

DIFFERENTIAL PULSE POLAROGRAPHIC ANALYSIS OF THIN-FILM TIN-CADMIUM ALLOY DEPOSIT OVER MILD STEEL

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ABSTRACT

A differential pulse polarographic method has been developed to estimate tin and cadmium simultaneously in presence of large excess of iron. Alloy deposits of Sn and Cd having different compositions were analysed and the percentages of alloy compositions were calculated in each case. It has been possible to estimate ppb levels of Sn and Cd by this method.

Key Words: Differential pulse polarography, Sn-Cd alloy deposition, mild steel substrate

INTRODUCTION

Pulse and Differential Pulse Polarographic techniques (DPP) have to a larger extent supplanted conventional polarography in the recent electroanalytical literature [1]. This is attributed to the lower detection limits of the pulse techniques. DPP is also widely employed for the determination of organic compounds and metal ions for which stripping voltammetry is unsuitable [1]. Analysis of various plating solutions by differential pulse polarography has been dealt with in recent literatures [2,3] especially in gold and nickel plating baths, estimation of cadmium down to 10^{-6} M to 10^{-8} M by DDP is reported [4]. Limit of detection of Cd by colorimetry is 10^{-7} M using dithiozone. However, in this procedure, the major interferences are zinc, copper, cobalt (>0.25 mg) and to a lesser extent silver, mercury, lead, bismuth, arsenic, antimony, tin, chromium, aluminium, iron, manganese, nickel (>2.5 mg). For a simultaneous determination of tin and cadmium in presence of large excess of iron, DPP was resorted to in view of the very low concentrations of Sn and Cd available in the sample and the difficulty met with in other analytical procedures. The results are discussed in the present communication.

EXPERIMENTAL

AR grade chemicals were used to prepare background electrolyte and standard solutions. The differential pulse polarographic experiments were conducted with PAR 174A Polarographic Analyzer incorporating DME set up and timer to adjust the drop time. The drop time was maintained at 1 sec throughout the experiment and the potential was scanned from +0.1 V - 1.0 V at a scan rate of 2 mV/sec.

Sample preparation

Samples of the thin film deposits of tin-cadmium alloy over mild steel were supplied for analysis from the Industrial Metal Finishing Division of the Institute. The plated samples were treated with hydrochloric acid to strip the Sn-Cd alloy deposit. In this process, large amounts of iron also dissolved. DPP of Sn and Cd was carried out in presence of large excess of iron.

Two sets of standards containing pure Sn and Cd salts, one in the

concentration range 0.5 mM - 2 mM for Sn and 0.1 to 4 mM for Cd and others in the range of 0.1 to 0.001 mM with respect to both Sn and Cd were prepared, so as to correspond to the alloy deposit. The solutions were deaerated by passing pure nitrogen before each experiment. A three electrode cell was employed. Mercury pool acted as the auxiliary electrode and 1N calomel was used as reference.

PRINCIPLE OF THE METHOD [5]

Stannic tin in 4M hydrochloric acid is known to give two distinct waves in DC polarography, first at -0.25 V and the second at -0.52 vs SCE. The second wave is fully developed making it ideally suitable for practical analyses. In differential pulse polarography also, these peaks seem to appear at the above potentials corresponding to the two stages of reduction, stannic to stannous and stannous to tin metal, in 4 M hydrochloric acid. Reduction of $Cd^{2+} + 2e \longrightarrow Cd$ manifests itself as a well defined peak at -0.6 V in DPP in 4 M hydrochloric acid. DPP's of these reference samples have typical features for the current peaks that are identical to those described for the samples.

By virtue of the potential difference between the reduction potentials of the two metal ions, simultaneous determination is thus seen to be feasible. Iron which is present in very large excess ($> 99\%$ in the present study) is seen to have no effect on the polarographic waves of tin and cadmium. This can be understood from the fact that the standard potential of the ferric-ferrous couple is +0.51 V vs SCE and the reduction potential of ferrous iron to the metal varies from -1.3 -1.5 V vs SCE in different supporting electrolytes including 4M hydrochloric acid. Therefore, iron which has dissolved from the substrate in hydrochloric acid medium either in ferrous, ferric or both forms does not interfere in the above determinations.

RESULTS AND DISCUSSION

The DPPs of representative samples are given in Figs. 1 and 2. As already remarked DPPs obtained using mixtures of pure cadmium and tin salts in the same supporting electrolyte viz. 4M HCl are identical in their polarographic peak characteristics, since the presence of excess iron has no influence on Cd and Sn polarographic behaviour.

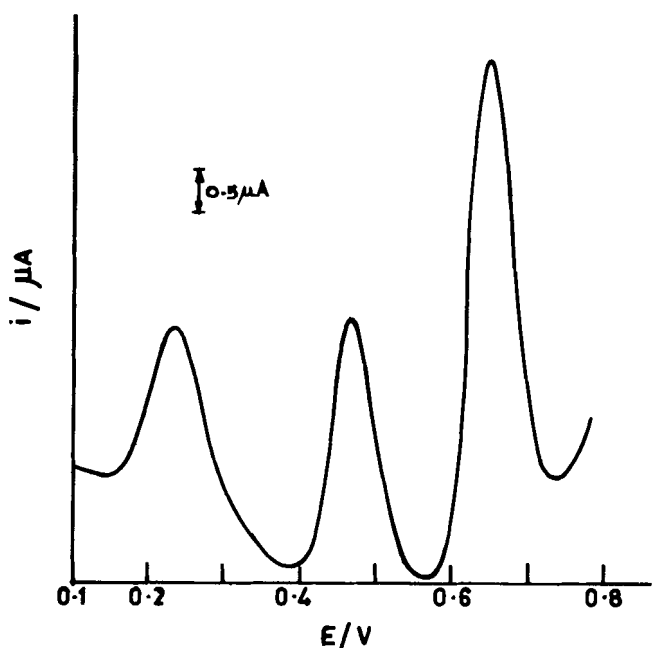


Fig. 1. Typical differential pulse polarogram of sample containing nearly equal quantities of cadmium and tin. Initial potential 0.1 V; Drop time - 1 sec; Scan rate 2 mV/sec.

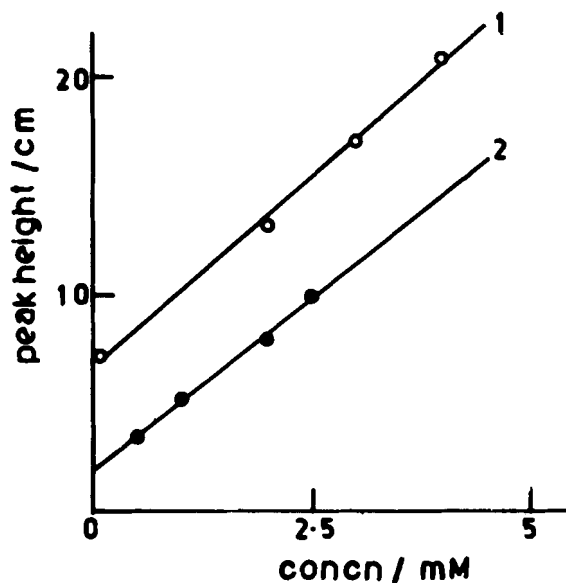


Fig. 3. Linear calibration graph for cadmium and tin in the concentration range 0 to 5 mM (1) cadmium (2) tin.

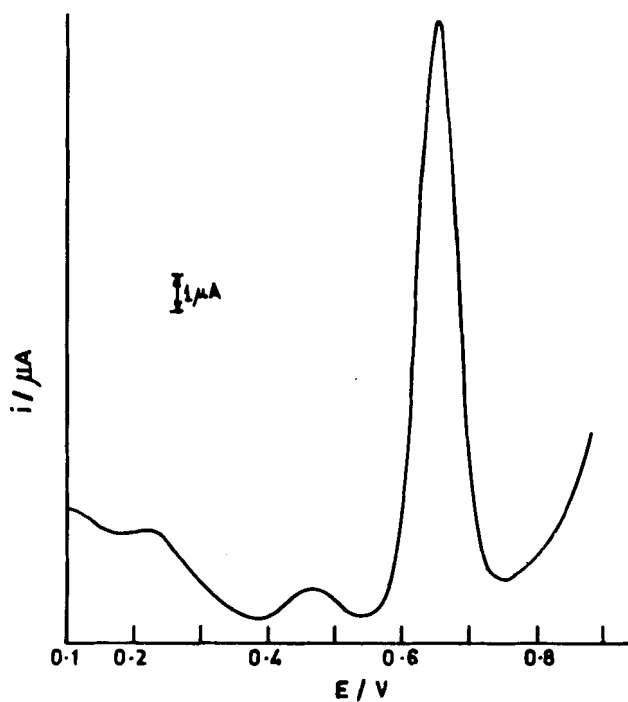


Fig. 2. Typical DPP of sample containing excess of cadmium and traces of tin. Initial potential 0.1 V; Drop time 1 sec; Scan rate 2 mV/sec.

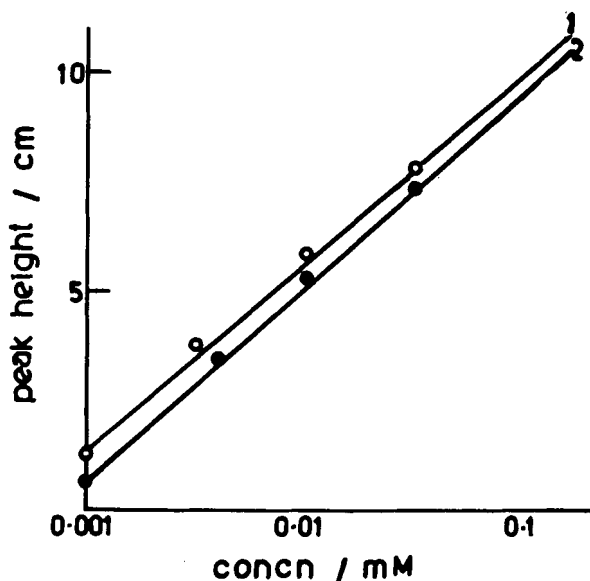


Fig. 4. Linear calibration graph for (1) cadmium in the concentration range 0.001 to 0.1 mM (2) tin in the concentration range 0.001 - 0.1 mM.

Now, making use of calibration plots (Fig. 3 and 4) constructed for the two concentration ranges of interest (0.001 to 0.1 mM and 0.1 to 4 mM for Cd) and (0.001 to 0.1mM and 0.5 to 2.5 mM for Sn), a number of samples have been analysed for their Cd and Sn contents and tabulated Table I). It may be remarked that the method allows the accurate estimation

Table-I:Composition of cadmium tin alloy found

Sample No.	Concentration found		Percentage composition in the deposit	
	mM (Cd)	mM (Sn)	(Cd)	(Sn)
1	0.097	0.015	86.0	13.9
2	0.050	0.039	55.2	44.7
3	0.050	0.002	96.0	3.8
4	1.200	0.054	95.4	4.6
5	3.000	0.001	100.00	traces

of the two components at widely varying ratios, to the extent of 1 : 3000 for tin to cadmium.

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