Determination of Cadmium by Adsorptive Stripping Voltammetry of a Cadmium-Calcein Blue Complex

Kunihiko YOKOI, Masayo MIZUMACHI and Tsutomu KOIDE

Division of Natural Science, Osaka Kyoiku University, Kashiwara, Osaka 582, Japan

A sensitive stripping voltammetry for the determination of cadmium, with an adsorptive accumulation of complexes on a hanging mercury drop electrode with Calcein Blue, 8-[*N,N*-bis(carboxymethyl)aminomethyl]-4-methylumbelliferone, has been developed. After accumulation of the complex, the electrode potential is scanned with differential pulse modulation and the reduction current for cadmium is observed at -0.8 V. Under optimum conditions ($1 \mu\text{M}$ Calcein Blue, pH 7.2, adsorption at -0.2 V for 3 min), the detection limit was 0.015 nM. Interference from iron can be reduced by the addition of citrate ion. The method was applied to the determination of cadmium in fresh water samples.

Keywords Adsorptive stripping voltammetry, cadmium, cadmium-Calcein Blue complex

The determination of such heavy metals as cadmium and lead is important because they are toxic to living organisms. Recently, atomic absorption spectroscopy and inductively coupled plasma atomic emission or mass spectroscopy have been used to determine heavy metals. Since the concentrations of heavy metals in natural water samples are frequently lower than their detection limit, tedious preconcentration procedures are occasionally required.

As a simple, sensitive and inexpensive technique, adsorptive stripping voltammetry is widely used to determine at least 20 heavy metals in natural water samples directly.¹⁻⁴ Among the ligands^{5,6} proposed for cadmium determination, only 8-quinolinol (oxine) is known to have a detection limit of 0.1 nM ($M = \text{mol dm}^{-3}$) upon 60 s accumulation. However, the selectivity of oxine is not sufficiently high; *e.g.*, uranium is reduced at nearly the same potential as cadmium.⁵ We examined Xylenol Orange (XO, 3,3'-bis[*N,N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein) and related compounds as complexing reagents for the adsorptive stripping voltammetric determination of cadmium. Among these, XO, Calcein Blue (8-[*N,N*-bis(carboxymethyl)aminomethyl]-4-methylumbelliferone), Calcein (3,3'-bis[*N,N*-bis(carboxymethyl)aminomethyl]fluorescein), Alizarin Complexone (3-[*N,N*-bis(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone), and Thymolphthalein Complexone (3,3'-bis[*N,N*-bis(carboxymethyl)aminomethyl]thymolphthalein) were found to be useful. Considering the sensitivity and the background current stability, Calcein Blue was chosen to establish a sensitive voltammetric method for the determination of cadmium.

Experimental

Reagents

Stock solutions of $500 \mu\text{M}$ Calcein Blue (Dojindo Lab.), 1 M PIPES (Dojindo Lab., piperazine-1,4-bis(2-ethanesulfonic acid)), 5 M sodium chloride (Wako Pure Chemicals) and 1 M sodium citrate (Wako Pure Chemicals) were purified by equilibration with Chelex-100 for 1 d. Water from a Milli-Q system was used throughout. Hydrochloric and acetic acids and ammonia were purified by isothermal distillation into Milli-Q water. A stock solution of cadmium was prepared from high-purity (99.999%) metal (Wako Pure Chemicals).

Equipment

A voltammetric analyzer (Model P-1100, Yanaco) was used for all voltammetric measurements. A PAR 303A static mercury drop electrode was used as the working electrode. The reference electrode was $\text{Ag}|\text{AgCl}|\text{stad. KCl}$.

Procedure

In experiments to optimize various analytical conditions, all of the voltammograms were recorded in a 50 mM NaCl solution. The solutions were purged with water-saturated nitrogen for 5 min, after which the working electrode potential was set to the deposition potential. After the deposition period under stirring of the solution, the stirrer was switched off and a quiescent period of 10 s was allowed; the potential was then scanned in a negative direction. The scan was made by differential pulse modulation with a pulse rate of 10 s^{-1} , a pulse height of 25 mV and a scan rate of 20 mV s^{-1} ; under

these conditions the optimum sensitivity and selectivity were obtained. The cadmium concentration was determined by a standard addition procedure. The samples were handled in a class-100 laminar-flow hood.

Results and Discussion

Cyclic voltammetry and analytical parameters

Figure 1 shows cyclic voltammograms recorded after 60 s adsorption at -0.5 V in the presence of $1\text{ }\mu\text{M}$ Calcein Blue at pH 7.2. The cadmium peak was observed at -0.81 V. Since the re-oxidation peak appeared at a similar potential, the redox process is considered to be reversible.

The cadmium peak current was measured against the Calcein Blue concentration (c_{CB}) at pH 7.2. The peak current increased with c_{CB} , and then leveled off for $c_{\text{CB}} > 600\text{ nM}$. Since the background current deteriorated at higher c_{CB} , the optimum c_{CB} was found to be around $1\text{ }\mu\text{M}$.

The effect of the pH on the peak current is shown in Fig. 2. In acidic solutions Calcein Blue could not coordinate to cadmium because of the only slight dissociation of protons from the iminodiacetyl group; accordingly, the peak current was not observed at a pH below 6. The peak current sharply increased at pH of around 6, passed through a maximum at $\text{pH} \approx 7$, and slightly decreased until a plateau was reached at a pH beyond 8. In view of this, pH 7.2 was concluded to be optimum.

The effect of the adsorption potential (E_{ad}) was also examined. The peak current changed only slightly at E_{ad} 's in the range from -0.05 to -0.6 V, and -0.2 V was concluded to be optimum.

The peak current in a solution containing 10 nM cadmium ion increased linearly with the adsorption time (t_{ad}) for up to 3 min.

Interference

The peak current for 20 nM cadmium in the presence of $1\text{ }\mu\text{M}$ Calcein Blue at pH 7.2 was not affected by the addition of 100 nM copper, zinc, iron cobalt, nickel, aluminum, manganese, molybdenum, palladium, chromium(III), chromium(VI), magnesium, calcium, strontium, barium, tungsten or tin(IV). The addition of 100 nM lead, titanium, vanadium and uranium decreased the cadmium peak height by 40, 25, 30 and 40%, respectively. However, no interference was observed at a comparable concentration of these metal ions, and there was no overlapping between the current peak of cadmium and that of one of these metals. Hence, the cadmium peak could be calibrated by the standard addition procedure. Although the coexistence of iron at the μM level suppressed the cadmium peak drastically, an increase of c_{CB} to $3\text{ }\mu\text{M}$ and the addition of 15 mM citrate ion recovered the sensitivity by about 30%. The addition of 1 mM magnesium and calcium, generally found in river water, showed no interference; however,

Fig. 1 Cyclic voltammogram of cadmium in the presence of $2\text{ }\mu\text{M}$ Calcein Blue at pH 7.2. Adsorption, 60 s at -0.5 V; scan rate, 50 mV s^{-1} ; broken curve, blank; solid curve, 200 nM cadmium.

Fig. 2 Effect of pH on the peak current (20 nM cadmium, $1\text{ }\mu\text{M}$ Calcein Blue, $t_{\text{ad}}=60\text{ s}$, $E_{\text{ad}}=-0.2\text{ V}$).

the addition of magnesium at a concentration above 30 mM reduced the cadmium sensitivity to nearly zero, and no recovery was noted upon the addition of a higher concentration of Calcein Blue and citrate. Therefore, the present method is applicable to fresh-water samples, but not to seawater.

Natural surface-active compounds are known to adsorb on a mercury electrode and to interfere with analyses by adsorptive stripping voltammetry. The

Fig. 3 Interference of surfactants (20 nM cadmium, 1 μ M Calcein Blue, pH 7.2, t_{ad} =60 s, E_{ad} =-0.2 V). See text for abbreviations.

Fig. 4 Calibration curves of cadmium (pH 7.2, t_{ad} =90 s, E_{ad} =-0.2 V); (a) with 1 μ M Calcein Blue, (b) with 1 μ M iron, 15 mM sodium citrate and 3 μ M Calcein Blue.

interfering effects of anionic surfactants (sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulfonate (SDBS)), a cationic surfactant (dodecyltrimethylammonium chloride (DTMAC)) and a non-ionic surfactant (Triton X-100 (TX)) were investigated. Figure 3 shows that all of these surfactants interfere with the cadmium determination when their concentrations are higher than a few ppm. In view of this, the surfactants have to be decomposed or removed in order to attain good sensitivity to cadmium.

Table 1 Results of cadmium determination in water samples

Sample		$[Cd^{2+}]^a$ /nM
River water	A	0.26 ± 0.06
	B	0.20 ± 0.01
Mineral water	A	0.14 ± 0.01
	B	1.77 ± 0.10
	C	0.18 ± 0.02
	D	0.15 ± 0.00
Tap water		0.14 ± 0.01

a. Average of duplicates runs.

Fig. 5 Voltammograms for mineral water A; (a) original, (b) 0.26 nM cadmium added, (c) 0.52 nM cadmium added.

Dynamic range and detection limit

Under the optimum conditions (1 μ M Calcein Blue, pH 7.2, E_{ad} =-0.2 V) the calibration curve was linear up to 100 nM of cadmium upon 1 min of adsorption; at higher concentrations the calibration curve tended to level off because of adsorption saturation.

The detection limit, defined as three-times the standard deviation of repeated determinations ($n=10$), was 0.015 nM for 0.207 nM of cadmium with an adsorption time of 3 min. For the determination of cadmium in fresh-water samples containing a μ M-level of iron, higher concentrations of Calcein Blue (3 μ M) and citrate (15 mM) were needed to avoid interference. In the

presence of these reagents and 1 μM iron the sensitivity was lowered and the detection limit was 0.1 nM with 90 s adsorption. Calibration curves with and without 1 μM iron are shown in Fig. 4. In both cases, linear responses were obtained for a low nM-level of cadmium.

Determination of cadmium in water samples

The present method was applied to fresh-water samples. The samples were filtered with a 0.22 μm Nuclepore filter and irradiated with ultraviolet light from a 70 W low-pressure mercury lamp for 6 h at pH 2 to decompose organic substances, and measured after the addition of 3 μM Calcein Blue and 15 mM citrate at pH 7.2. The results are listed in Table 1, and voltammograms for samples are shown in Fig. 5. These cadmium concentrations found coincide with the reported ones for natural-water samples.⁷⁻¹⁰

References

1. C. M. G. van den Berg, *Anal. Chim. Acta*, **250**, 265 (1991).
2. J. Wang, *Fresenius' Z. Anal. Chem.*, **337**, 508 (1990).
3. C. M. G. van den Berg, *Analyst* [London], **114**, 1527 (1989).
4. R. Kalvoda and M. Kopanica, *Pure Appl. Chem.*, **61**, 97 (1989).
5. C. M. G. van den Berg, *J. Electroanal. Chem.*, **215**, 111 (1986).
6. Z.-Q. Zhang, S.-Z. Chen, H.-M. Lin and H. Zhang, *Anal. Chim. Acta*, **272**, 227 (1993).
7. Y. Nojiri, T. Kawai, A. Otsuki and K. Fuwa, *Water Res.* **19**, 503 (1985).
8. C. J. Cheng, T. Akagi and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **58**, 3229 (1985).
9. K. Vermeiren, C. Vandecasteele and R. Dams, *Analyst* [London], **115**, 17 (1990).
10. S. Taguchi, S. Yamazaki, A. Yamamoto, Y. Urayama, N. Hata, I. Kasahara and K. Goto, *Analyst* [London], **113**, 1695 (1988).

(Received August 29, 1994)

(Accepted December 16, 1994).