of HMDE. A silver-silver chloride (KCl 3 M) electrode was used as the reference. Stirring was carried out with a large Teflon stirring bar at 2000 rpm. A Metrohm-692 digital pH-meter was used for pH measurement. Solutions were purged with high purity nitrogen for 5 min prior to each experiment, which was performed under a nitrogen atmosphere.

## Procedure

Ten milliliters of borax buffer solution (pH 9.5) was pipetted into the voltammetric cell. Then an appropriate volume of DTSA was added, giving a final concentration of 11 nM. The solution was purged with water nitrogen for 5 min in the first cycle and 30 s for each successive cycle. The preconcentration (adsorption) potential ( $-300$  mV) was applied for 60 s to a fresh mercury drop while the solution was stirred. The stirring was stopped for a period of 10 s (equilibration time) and then the potential was scanned from  $+100$  mV toward more negative values using differential pulse (DP) modulation (modulation time, 40 ms; modulation amplitude,  $-50$  mV; interval time, 0.2 s; potential step, 8 mV, resulting in a scan rate of  $40$  mV s $^{-1}$ ). Each scan was repeated 3 times with a new drop for each analyzed solution and the mean of these voltammograms obtained. Cadmium and copper stripping peaks were registered at about  $-8$  mV and  $-685$  mV, respectively, and their currents used as a measure of cadmium and copper concentrations. All experiments were carried out at room temperature.

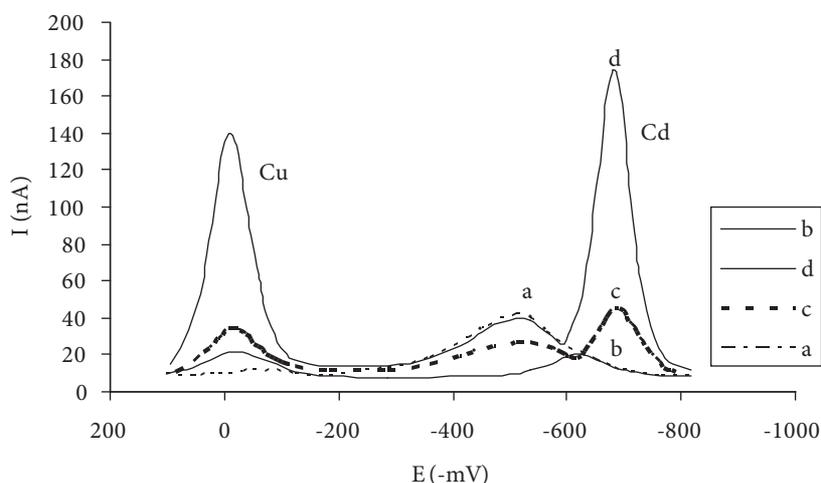
## Result and discussion

### Adsorptive characteristics of the Cu- and Cd-DTSA complexes

Preliminary experiments were carried out to identify the general features that characterize the behavior of the Cu- and Cd-DTSA systems on a mercury electrode. Figure 1 displays differential pulse voltammograms of the copper- and cadmium-DTSA system between 100 and  $-800$  mV (versus Ag/AgCl), in the absence of metal ions (curve a) and DTSA (curve b) after 60 s accumulation at  $-300$  mV. The voltammograms of metal ions in the presence of DTSA after 0 (curve c) and 60 s (curve d) accumulations at  $-300$  mV are also shown. Comparison of the voltammograms shows that the heights of copper and cadmium reduction peaks depend on the duration of the concentration stage and also on the presence or absence of DTSA, which reveals the adsorption nature of the currents.

### Effect of pH

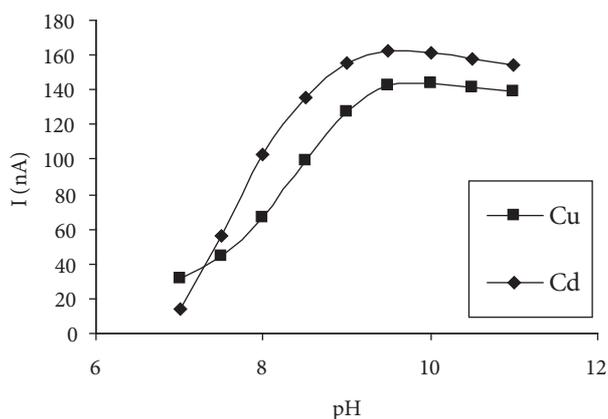
The influence of pH on the cathodic stripping peak currents of copper and cadmium was studied in the pH range of 7.0-11.0 (Figure 2). It was found that at pH 9.5 the peaks current of copper and cadmium were at their maximum values. At pH values lower than 9.5 the peaks current decreased, possibly due to diminished complexation ability of DTSA at such pHs. Thus, pH 9.5 was adopted for further studies.



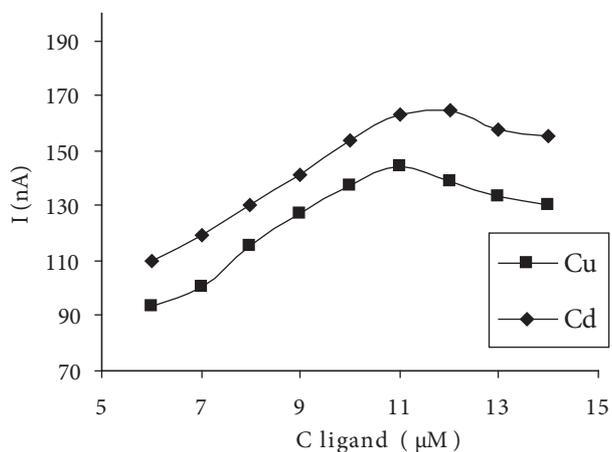
**Figure 1.** Differential pulse voltammograms of: (a) 11 nM of DTSA solution at pH 9.5 after 60 s accumulation time at  $-300$  mV vs. Ag/AgCl reference electrode; (b)  $20 \text{ ng mL}^{-1}$  of copper and  $50 \text{ ng mL}^{-1}$  of cadmium at pH 9.5 after 60 s accumulation time at  $-300$  mV; (c)  $20 \text{ ng mL}^{-1}$  of copper and  $50 \text{ ng mL}^{-1}$  of cadmium and 11 nM of DTSA without accumulation and (d) after 60 s accumulation time.

### Effect of ligand concentration

The effect of DTSA concentration on the sensitivity of the proposed method was also studied. The obtained results (Figure 3) show that the cathodic stripping peak current of Cu- and Cd-DTSA complexes increased with increasing DTSA concentration up to 11 nM. At higher concentrations, peak current decreased with increasing DTSA concentration. The DTSA concentration of 11 nM was selected as the optimum ligand concentration for the determination of both elements.



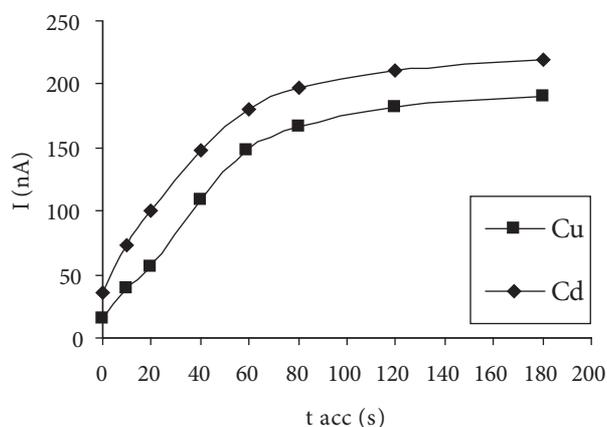
**Figure 2.** Effect of pH test solution on the differential pulse cathodic stripping voltammetric peaks current of  $20 \text{ ng mL}^{-1}$  of copper and  $50 \text{ ng mL}^{-1}$  of cadmium ions and 11 nM of DTSA after 60 s accumulation at  $-300$  mV.



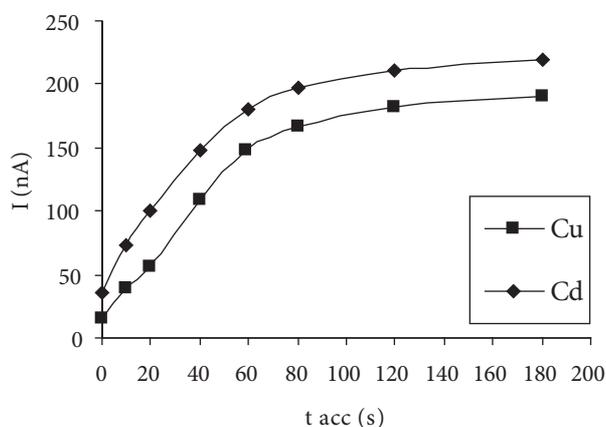
**Figure 3.** Effect of DTSA concentration on the peaks current of metal ions at pH 9.5. Other conditions are as Figure 2.

## Effect of accumulation parameters

The effect of accumulation potential on the stripping peak currents of copper and cadmium complexes with DTSA was examined individually over the potential range of 0 to  $-700$  mV. The plots of stripping peaks current of both metal ions as a function of preconcentration potential are shown in Figure 4. As is obvious, the peak currents of cadmium are independent of accumulation potential at the potential range of  $-200$  to  $-500$  mV, and at potentials more negative than about  $-500$  mV the sensitivity of reduction of cadmium decreased. However, in the case of copper the maximum peak current was achieved at  $-300$  mV. Thus, this accumulation potential was selected for both metal ions. At this potential the copper and cadmium ion complexes were adsorbed on the surface of the mercury drop and the response signals are due to reduction of both metal ion complexes during the cathodic sweep. The influence of accumulation time on the stripping peaks of copper and cadmium was investigated and the results are summarized in Figure 5. As expected for adsorption processes, the dependence of the peak current on the accumulation time is limited by the saturation of the electrode surface, resulting in the current reaching a plateau at high accumulation times, as shown in Figure 5. Thus, a deposition time of 60 s was used throughout, as it combines good sensitivity and relatively short analysis time.



**Figure 4.** Effect of accumulation potential on the peak currents of  $20 \text{ ng mL}^{-1}$  of copper and  $50 \text{ ng mL}^{-1}$  of cadmium at pH 9.5. Other conditions are as Figure 2.

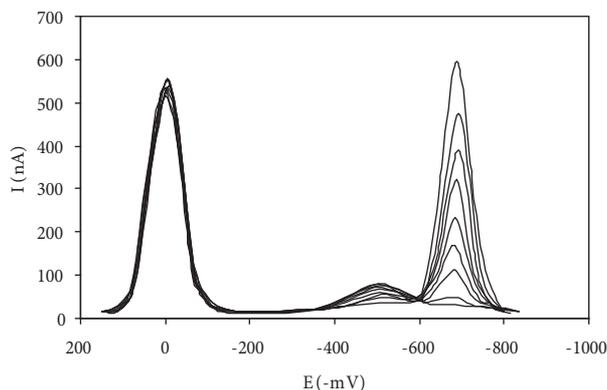


**Figure 5.** Effect of accumulation time on the current of metal ions. Other conditions are as Figure 2.

## Analytical figures of merit

To verify the linear relationship between peak currents and metal concentrations, 4 calibration graphs were constructed under optimum conditions, after 60 s accumulation time. The calibration graphs were determined for copper and cadmium separately and in the presence of each other. As an example, Figure 6 shows the peak currents of various concentrations of Cd(II) while the concentration of copper is constant. As seen from Figure 6, there is no cross reactivity between copper and cadmium ions. The results of this study (correlation coefficients greater than 0.99) indicated that in all cases the current–concentration relationships were linear in the concentration range of  $1\text{--}80$  and  $1\text{--}240 \text{ ng mL}^{-1}$  with regression equations of ( $I = 2.42C + 9.83$ ,  $R^2 = 0.999$ ) and ( $I = 6.91C + 12.67$ ,  $R^2 = 0.999$ , C is concentration of metal ion) for copper and cadmium, respectively.

The detection limits ( $S/N = 3$ ) of  $0.5$  and  $0.3 \text{ ng mL}^{-1}$  were obtained for copper and cadmium, respectively.<sup>18</sup> The precision obtained, RSD (%), for  $30 \text{ ng mL}^{-1}$  of copper(II) was 2.3%, and for the same concentrations of cadmium(II) it was 1.5%



**Figure 6.** Differential pulse cathodic stripping voltammograms for different concentrations of Cd(II) under the optimized conditions, in the presence of  $80 \text{ ng mL}^{-1}$  Cu(II); Cd(II) concentration of: (a) 1, (b) 10.0, (c) 40.0, (d) 60.0, (e) 90.0, (f) 120.0, (g) 160.0, (h) 200.0 and (i)  $240.0 \text{ ng mL}^{-1}$ .

### Effect on interferences

Possible interference by other metals with the cathodic adsorptive stripping voltammetry of copper and cadmium was investigated by the addition of the interfering ion to a solution containing  $20.0 \text{ ng mL}^{-1}$  of both metal ions under optimized conditions. The results of this study are summarized in Table 1, from which it can be concluded that the method is free from interferences of foreign ions.

**Table 1.** Tolerance limit to foreign ions on the recovery of  $20.0 \text{ ng mL}^{-1}$  of copper and cadmium.

Tolerance limit		Ions
$(C_{ion}/C_{Cd})$	$(C_{Ion}/C_{Cu})$	
$K^+, Mg^{2+}, Na^+, Ca^{2+}$ Bi(III), Mn(II), Mo(VI), Co(II), Fe(II), Triton X-10	10000	10000
Zn(II), As(III), Cr(III), Al(III)	5000	5000
$C_2O_4^{2-}, SO_3^{2-}, I^-$	4000	4000
U(VI), Cr(VI), Pb(II)	500	1000
Ni(II)	20	100

### Analytical application

The proposed method was successfully applied to the simultaneous determination of copper and cadmium in sea and river water and tea samples. The seawater sample was collected from the Khazar Sea, Gilan, Iran. The

river water sample was collected from the Gharasoo River, Kermanshah, Iran. Water samples were injected into a polarographic cell after filtering and UV irradiation. The standard addition technique was used to estimate the accuracy of the developed method based on recovery of each analyte. The results obtained by this method (Table 2) reveal the capability of the method for simultaneous determination of these metals in environmental water samples. Tea samples (Fooman, Gilan, Iran) were prepared in a way similar to that reported in the literature.<sup>19</sup> A 1-mg tea sample was dried at 105 °C and placed in a beaker, followed by the addition of 7 mL of concentrated nitric acid, and the beaker was covered with a watch glass. The mixture was allowed to stand overnight, and the content was heated on a hot plate (150 °C for 15 min). Then the sample was cooled and filtered. The solution was heated to dryness at 150 °C. The residue was dissolved in 5 mL of 1 mol L<sup>-1</sup> nitric acid and the solution was transferred into a 100-mL calibrated flask. At least 100 μL of this solution was pipetted into 10 mL of supporting electrolyte. The tea samples were also analyzed for copper and cadmium content by electrothermal atomic absorption spectrometry (ET-AAS). The results are shown in Table 3. A comparison of the results obtained by the proposed method and ET-AAS, using common statistical tests (ANOVA, Student's t test, 95% confidence level) shows good agreement, thus conforming the suitability of the method for simultaneous determination of copper and cadmium.

**Table 2.** Simultaneous determination of copper and cadmium in seawater and river water samples.

	Added (ng mL <sup>-1</sup> )		Found (ng mL <sup>-1</sup> )		Recovery %	
	Cu	Cd	Cu	Cd	Cu	Cd
Seawater	0	0	27.10 ± 0.21	-	-	-
	10	20	37.60 ± 0.19	20.47 ± 0.12	101.3	102.0
	20	40	49.11 ± 0.11	38.29 ± 0.13	104.3	98.0
	40	80	68.33 ± 0.13	82.10 ± 0.22	101.8	102.7
River water	0	0	21.31 ± 0.22	-	-	-
	10	20	30.62 ± 0.18	20.62 ± 0.21	97.8	103.0
	20	40	42.00 ± 0.21	39.20 ± 0.11	101.6	98.0
	40	80	62.51 ± 0.20	78.99 ± 0.18	102.0	98.7

**Table 3.** Simultaneous determination of copper and cadmium in tea samples.

Tea samples	Proposed method		ET-AAS method <sup>a</sup>	
	Copper (ng mL <sup>-1</sup> )	Cadmium (ng mL <sup>-1</sup> )	Copper (ng mL <sup>-1</sup> )	Cadmium (ng mL <sup>-1</sup> )
1	3.12 ± 0.12	3.59 ± 0.18	2.07 ± 0.19	2.39 ± 0.20
2	2.22 ± 0.10	2.98 ± 0.16	2.09 ± 0.08	2.43 ± 0.09
3	2.87 ± 0.13	2.29 ± 0.09	3.00 ± 0.10	2.53 ± 0.11

<sup>a</sup> Results obtained with a Shimadzu model 6650 furnace atomic absorption spectrophotometer.

## Conclusion

A study was conducted on the simultaneous determination of copper and cadmium by AdCSV on a HMDE. The relevant chemical and instrumental parameters were investigated, enabling the selection of the most appropriate conditions for the determination of copper and cadmium. The method has practical potential for simultaneous determination of ultratrace amounts of copper and cadmium in environmental water and tea samples with high selectivity, sensitivity, simplicity, and speed.

## References

1. Gonzalez, M. J.; Martinez, M. C.; Aguilar, M. V. Z. *Z. Lebensm. Unters. F. A.* **1998**, *186*, 325-329.
2. Goyer, R. A.; Clarkson. T. W. *Toxic Effects of Metals*, New York: McGraw-Hill, 2001.
3. Turnlund, J. R. *Am. J. Clin. Nutr.* **1998**, *67*, 960-964.
4. Gaetke, L. M.; Chow, C. K. *Toxicology* **2003**, *189*, 147-163.
5. Pizarro, F.; Olivares, M.; Uauy, R.; Contreras, P.; Rebelo, A.; Gidi, V. *Environ. Health Persp.* **1999**, *107*, 117-121.
6. Winge, D. R.; Mehra, R. K. *Int. Rev. Exp. Pathol.* **1990** *31*, 47-83.
7. Hsu, P. C.; Guo, Y. L. *Toxicology* **2002**, *180*, 33-44.
8. Kim, M. *Food Add. Contam.* **2004**, *21*, 154-157.
9. Weisel, C.; Demak, M.; Marcus S.; Goldstein, B. D. *Am. J. Public Health* **1991**, *81*, 756-758.
10. Williams, S. R. *Basic Nutrition and Diet Therapy*, Mosby Year Book, Inc, Missouri, USA, 1995.
11. Czae, M.; Wang, J. *Talanta* **1999**, *50*, 921-928.
12. Bobrowski, A.; Zarebski, J. *Electroanalysis* **2007**, *12*, 1177-1186.
13. Zhang, Z.; Chen, S. Z.; Lin, H. M.; Zhang, H. *Anal. Chim. Acta* **1993**, *272*, 227-232.
14. Van den berg, M. G. *J. Electroanal. Chem.* **1986**, *215*, 111-121.
15. Yantasee, W.; Lin, Y.; Fryxell, G. E.; Busche, B. J. *Anal. Chim. Acta* **2004**, *502*, 207-212.
16. Ensafi, A. A.; Khyamian, T.; Bendavi, A.; Mirmomtaz, E. *Anal. Chim. Acta* **2006**, *561*, 225-232.
17. Babaei, A.; Babazadeh M.; Shams, E. *Electroanalysis* **2007**, *19*, 978-985.
18. Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*, Ellis Horwood, Chichester, UK, 1984.
19. Ichinoki, S.; Yamazaki, M. *Anal. Chem.* **1985**, *57*, 2219-2222.