

A SIMPLE POTENTIOMETRIC STRIPPING METHOD FOR COPPER IN PLATING WASTE

H GOMATHI and G PRABHAKARA RAO

Central Electrochemical Research Institute, Karaikudi-623 006

ABSTRACT

A potentiometric stripping analysis of copper applicable to raw waste streams from common metals plating industry is described. Glassy carbon is employed as the working electrode. The possible reactions that would take place during the stripping process are discussed. It has been possible to estimate less than 1 ppm of Cu by this method and it is free from interference by other metallic impurities present in common metal plating effluent.

Key Words: Potentiometric stripping analysis, metal plating wastes, copper estimation .

INTRODUCTION

Copper tops the list of toxic pollutants met with in raw waste streams from common metals plating industry [1]. A detailed review of anodic stripping voltammetric procedures available for copper in various composite materials has appeared in the seventies [2]. Recently potentiometric stripping analysis (PSA) procedure has been developed for analysing Cu, Cd, Pb, Sn, Bi, Zn, Th etc. on mercury film glassy carbon electrode (MFGCE) using Hg (II) [3] compounds or dissolved oxygen [4] as oxidants. The mechanistic aspects of this method have been dealt in detail subsequently [5]. The present investigations are aimed at assessing the usefulness of Glassy Carbon (GC) as such as working electrode without any mercury film coated over it. Results of such PSA studies are reported and discussed here.

EXPERIMENTAL

A three electrode cell with GC working electrode, a platinum counter electrode and 1N calomel reference electrode was used. The working electrode (GC) was polished successively with 1/0, 2/0, 3/0 and 4/0 emery sheets. The solution was deaerated with nitrogen wherever necessary. The potential of the working electrode was expressed with reference to 1N calomel electrode. A magnetic stirrer was employed to stir the sample solution during experiment. An X-Y recorder (Rikadenki Model RW 201T) was used for recording E-t profiles.

PROCEDURE

The working electrode was held potentiostatically at a sufficiently negative potential for copper deposition and at the end of the stipulated-time, the potentiostatic circuitry was disconnected and potential-time response was recorded under the same hydrodynamic conditions as for deposition.

RESULTS AND DISCUSSION

In Figs.1 and 2, typical potential-time curves obtained in an unbuffered medium (0.5M H₂SO₄ - pH 2.2) and a buffered medium (0.1M HCl + 0.1M NaOOCCH₃ pH 2.87) at a copper concentration of 10⁻⁴M are presented. In both the media the preconcentration was carried out for 5 mins. at -700 mV. Stripping times obtained, show that time taken for complete stripping is nearly the same in the case of sulphuric acid and (hydrochloric acid + sodium acetate buffer). It is also of interest to note that no stripping signal was observed in acetic acid - sodium acetate buffer of pH 4-5.

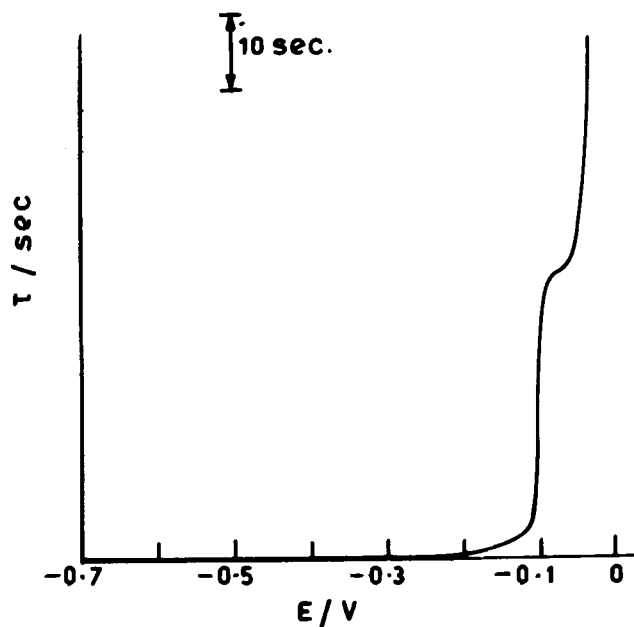


Fig.1. Potentiometric stripping curve for copper deposited from 10⁻⁴M CuSO₄ in H₂SO₄ medium (pH 2.2) Preconcentration - 5 mins

These observations point to the fact that pH plays a very crucial role in the stripping process. Therefore, a pH 2-3 of either buffered or unbuffered medium is suitable. It is clear from Figs. 1 and 2 that a plateau occurs at the equilibrium dissolution potential of the metal and it is characteristic for each medium and also varies with the nature of the substrate over which the metal is deposited. This potential was found to be -100 to -60 mV for Cu²⁺ deposited over glassy carbon in sulphuric acid medium and -160 to -100 mV in hydrochloric acid + sodium acetate medium. A linear calibration plot for Cu²⁺ in the concentration range

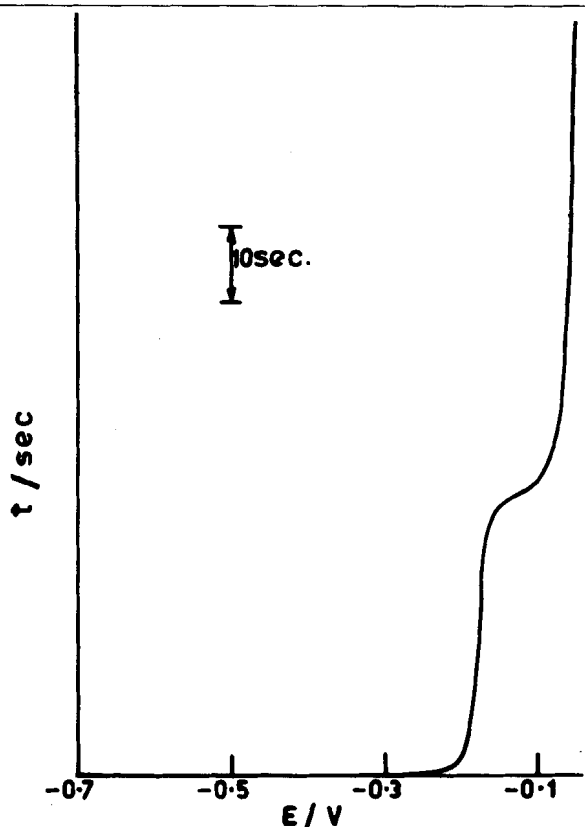


Fig. 2. Potentiometric stripping curve for copper deposited from $10^{-4}M$ $CuSO_4$ in $0.1N$ CH_3COONa + $0.1N$ HCl (pH 2.87) Preconcentration - 5 mins

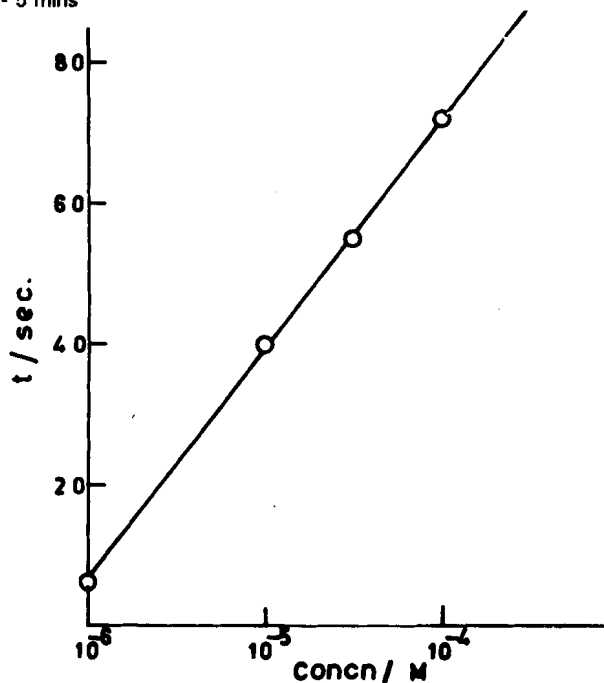


Fig. 3. Linear calibration plot of stripping time versus concentration of copper in the concentration range $10^{-6}M$ to $10^{-4}M$; Background - $0.5M$ H_2SO_4 Preconcentration - 5 mins

$10^{-4}M$ to $10^{-6}M$ vs stripping time, in $0.5 M$ sulphuric acid medium is represented in Fig. 3. The above procedure was then applied for the estimation of copper in synthetic samples of waste streams from common metal plating industries, taking a typical composition for the effluent [1] .

It is noted that the stripping time for copper deposited from the effluent in the concentration range 10^{-6} to $10^{-4}M$ was comparable to the stripping time from pure sample solutions when other metal ions like Cd, Pb, Sn are present in their lower limits. The potentiometric stripping curve for copper deposited from the effluent containing one tenth of the upper limit of the constituents (Table I) is shown in figure 4.

Table-I:Composition of raw waste streams from common metals plating

Metal or other constituent		mg / l
Copper	0.032 -	272.5
Nickel	0.019 -	295.4
Chromium (total)	0.088 -	525.9
Chromium (hexavalent)	0.005 -	334.5
Zinc	0.112 -	252.0
Cyanide (amenable to chlorination)	0.003 -	130.0
Flouride	0.022 -	141.7
Cadmium	0.077 -	21.6
Lead	0.663 -	25.4
Iron	0.410 -	1482
Tin	0.060 -	103.4
Phosphorus	0.020 -	144.0
Total suspended solids	0.100 -	9970

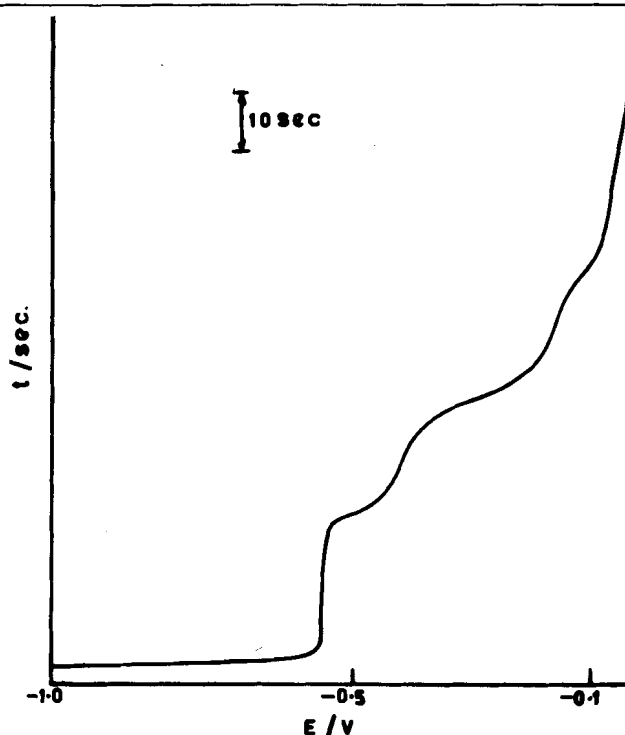


Fig. 4. Potentiometric stripping curve for copper deposited from synthetic common metals plating effluent containing one tenth of the upper limit of the constituents in Table I

In this case stripping time for copper is less than that for pure sample solution. This is understandable because at the potential (-1.0V) applied for preconcentration, codeposition of other metals like Pb, Cd, Sn etc. also occurs and the efficiency of copper deposition is reduced. Such difficulty can be circumvented by obtaining special calibration graph, making the standards identical to that of the sample solution. A simultaneous determination of various metal ions like Pb, Cd, Sn, Cu, etc. in the effluent is possible by this procedure and attention is being paid to this aspect presently.

The observed potentiometric stripping can be understood in terms of the oxidation of the metal with the agency of dissolved oxygen analogous to the potentiometric stripping curves that one gets on mercury coated glassy carbon. This has been substantiated in the present work by carrying out experiments with completely deaerated solutions in which no well defined potentiometric stripping signal could be recorded.

CONCLUSION

The results obtained showed that glassy carbon (without mercury film) could be successfully employed as an electrode material for potentiometric stripping analysis of Cu^{2+} in buffered and unbuffered solutions.

REFERENCES

1. U S Environmental Protection Agency Development Document for proposed Existing Source Pretreatment Standards for the Electroplating Point Source Category Report EPA 440/1-78/085, Washington, D.C. (February 1978)
 2. F Vydra, K Stulik and E Julakova, *Electrochemical Stripping Analysis*, John Wiley & Sons Inc, New York (1976)
 3. D Jagner, *Anal Chem*, 50 (1978) 1924
 4. D Jagner, *Anal Chem*, 51 (1979) 342
 5. D Jagner, *Analyst*, 107 (1982) 593
- 