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# ADSORPTIVE-CATALYTIC STRIPPING VOLTAMMETRY FOR DETERMINATION OF ULTRATRACE TITANIUM

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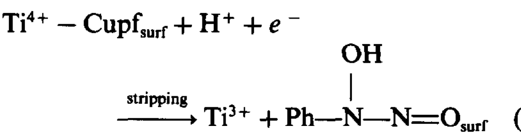
**Summary**—An extremely sensitive stripping voltammetric procedure for determination of ultratrace titanium is reported. The method is based on the interfacial preconcentration of titanium–cupferron complex onto the hanging mercury drop electrode, followed by catalytic reduction of the adsorbed complex for the presence of cupferron. The peak currents are directly proportional to titanium in the ranges of 0.06–1.0 ng/ml and 1.0–30.0 ng/ml. Moreover, the character of stripping current has also been studied with various polarographic methods. Such coupling of catalytic and adsorptive collection processes holds great promise for the development of an ultrasensitive voltammetric procedure for other metals.

Titanium is an important metal and occurs in extremely low levels in various materials. Trace amounts of titanium markedly affect the mechanical working properties of steel and alloys of copper and nickel as well as human health,[1,2] so an ultrasensitive method is required for its reliable quantification. It has been reported that the polarographic waves of chelates of titanium with various reagents in DC polarography[3,4] and oscilloscopic polarography,[5–7] but the detection limits are not satisfactory for ultratrace measurements of titanium. Voltammetry has been shown to be useful. This paper reports an ultrasensitive stripping voltammetric procedure for ultratrace measurements of titanium based on the coupling adsorptive and catalytic processes. The procedure can be written as:

$$Ti^{4+}-Cupf_{soln}\xrightarrow{\text{adsorptive preconc.}}Ti^{4+}-Cupf_{surf} \quad (1)$$



$$Ti^{4+}-Cupf_{surf}+H^{+}+e^{-}\xrightarrow{\text{stripping}}Ti^{3+}+Ph\text{—}\overset{\overset{OH}{|}}{N}\text{—}N{=}O_{surf} \quad (2)$$

$$Ti^{3+}+Cupf_{surf}+6H^{+}\xrightarrow{\text{Catalysis}}Ph-NH-NH_2+Ti^{4+}+2H_2O \quad (3)$$

The cycling catalytic reactions (2) and (3) associated with adsorptive collection offer remarkable sensitivity, with detection limit 0.04 ng/ml, and high selectivity. Analogous procedures have been reported recently for detection of picomolar levels of molybdenum[8] and platinum.[9]

## EXPERIMENTAL

### *Apparatus*

A Model 79-1 voltammetric analyzer (Jinan Instrumental Co., China) was used in connection with a Model L-204 X-Y recorder (Shanghai Instrumental Co., China) and a Model JM-01 hanging mercury drop electrode (Jiangsu Instrumental Co., China) with an area of 3.00 mm$^2$.

### *Reagents*

*Stock titanium solution (1.000 mg/ml).* Dissolve 0.5000 g of titanium powder (purity 99.9%) in 5 ml of sulphuric acid and 0.5 ml of nitric acid (heated to boiling). Quantitatively transfer the solution into a 500-ml standard flask and dilute to the mark with 5% sulphuric acid. The stock titanium solution was diluted to the required concentration with 1% sulphuric acid.

*Cupferron solution (0.025*M*).* Dissolve 0.2 g of cupferron solid reagent in 50 ml of non-aqueous alcohol. This solution was prepared daily.

All reagents used were of analytical reagent grade and water was doubly distilled in a quartz still.

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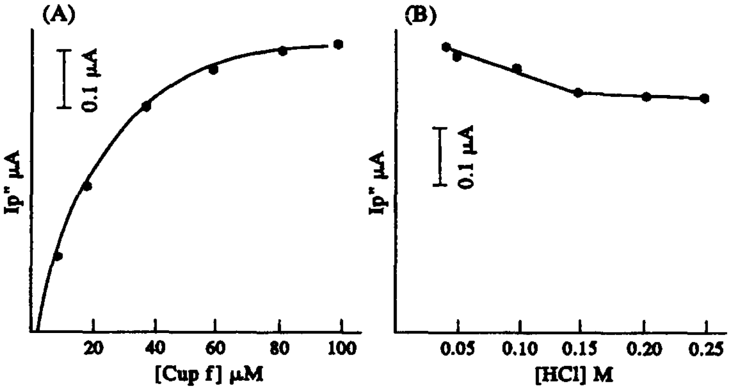

Fig. 1. Dependence of $I''_p$ for 5 ng/ml titanium on cupferron (A) and hydrochloric acid (B) conc. Cupferron $1.0 \times 10^{-4}M$ (B). Hydrochloric acid $0.1M$ (A). Alcohol 10% v/v. Opening electric circuit preconc. for 1 min. Scan rate with 100 mV/sec.

### *Procedures*

Into a 25-ml flask, a known volume of 1.000 $\mu$g/ml titanium solution, 2.5 ml of $1.0M$ hydrochloric acid, 0.1 ml of $0.025M$ cupferron and 2.5 ml of non-aqueous alcohol were placed, followed by dilution to the mark with water. This base solution (25 ml) was pipetted into the cell. The preconcentration potential, $-0.2$ V (or an opening electric circuit), was applied to a fresh mercury drop while the solution was stirred. After preconcentration for about 2 min the stirring was stopped and after 30 sec, a cathodic linear scan was carried out from $-0.2$ to $-0.7$ V (with a 100 mV/sec scan rate). The second derivative peak current ($I''_p$) was measured at $-0.45$ V. The procedure was repeated using a new mercury drop. All data were obtained at room temperature.

## RESULTS AND DISCUSSION

### *Optimization*

*Alcohol, cupferron and acidility.* The cupferron is so unsteady in acidic solution that the reproducibility of the peak current is very poor. It was found that adding alcohol could enhance the stability of cupferron and the steady time was proportional to the amount of alcohol, but the peak current was decreased by adding alcohol. When the solution contains 10% (v/v) alcohol, the cupferron concentration cannot be changed within 3 hr in $0.1M$ hydrochloric acid. Figure 1 shows the dependence of $I''_p$ on cupferron (A) and hydrochloric acid (B).

The concentration of cupferron has a profound effect on the $I''_p$. The $I''_p$ increases rapidly with increasing cupferron concentration up to $4 \times 10^{-5}M$ and then more slowly. However, the concentration of hydrochloric acid has a slight effect on the $I''_p$ [Figure 1 (B)]. The optimum supporting electrolyte solution contains $1.0 \times 10^{-4}M$ cupferron, $0.1M$ hydrochloric acid and 10% (v/v) alcohol.

*Preconcentration potential ($E_p$) and time ($T_p$).* Figure 2 shows the effect of $E_p$ (A) and $T_p$ (B) on $I''_p$. In this procedure, two ways of preconcentration can be selected: opening electric

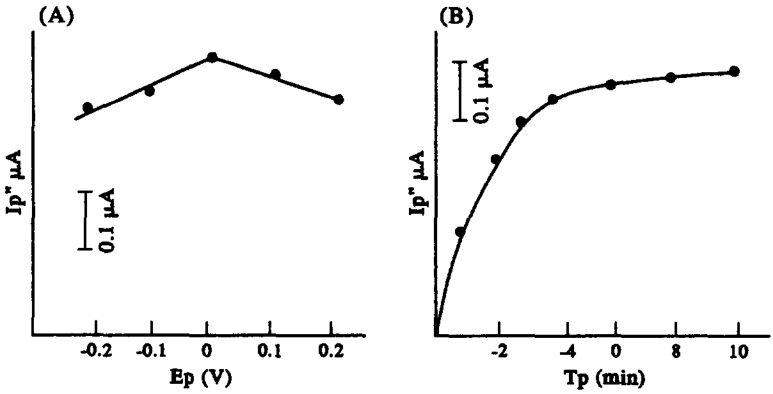

Fig. 2. Effect of $I''_p$ by preconc. potential (A) and time (B). Preconc. 1 min (A). Opening electric circuit preconc. (B). Scan rate 100 mV/sec. Solution, cupferron $1.0 \times 10^{-4}M$, hydrochloric acid $0.1M$, 10% v/v alcohol and 5 ng/ml titanium.

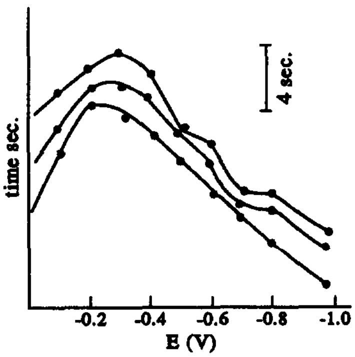

Fig. 3. The electrocapillary curve. (A) 10% v/v alcohol and 0.1$M$ hydrochloric acid; (B): (A) and $1.0 \times 10^{-4}M$ cupferron; (C): (B) and 10 ng/ml titanium.

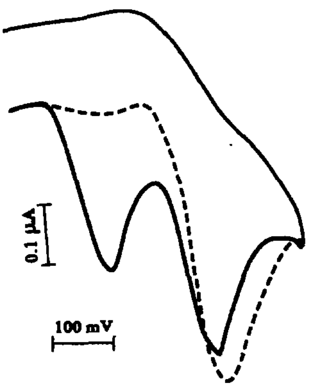

Fig. 4. Cyclic voltamperogram. Conditions as in Fig. 1. Solution as in Fig. 2.

circuit and controlling potential. The former sensitivity is slightly higher than that of the latter. Figure 2 (A) shows that, at $E_p$ 0.00 V, the maximum $I_p''$ can be obtained. By scanning from 0.00 V to negative, the reduction peak of oxygen was found at −0.2 V and it interfered with the measurement of titanium's peak current. Selecting $E_p$ at −0.2 V and scanning from −0.2 to −0.7 V the oxygen peak was disappeared. In this procedure, purging oxygen is not needed. Obviously, that the $E_p$ shows a relatively weak effect on $I_p''$ and opening electric circuit preconcentration can be used which indicates that the process of preconcentration is mainly a process of adsorption. Figure 2B shows that $I_p''$ increases linearly with $T_p$ after less than 4 min because the complex adsorption is not saturated on the electrode surface. However, the adsorption tends to saturate when $T_p$ longer than 4 min, so it would not be available for increasing $I_p''$ by prolonging $T_p$.

### *Catalytic wave mechanism*

The catalytic character of the $Ti^{4+}$–cupferron complex has been studied extensively. Figure 3 shows the electrocapillary curve under selected conditions. The curve (A) lower than curve (B) and the curve (B) lower than curve (C) express that both cupferron and $Ti^{4+}$–cupferron complex possess the character of adsorption. Curve (B) at about −0.7 V, curve (C) at about −0.5 V and −0.7 V appearing as a small peak respectively express that cupferron (at about −0.7 V) and $Ti^{4+}$–cupferron complex (at about −0.5 V) are reduced, which correspond to the positions of $I$p in the cyclic voltamperogram (Fig. 4). The uncontinued curve refers to the basic solution in the absence of titanium and the continued curve is obtained by adding titanium into the basic solution. There are no oxidation peaks in the two curves, which show that the electrode reactions of cupferron and its complex are all irreversible. In addition, the temperature coefficient −6.2%/deg. in the range 20–50° and the $\beta$ value of 0.63 obtained from the instantaneous current–time curve confirm the character of adsorption and parallel catalysis.[10] Moreover, the complex ratio was studied by the method described in Ref.[11] The titanium–cupferron complex is 1:1. According to these studies, the processes may be represented in the following equations:

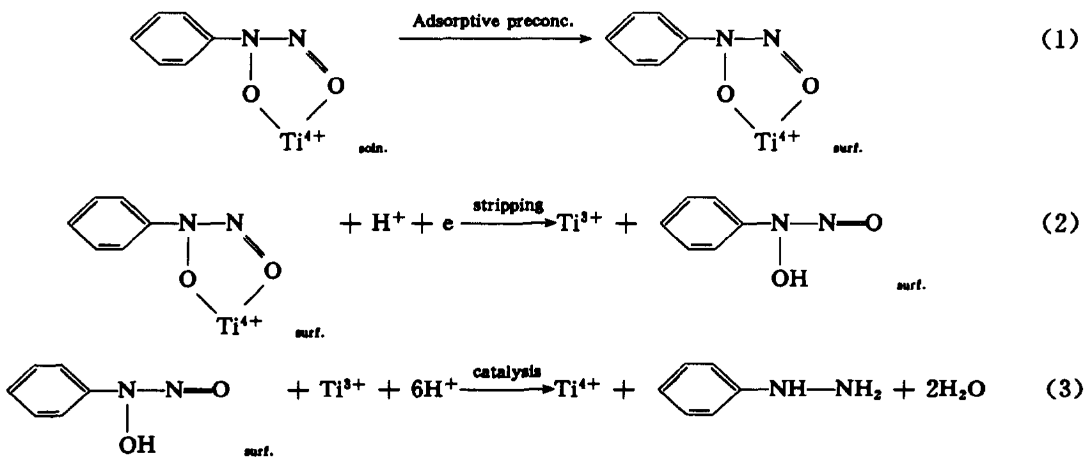

Table 1. Interference ions and their max. amount allowed (error $\leqslant 10\%$)

| Interference ions | $Se^{4+}$ | $W^{6+}$ | $V^{5+}$ | $Fe^{3+}$ | $Mo^{6+}$ | $UO_2^{2+}$ |
|---|---|---|---|---|---|---|
| Max. amount, *µg/ml* | 1.6 | 2 | 0.6 | 1.6 | 0.1 | 0.6 |
| Times (ion)/(titanium) | 320 | 400 | 120 | 320 | 20 | 120 |

### *Interferences*

High selectivity is one character of the adsorptive–catalytic stripping voltammetry. Table 1 shows the results of several interfering metal ions and their maximum presence amount allowed with the measurements of 5 ng/ml titanium. Many other metal ions, such as $Sn^{4+}$, $Tl^{+}$, $Sb^{3+}$, $Bi^{3+}$, $Pb^{2+}$, $Cu^{2+}$, $Ba^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Zn^{2+}$, $Ag^{+}$, $Cd^{2+}$, $Al^{3+}$, $Co^{2+}$ and $Ni^{2+}$, do not interfere with the measurement.

### *Calibration curve*

Under the condition as in procedures, $I''_p$ is proportional to the titanium concentration in ranges of 0.06–1.0 ng/ml ($T$p: 3 min) and 1.0–30.0 ng/ml ($T$p: 1 min). The linear regression equations are:

$$I''_p = -0.0986 + 37.3C_{Ti}\ (\text{ng/ml})$$

$$r = 0.999\ (T\text{p: 3 min})$$

$$I''_p = 8.51 + 3.13C_{Ti}\ (\text{ng/ml})$$

$$r = 0.985\ (T\text{p: 1 min})$$

The relative standard deviation for 1.0 ng/ml is 4.6%.

### *Application*

This method was used to determine trace levels of titanium contained in high pure aluminium standard samples. The results are in good agreement with their standard values. The relative errors are 4–6%.

## CONCLUSION

This study demonstrates that the coupling of the adsorptive and catalytic process can constitute the basis of an ultrasensitive voltammetric procedure for detecting titanium. This stripping procedure offers a remarkably low detection limit and high selectivity. Compared to analogous catalytic–polarographic measurement,[5–7] the adsorptive preconcentration results in a 2 or 3 orders of magnitude lowering of the detection limit.

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