

POLAROGRAPHIC ANALYSIS OF COPPER BASE ALLOYS

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(Received November 6, 1969)

Two alloy systems Cu-Zn-Pb and Cu-Zn-Pb-Sn have been studied. Their polarography has been carried out in aqueous media using potassium chloride as the base electrolyte and normal calomel electrode (N.C.E.) as reference electrode. Since Sn (IV) forms a colloidal precipitate of Sn(OH)_4 in warm aqueous medium, it was separated from the system by ion exchange method and determined polarographically in hydrochloric acid medium.

Since Heyrovsky's first polarographic measurements in 1921, polarography has become a useful instrumental technique for the analysis of a wide variety of materials. This technique is now well established in many analytical laboratories along with other modern physicochemical methods such as spectrophotometry and emission spectroscopy. The importance of the method has further been increased by the fact that several elements can be quantitatively determined in a single solution in a short time. The technique is also most versatile as it can be employed to macro and micro-analytical problems and is ideal for the determination of trace metallic impurities.

Apparatus and Reagents

A Cambridge pen writing polarograph, dropping mercury electrode capillary and thermostat, as supplied by the manufacturer, were used for recording the polarograms. The experiments were carried out in a cell as described by Vogel,¹ with reference to a normal calomel electrode at 25°C. Dissolved air was removed from the solution by passing pure and dry nitrogen gas for about 10 min. The m value of the capillary was determined and found to be constant at 1.47 mg/sec at 25°C for over 6 months. The drop time was adjusted at 3.0 sec in KCl-supporting electrolyte for Cu, Pb and Zn and 3.0 sec in HCl-supporting electrolyte for Sn(IV) measured at the particular applied potential at which the diffusion current started.

Stock solutions of Cu, Pb, Zn and Sn (5.0 mM) were prepared in concd HCl from reagent quality metals. 0.1 M KCl supporting electrolyte and 0.2% Triton X-100 maximum suppressor stock solutions were prepared in distilled water. Potassium ferrocyanide, quinaladic acid, potassium chromate and sodium sulphide were used for qualitative identification of metal cations during ion-exchange separations.

Experimental

Leaded brasses, non-leaded brasses, leaded tin bronze, leaded high tin bronzes etc. are amongst the commonly used foundry alloys containing varying amounts of copper, lead, zinc and tin. Additions of other elements like nickel, aluminium, iron, manganese, silicon, phosphorus etc. are made to acquire special purpose alloys.

Copper gives reduction steps near to zero applied potential in most base electrolytes.² Therefore, the current due to this reduction greatly restricts the determination of elements reducing at more negative potentials. Tin also reduces near to zero applied potential whereas lead and zinc have half wave potentials far removed from copper and tin. Separation of these elements is, therefore, essential. Whereas copper is usually removed by (i) forming copper cyanide complexes, (ii) precipitation, (iii) electrolytic deposition and (iv) precipitating other cations from the composite solution and determining copper separately, tin, lead and zinc are separated by conventional methods. The authors have employed ion exchange method for the separation of these cations, because it is not only quick but also quantitative.

(a) Ion Exchange Separation of Cu, Zn, Pb and Sn

A Pyrex glass column (20 × 1.5 cm) containing a strongly basic anion exchange resin (Amberlite IRA-400 Cl) was used for the separation of the above cations, using 2M HCl as the complexing medium. A mixture of 5 ml each of 5mM Cu^{++} , Zn^{++} , Pb^{++} and Sn(IV) was fed to the column at the rate of 1 ml/min. Copper was not adsorbed and passed through the column as such. It was collected in a 100-ml beaker. Pb^{++} , Zn^{++} and Sn(IV) were held by the resin, wherefrom Pb^{++} and Zn^{++} were eluted with water and their combined solution preserved in another 100-ml beaker. Lastly, Sn(IV) was stripped off the column with 1M HNO_3 and collected in another 100-ml beaker.

The various eluates collected as above were then treated for polarography and polarograms recorded as described below.

(b) Polarographic Determination of Copper

Copper has been found to give a single step reduction wave when 1N H_2SO_4 or 1N HNO_3 is used as supporting electrolyte. The wave form in 1N HNO_3 is normal, but in 1N H_2SO_4 a peculiar semblance of a minimum is noted in diffusion current. Therefore, 1N H_2SO_4 is not recommended for the quantitative determination of copper.³

In the present case, however, the procedure is as follows: The solution containing cupric ions was evaporated to dryness to expel the acid and taken up with distilled water to make 5 ml of the solution. Then 1 ml of this neutral solution was fed to the polarographic cell along with 1 ml each of 0.1M KCl and 0.2% Triton X-100 as base electrolyte and maximum suppressor respectively. The solution was deaerated with pure dry nitrogen for 10 min and the polarogram recorded at 25°C as shown in Fig. 1(c).

It may be seen from Fig. 1(a) that copper reduces in two steps, probably, from $CuCl_4^{-2}$ to $CuCl_2^-$ and then to the metallic state, the reduction steps having half-wave potentials of -0.035 and -0.175 V respectively. If, however, proper applied voltage range is selected, the reduction is completed in a single step with $E_{1/2} = -0.125$ V as shown in Fig. 1(b). It is observed that the total step height in the two cases is the same.

(c) Polarographic Determination of Zinc Plus Lead

Zinc cannot be determined in large concentrations of hydrogen ions because the wave is masked by hydrogen evolution.⁴ However, good quantitative steps are obtained in alkali chloride or nitrate base electrolytes.⁵ Ammoniacal media have been found extremely useful for the determination of zinc in copper base alloys⁶ and lead base alloys.⁷

Lead gives excellent reduction steps in a number of base electrolytes and since it is not easy to determine lead by other physical methods, the polarographic method is now extensively used for its determination in pure metals and metallurgical alloys.⁸

In this case, the authors proceeded with the combined zinc and lead eluate as follows: The solution was evaporated to dryness and taken up

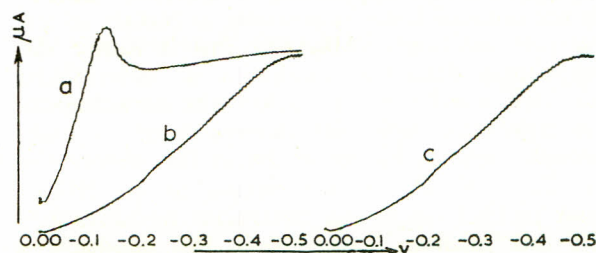


Fig. 1.—Polarograms of Cu^+ showing (a) two step reduction wave, (b) single step standard wave, (c) single step wave after separation, at sensitivity 1/100 and damping 3.

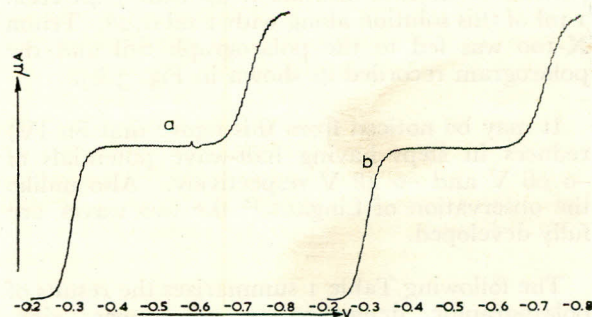


Fig. 2.—Polarograms of $Pb^{++} + Zn$ showing (a) standard wave, (b) after separation, at sensitivity 1/100 and damping 3.

with distilled water to make 5 ml of the solution. 1 ml of this solution was then fed to the polarographic cell along with 1 ml each of 0.1M KCl and 0.2% Triton X-100 as supporting electrolyte and maximum suppressor respectively. The solution was deaerated as before and polarogram recorded as shown in Fig. 2(b).

From Fig. 2, it is quite clear that Pb and Zn give excellent reduction waves with half-wave potentials of -0.59 V and -1.43 V respectively. Since the two cations are widely separated with respect to their half-wave potentials, they are polarographed together, otherwise their separation would have to be affected from the combined eluate.

(d) Polarographic Determination of Tin

Several studies of the polarographic characteristics of tin have been made by various authors but the first systematic study was conducted by Lingane for its determination in various kinds of copper-based alloys.¹⁰ Stannic tin in either 1N H_2SO_4 or HNO_3 is too greatly hydrolysed with the precipitation of basic salts to permit the use

of these media as supporting electrolytes. Sn(IV) is not reduced from its solutions in NaOH or any tartrate solutions. Although this is rather disappointing from the standpoint of determining tin itself, it will probably prove to be advantageous in connection with the determination of other metals, such as Sb, Bi or Pb in the presence of Sn(IV).⁹ Sn(IV) is determined in 4M NH₄Cl and 1M HCl supporting electrolyte by Lingane.¹⁰ In this medium although Sn(IV) produces a double wave corresponding to stepwise reduction first to the Sn(II) state and then to the metal, but the first diffusion current wave is not fully developed before the second wave begins.

The eluate containing Sn(IV) ions was evaporated to dryness and taken up with 7.4N HCl. 1 ml of this solution along with 1 ml 0.2% Triton X-100 was fed to the polarograph cell and the polarogram recorded as shown in Fig. 3(b).

It may be noticed from this figure that Sn(IV) reduces in steps having half-wave potentials of -0.06 V and -0.48 V respectively. Also unlike the observation of Lingane,¹⁰ the two waves are fully developed.

The following Table 1 summarizes the results of polarographic determination of copper, zinc, lead and tin after their separation from each other by ion exchange method.

TABLE 1.

Element	Taken mg/ml	Found mg/ml	Error %
Copper	0.3175	0.3146	0.91
Lead	1.035	1.029	0.57
Zinc	0.3268	0.3268	nil
Tin	0.5935	0.5920	0.25

In unknown solutions of copper base alloys elements like antimony, bismuth, iron, nickel, manganese and aluminium may be encountered. These elements are usually present in small quantities for giving special properties to the copper alloys. They can be separated from the solution by ion exchange methods using suitable eluting agents and complexing media and their polarography conducted separately. A knowledge of the diffusion current constants further simplifies the position as regards the calculation of the quantities of various elements. For example, Ni and Al^{III} can easily be collected in the effluent from the ion exchange column because they do not form anionic chloro complexes in any strength

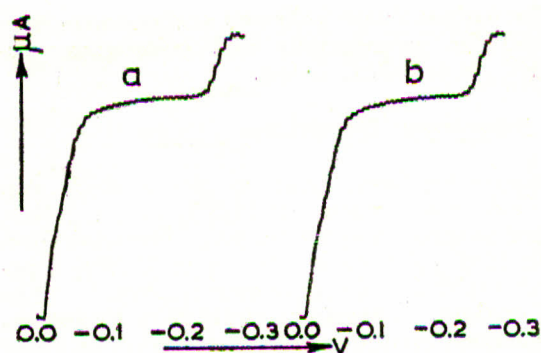


Fig. 3.—Polarograms of Sn(IV) showing (a) standard wave, (b) wave obtained after separation, at sensitivity 1/20 and damping 3.

of HCl. They can further be separated quantitatively by passing the solution over a cation exchange column and subsequently eluting Al with 0.8M HF-0.06 M HCl and Ni with 4M HCl.² Antimony, bismuth, iron and manganese which are effectively taken up in concd HCl, can be eluted from the column with 6N HCl (manganese¹³), 0.5N HCl (iron¹⁴), 1N NaOH (antimony¹⁵) and 1N H₂SO₄ (bismuth¹⁶), thus enabling a complete quantitative analysis of any copper base alloy.

Diffusion Current Constants and their Application to Analysis

It was first demonstrated by Ilkovic and later confirmed by others,¹⁶ that the diffusion current is expressed completely and quantitatively by the following equation:

$$i_d = KnD^{1/2} Cm^{2/3} t^{1/6}$$

in which i_d is the diffusion current in microamperes, n is the number of electron equivalents per molar unit of the electron reaction, D is the diffusion coefficient (cm²/sec) of the reducible or oxidisable substance, C is its concentration in millimoles per liter, m is the rate of Hg flow from the dropping electrode in mg/sec and t is the drop time in sec. In this relation K , n and D are independent of the characteristics of the dropping electrode capillary. Therefore, the quantity $KnD^{1/2}$, which is experimentally determinable as $i_d/(Cm^{2/3} \times t^{1/6})$ is a fundamental constant referred to as "diffusion current constant".

Table 2 gives the diffusion current constants for the elements studied at 25°C using normal calomel electrode as the reference electrode.

TABLE 2.

Cations	Solution	Diffusion current constant
Copper	5 mm	16.23
Lead	5 mm	5.71
Zinc	5 mm	15.28
Tin	5 mm	2.05

The data can be applied directly to the analysis of unknown solutions of these metals in the particular supporting electrolytes. If we represent diffusion current constant by I , then the concentration in an unknown case will be given by

$$C = \frac{i_d}{I m^{2/3} t^{1/6}}$$

In addition to a knowledge of the I , this method requires that the quantity $m^{2/3} t^{1/6}$ be known for the capillary that is used, but the determination of m and t by a technique that has already been described¹⁷ requires only a few minutes time, and obviously it is much simpler than the preparation of a standard solution for each substance.

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