

VOLTAMMETRIC TECHNIQUES FOR ANALYTICAL APPLICABILITY AND METAL PLATING INDUSTRIES

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Modern voltammetric techniques such as pulse polarography, differential pulse polarography and differential pulse stripping voltammetry have found widespread application in industrial and pollution laboratories. An increasing interest in the detection and assay of heavy metals in a variety of materials (e.g., biological fluids, food, sewage, fresh water, sea water etc.) at trace levels, has created an anxiety for sensitive and reliable analysis methods. Modern pulse polarography extends these techniques to the identification and determination of many substances at parts per billion concentration ranges. These techniques give wide application for identification and detection in the analysis of pharmaceuticals, polluting metals and a broad variety of substances (drugs in biological fluids, plasma or serum samples, detection of liver poisoning in human liver, pesticides, plastics polymer, inhibitors, fertilizers etc.)

In the plating industry, the control of the plating baths is a difficult analytical problem. It is necessary to continuously monitor not only the plating metal concentration but also the concentration of other metals which may be present in both major and tracer amounts. Some of these metals may be harmful if they exceed certain limits as they can have a deleterious effect upon the physical and chemical properties. Differential pulse polarography is most suitable to solve the analytical problems of the plating industry. Depending upon the nature of the plating solution and the other type of species which are present, it is convenient to adjust the solution composition to increase the sensitivity and to avoid interferences.

Keywords : Voltammetric Techniques; Metal Plating Industry

INTRODUCTION

THE techniques by which composition of solution is studied through current-potential relationships are termed electrochemical techniques. The main branches of electrochemistry are :

- (i) voltammetry; (ii) coulometry; (iii) chronopotentiometry; and (iv) chronoamperometry;

For quantitative and qualitative analysis of solution voltammetry technique is the most important. The sub-divisions of voltammetry are : (i) polarography; (ii) stripping analysis; (iii) cyclic voltammetry; and (iv) linear sweep. Out of these subdivisions, polarography is a well-established technique for the detection of kinetic

parameters, study of complexes and for the qualitative and quantitative determinations of organics, metals and ions. It is rapid, reliable, accurate and low cost of analysis.

Polarography was developed by Heyrovsky in 1922. He was awarded Noble Prize in 1959. His method, developed about fifty seven years ago, is still used with undiminished success. Though it is unchanged in principle, numerous modifications have been made to improve the sensitivity because dc polarography is not satisfactory at concentration below $10^{-5}M$ because it suffers from the disadvantage of having a relatively unfavourable faradaic to charging current ratio. Hence, the d.c. polarography has been modified by A.C. square wave and pulse polarography.

In A.C. polarography, capacity current is recorded in addition to the faradaic current and therefore this method is a little more sensitive than classical polarography. It does not give the analysis of solutions which are more dilute than $10^{-5}M$. Although A.C. polarography is more sensitive than d.c. polarography in analytical method, it makes possible to study the kinetics of electrode reactions faster than those which are studied by the conventional method. In analytical method the peaked nature of the waves permits their resolution when they are too close together for resolution by d. c. polarography. It is shown in Fig. 1.

SQUARE WAVE POLAROGRAPHY

Square wave polarography was developed by Barker and Jenkins (1952) with the object of establishing a method of increasing the sensitivity of A. C. polarography.

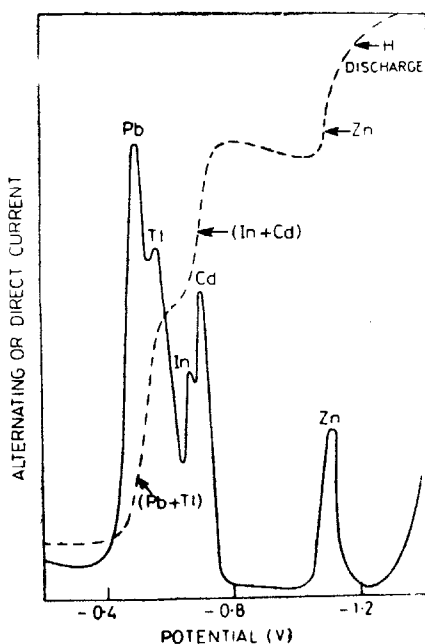


FIG. 1.

In order to increase the sensitivity, the capacitance current must be eliminated from the current that is measured.

The time dependence of the potential in the square-wave A. C. polarography is shown in Fig. 2. The capacitance current resulting from the growth of the drop is eliminated by measuring the current only at the end of the drop life. The A. C. caused by changes of the square wave potential is usually having a frequency of 225–250 Hz (cycles). The capacitance current disappears very rapidly after the change of the electrode potential by E , according to the equation: $i_c = \frac{E}{R} \exp\left(-\frac{T}{Rc}\right)$ where R and c are the resistance and capacity of the electrolytic system respectively and T is the time, elapsing the last potential change. The faradaic current on the other hand disappears at a much slower rate. The elimination of the capacitance current makes it possible to use this method for determining the concentration in the order of $10^{-8}M$ (Fig. 3). For irreversibly reduced depolarisers the lower limit of sensitivity is $10^{-6}M$.

PULSE POLAROGRAPHY

Pulse polarography was introduced by Barker and Gardner (1960) in which only one square wave impulse having a duration of $1/25\text{sec}$ is applied during the life of a drop. There are two sources of current which result from pulse application: (i) the faradaic current which is proportional to the concentration of depolariser; and (ii) the capacity current which charges the electrode double layer. In pulse polarography, the capacity current decays exponentially in response to potential pulse whereas the faradaic current decays at a very much lower rate.

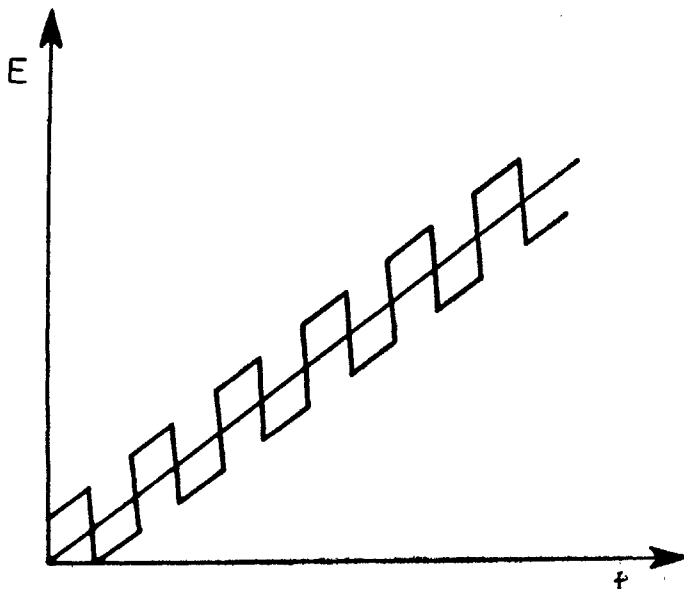


FIG. 2.

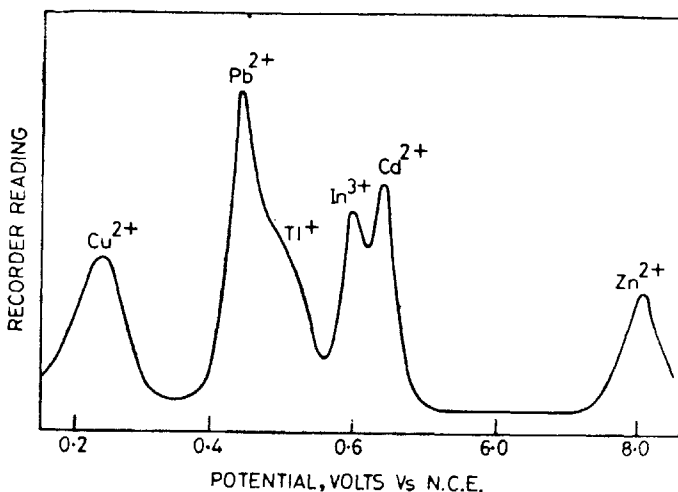


FIG. 3.

In pulse polarography there are basically two different ways of working: (i) In the first variant of pulse polarography, the electrode is polarised with a pulse having a linearly increasing amplitude. The potential changes and resulting currents are shown in Fig. (4). (ii) In the second variant one pulse of rectangular voltage, usually having a duration of $1/25$ and amplitude of about 30mm is applied to the slowly and linearly increasing potential after a definite time in the life of each mercury drop. The changes of the dropping electrode potential in this method are shown in Fig. (5). This method is characteristic of 'derivative' pulse polarography. The current is again measured during the second half of the pulse, so that the capacity current is eliminated. The current is measured twice—once before applying the pulse and once during the last 17ms of the pulse. The first current is instrumentally subtracted from the second current and the differential pulse polarogram is thus a plot of current difference vs. applied potential. The measurement of current difference gives the differential pulse polarogram of a peak shape, which is like the derivative d. c. polarogram.

A.N.P.P. vs. d. c. polarogram for Fe(III) in 0.2 M NH_4 tartrate buffer $\text{pH} = 9$ is shown in Fig. (6). An improvement in detection limit 5–10 times is observed for NPP over d. c. polarography.

A comparison of differential pulse and d. c. polarogram is shown in Fig. (7). The peak current of DPP is a quantitative measurement of concentration and peak potential is analogous to $E_{1/2}$.

CURRENT CONCENTRATION RELATIONSHIP OF NORMAL PULSE POLAROGRAPHY

Pulse polarography is applicable to a number of variety of electrodes and geometries. The normal pulse current on the diffusion plateau is given by (Parry & Osteryoung, 1964)

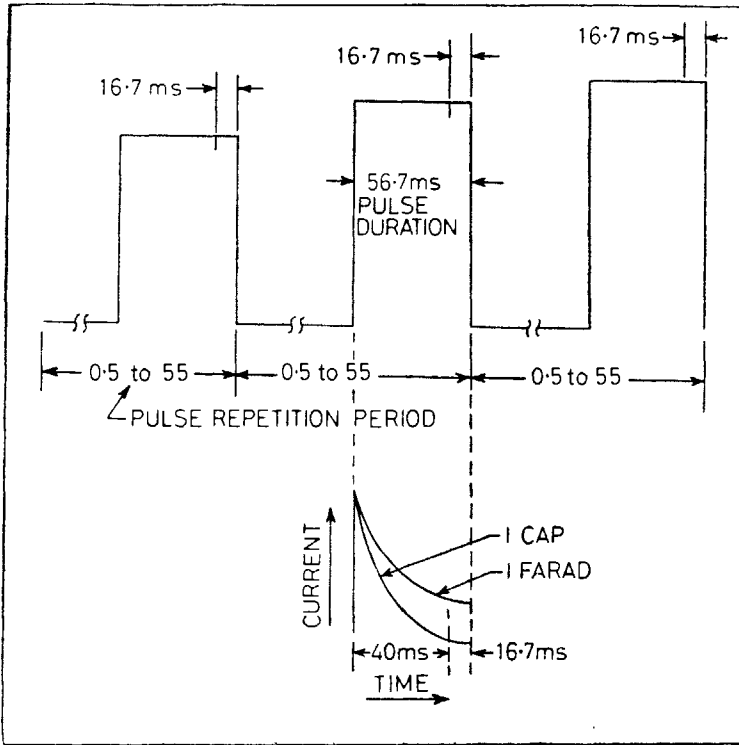


FIG. 4.

$$i_d = nFAD^{1/2} C_b / (\pi t_m)^{1/2} \quad \dots(1)$$

where i_d is the current in microamperes (μA), n the number of equivalents per mole, F the Faraday (96500 Coulombs/equivalent). A is the electrode area in cm^2 . C_b is the bulk concentration in m and t_m is the time in seconds at which current is measured from pulse application. In Fig. (A) time interval over which the current is averaged is illustrated, while in equation (1) we refer to instantaneous measurement time. The correct measurement time t_m to use equation (1) is given by

$$t_m^{1/2} = t^{1/2} + (t - \delta t)^{1/2} / 2 \quad \dots(2)$$

the pulse width ($t_2 - t_1$) as shown in Fig. (A) and t is the sample width. However, the time here is equal to the average time.

$$t_m = t - \delta t / 2 \quad \dots(3)$$

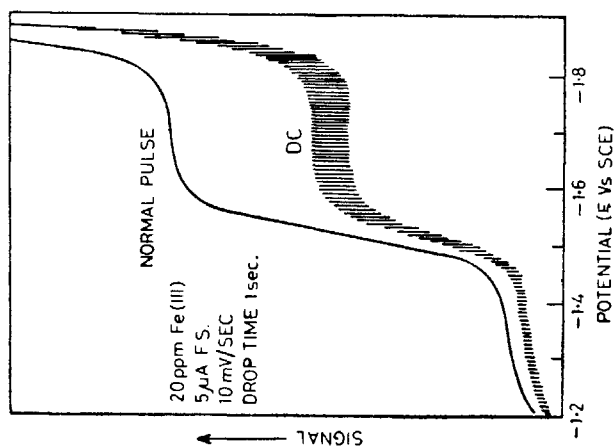


FIG. 6.

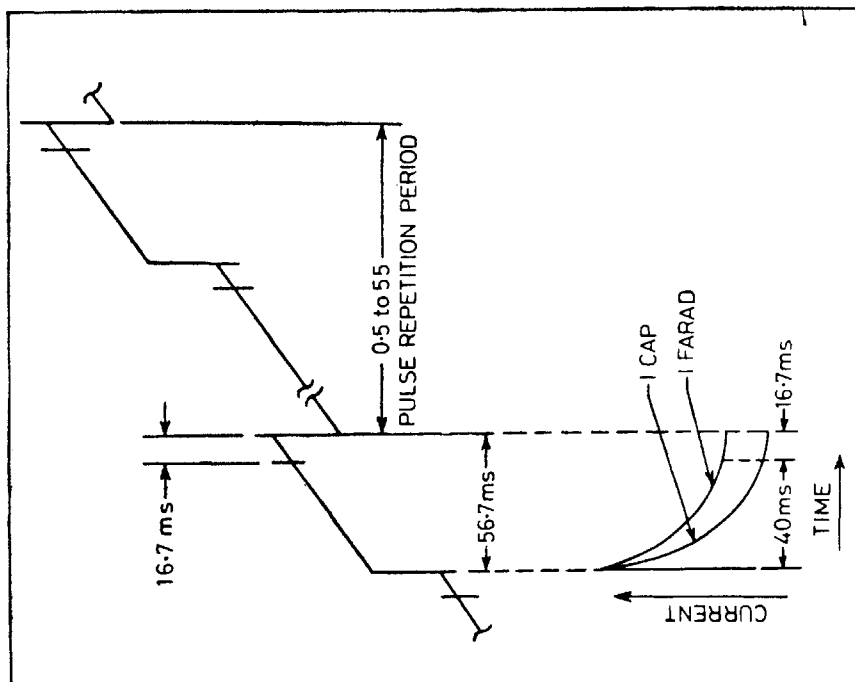


FIG. 5.

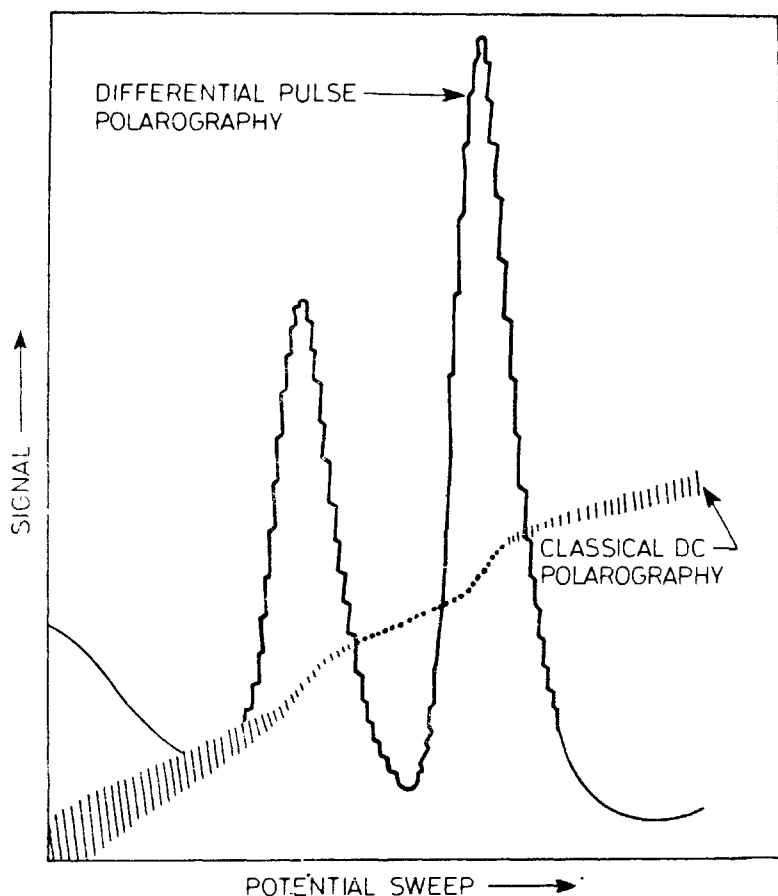


FIG. 7.

The sensitivity of NPP with respect to d. c. polarography can be calculated from equation (1) by substituting the area term for the growing drop and including the factor $(7/3)^{1/2}$ of the Ilkovic equation :

$$i_{\text{NPP}} = \frac{462 n D^{1/2} C_b m^{2/3} t_d^{2/3}}{t_m^{1/2}} \quad \dots(4)$$

$$i_{\text{DC}} = (7/3)^{1/2} 462 n D^{1/2} C_b m^{2/3} t_d^{1/6} \quad \dots(5)$$

$$i_{\text{NPP}}/i_{\text{DC}} = (3t_d/7t_m)^{1/2} \quad \dots(6)$$

For reasonable value of t_d and t_m this ratio is in the range 3-6 i.e., the N.P.P. detection is lower than 1/3 to 1/6 of the D.C. values.

ANALYTICAL APPLICATIONS

The needs of analytical chemists have undergone significant change over the last decade. As for example ppm (parts per million) determination were used to be sufficient applications. However, to-day's stringent environmental regulations and demand for ultra-pure chemicals in ppb determination are required. This technique has found widespread application in industrial, university and pollution laboratories. Differential pulse polarography is the most sensitive electroanalytical technique. The process is not limited to dme but it is extremely useful with stationary electrodes like carbon and platinum. Combination of stripping voltammetry with differential pulse wave-form gives a facility to detect solution concentration at sub-parts per billion levels.

Some examples are given of the detection of concentration of inorganic and organic compounds.

ANALYSIS OF TAP WATER BY DIFFERENTIAL PULSE STRIPPING VOLTAMMETRY

The heavy metal content of water which remained in copper plumbing overnight is compared to the metal content present after the pipes are flushed for several minutes. This water which was in the plumbing overnight showed higher concentration of Cu, Zn, and Pb.

Two different water samples were collected from two locations. Samples A were collected after running the water for approximately 30 minutes to flush the pipes and samples B were collected early in the morning which represented water which remained in Cu plumbing overnight. In each case 500ml samples were collected and preserved with 1.5ml of 1 : 1 HNO₃. Samples have a pH 1.5. Since at this pH hydrogen reduction interferes with analysis of Zn, first Cd and Pb were analysed in the water samples.

After this pH was raised to 8.9, Zn and Cu were estimated (Figs. 8 and 9). The determination of concentration of metal ions present in tap water is best received by addition of known volumes of standard metal-ion solution to the sample. After addition, the solution should be deaerated to remove the dissolved oxygen. The peak is taken then and the concentration of the given sample is calculated from the equation :

$$C_u = \frac{i_1 V_1 C_s}{i_2 V_1 + (i_2 - i_1) V_2}$$

C_u = original concentration; C_s = concentration of standard solution and for spiking
 ϕi_1 = original peak height; i_2 = spiked peak height; V_1 = volume of standard solution; V_2 = volume of original sample.

Differential Pulse Polarographic Determination of Drugs in Biological Fluids :

The determination of drugs in biological materials are required for evaluation of the bioavailability and the pharmacokinetic profile of a drug in its earlier stages of development, and later on in clinical efficacy trials, in which the drug concentration

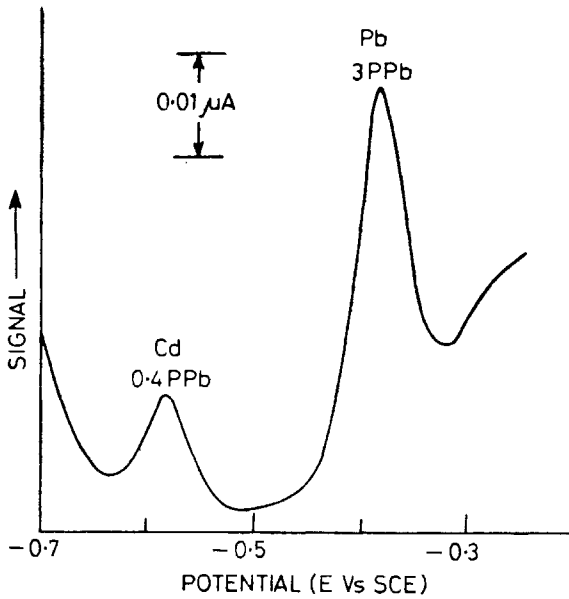


FIG. 8.

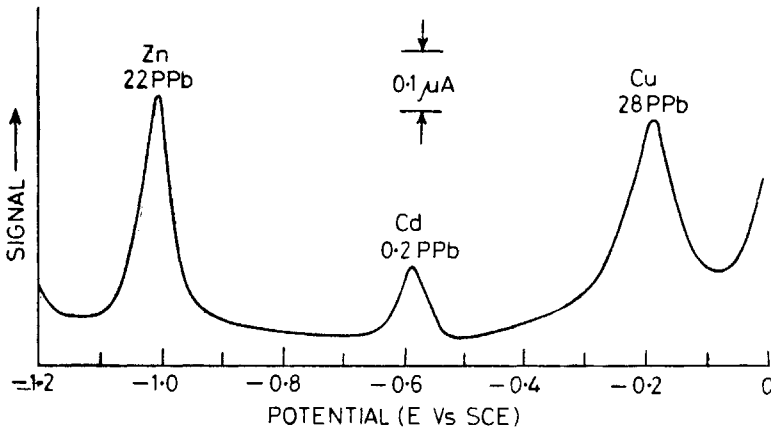


FIG. 9.

in the blood are co-related with clinical responses. The assays that are developed must be capable of measuring levels of the drug in both blood and urine in different species with sufficient sensitivity to follow the elimination of the drug for a period of 24 hours to 28 hours after single dose administration.

Dr M. A. Brooks, J. A. F. de Silve and L. M. D. Arcoute (Brooks *et al.*, 1973) have investigated the concentration of (i) 1-(2-nitro-1-imidazolyl)-3-methoxy-2-propanol and (ii) -chloromethyl-2-methyl-5-nitro-1-imidazole-ethanol in blood. The

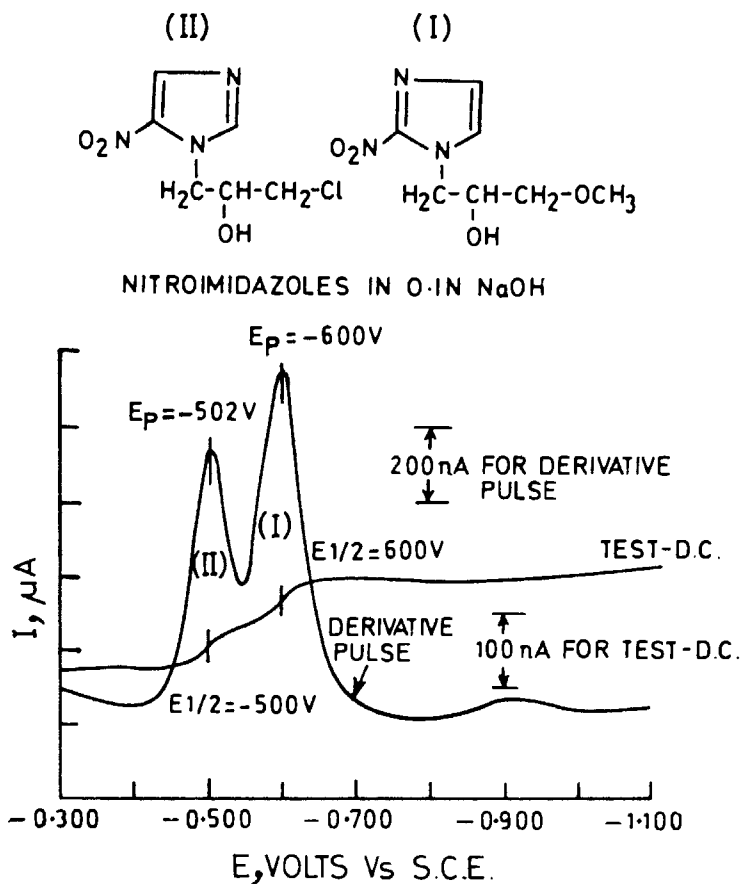


FIG. 10.

compounds were extracted in ethyl acetate, the residue of which is dissolved in 0.1N NaOH and analysed by DPP, by reduction of the nitro group Fig. (10). The sensitivity limit of both the compounds is 0.2–0.3 μ g/ml of blood.

APPLICATION OF DPP IN THE PLATING INDUSTRY

In the plating baths it is necessary to continuously monitor not only the plating metal concentration, but also the concentration of other metals which are present in both major and trace amounts. The concentration of these metals may be sometimes critical because the presence of certain elemental impurities can have a deleterious effect on the physical and chemical properties of the final product. These impurities give a demolishing effect on the marketability of the final product. The organic compounds are present in plating bath as chemical reagents or as inert reagents to improve the quality and brightness of the plate. The outline of the compositions of the plating baths of some metals is given in Table I. It consists of three sections

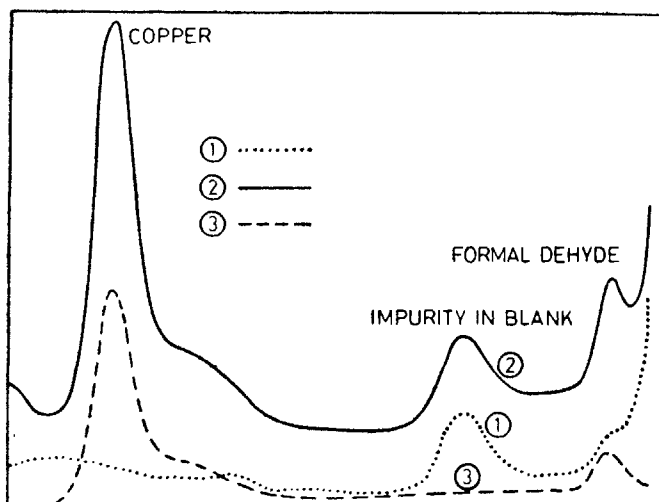


FIG. 11.

(a) Major components (b) trace metals and (c) organic additives. In the plating industry monitoring of high concentration of metal which is plated is necessary. Polarography technique is excellent for this determination. The concentration of major components, trace metals, and organic additives are estimated by this process. Estimation of some metal platings are shown in Fig. 11.

TABLE I

Examples of polarographic analyses of several plating baths

In these baths	Polarography can determine these		
	Major components	Trace metals	Organic Additives
1. Zinc Sulphate	Zinc	Copper, Cadmium, Arsenic	<i>o</i> -Chlorobenzaldehyde
2. Palladium	Palladium, Chloride	Tin	Hydroquinone
3. Gold (I) Cyanide	Gold, Free Cyanide	Cadmium, Cobalt, Copper, Zinc, Iron, Tin, Chromium	
4. Watt's Nickel	Nickel, Chloride, Boric Acid		Saccharin, <i>o</i> -Benzaldehyde sulphonic acid
5. Electroless Copper	Copper, Formaldehyde		Mercaptobenzothiazole
6. Copper sulphate	Copper		Thiourea and Thiourea derivatives
7. Solder Bath	Lead, Tin (II)	Tin (IV)	
8. Brass	Copper, Zinc	Lead, Arsenic	
9. Nickel-Cobalt	Nickel, Cobalt		

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