Apparatus for Automatic Control of Electrodeposition with Graded Cathode Potential

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An apparatus is described for carrying out graded cathode potential electrodepositions automatically, whereby a metal may be separated by cathodic deposition from a metal lying closely above it in the electromotive series. The device consists of a vacuum tube amplifier which magnifies the cathode-calomel voltage sufficiently to actuate a relay and motor which drives a Variac; the Variac governs the size of an alternating current, which when rectified is used to effect the deposition. The entirely automatic operation of the apparatus frees the analyst for the entire period of the electrodeposition and shortens the time normally taken for such an analysis. The apparatus has been tested on the separation of copper from tin in hydrochloric acid solution.

IN THE normal practice of analysis by the electrodeposition of a metal at the cathode, the voltage necessary to yield a current of convenient size is applied initially to the cathode and anode and no further attention paid to it other than to change its value occasionally to maintain the current as the composition of the electrolyte changes. By such a constant current electrodeposition the possible separations are limited to those metals below hydrogen in the electromotive series from those above hydrogen, hydrogen being evolved after the deposition of the lower metal in preference to deposition of the higher metal. The change in the cathode-anode voltage during the electrolysis is no clue to the extent of the deposition of a metallic ion, but is the algebraic difference of the voltages between the solution and the cathode and anode and the IR drop through the solution, all of which may undergo change during the electrolysis.

By inserting a reference half-cell into the solution and measuring the voltage between the cathode and the reference cell it becomes possible to isolate the effect at the cathode. The voltage between the solution and the cathode consists of the equilibrium

voltage of the electrode metal toward the solution containing its ions and concentration polarization caused by the flow of current. Neglecting the latter for the time being, there is thus provided a means of following the change in the concentration of the metal ion during the deposition, the reversible voltage being given by the Nernst equation:

$$E = E_0 + \frac{RT}{nF} \ln [M^{n+}]$$

Thus, for example, to separate copper from tin, the apparatus shown in Figure 1 is employed, a calomel half-cell being used as

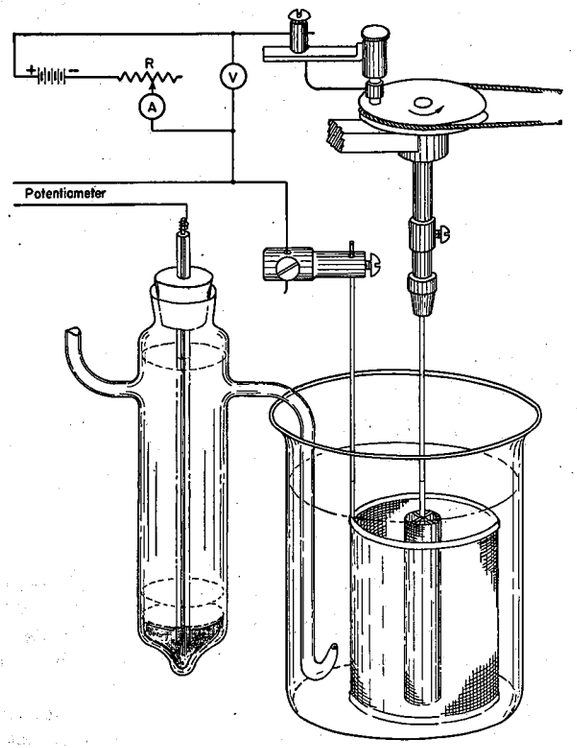

Figure 1. Circuit and Apparatus for Graded Cathode Potential Electrodeposition

the reference electrode. The cathode-calomel voltage, measured by the potentiometer, increases as the copper is deposited. Using a 0.1 *N* calomel reference half-cell, this voltage is not allowed to exceed 0.45 volt, the electrolyzing current being decreased progressively by increasing the resistance, *R*, to accomplish this. The last copper will be gradually deposited by the successively smaller current without the deposition of any tin.

Since their first use by Sand (*3*) such graded cathode potential separations have not become popular, even though a number of very useful applications of the method have been devised, notably by the English workers Sand, Lindsey, Collin, and Torrance. The continuous attention of the analyst is required throughout the electrolysis and the deposition can seldom be completed in less than 60 minutes, since it is necessary to use a relatively low initial current, less than 2 amperes. At greater currents the changes of the cathode voltage occur so rapidly that the manual operations of balancing the potentiometer and adjusting the current cannot be carried out sufficiently rapidly. Clearly then, this is a case for automatic control.

The apparatus described, which accomplishes the graded cathode potential separation automatically, consists of three main units:

1. A rectifying unit by which a direct current output of low voltage can be obtained from the 110-volt alternating current line to perform the electrolysis.
2. A control circuit consisting of a vacuum tube amplifier, a relay, and a motor-driven Variac by which the cathode voltage is made to govern the electrolyzing current.
3. A vacuum tube voltmeter for convenience in measuring the cathode-calomel voltage.

The circuit and appearance of the apparatus are shown in Figures 2 and 3.

RECTIFYING CIRCUIT

The direct current needed for the electolysis is obtained from the 110-volt alternating current line, the circuit elements being, successively, a switch in the 110-volt alternating current input, a Variac, a step-down transformer, a selenium rectifier, a milliammeter-shunt combination, and a filter.

The Variac is driven by a motor activated in turn by the amplifier-relay (control) circuit and is the mechanism whereby the electrolyzing current is decreased as a result of increases in the cathode-calomel voltage. The Variac may be set by hand after turning a knob which disengages it from the motor.

The secondary of the step-down transformer has taps to provide voltages of 2, 3, 4, 6, 8, and 10 volts when 110 volts are supplied the primary of the transformer by the Variac. Thus, no more than a safe load can be supplied the selenium rectifier which is capable of handling up to 10 volts.

The rectifier is followed by a filter consisting of an inductance of 2 henrys in series and two capacitances of 1500 μf in parallel, one before and one after the choke. The purpose of the filter is to smooth out the 120-cycle ripple which otherwise affects the control circuit adversely.

The direct current drawn is measured by a milliammeter suitably arranged with three shunts, so that it can be made to read three current ranges, 0 to 0.05 ampere, 0 to 0.5 ampere, and 0 to 5.0 amperes, by changing the position of the range selector knob on the lower right front panel of the instrument.

CONTROL CIRCUIT

The cathode-calomel voltage is amplified by a two-stage vacuum tube amplifier which drives a gas-filled tube which provides enough power to operate a relay. The relay in turn controls a motor which turns the Variac.

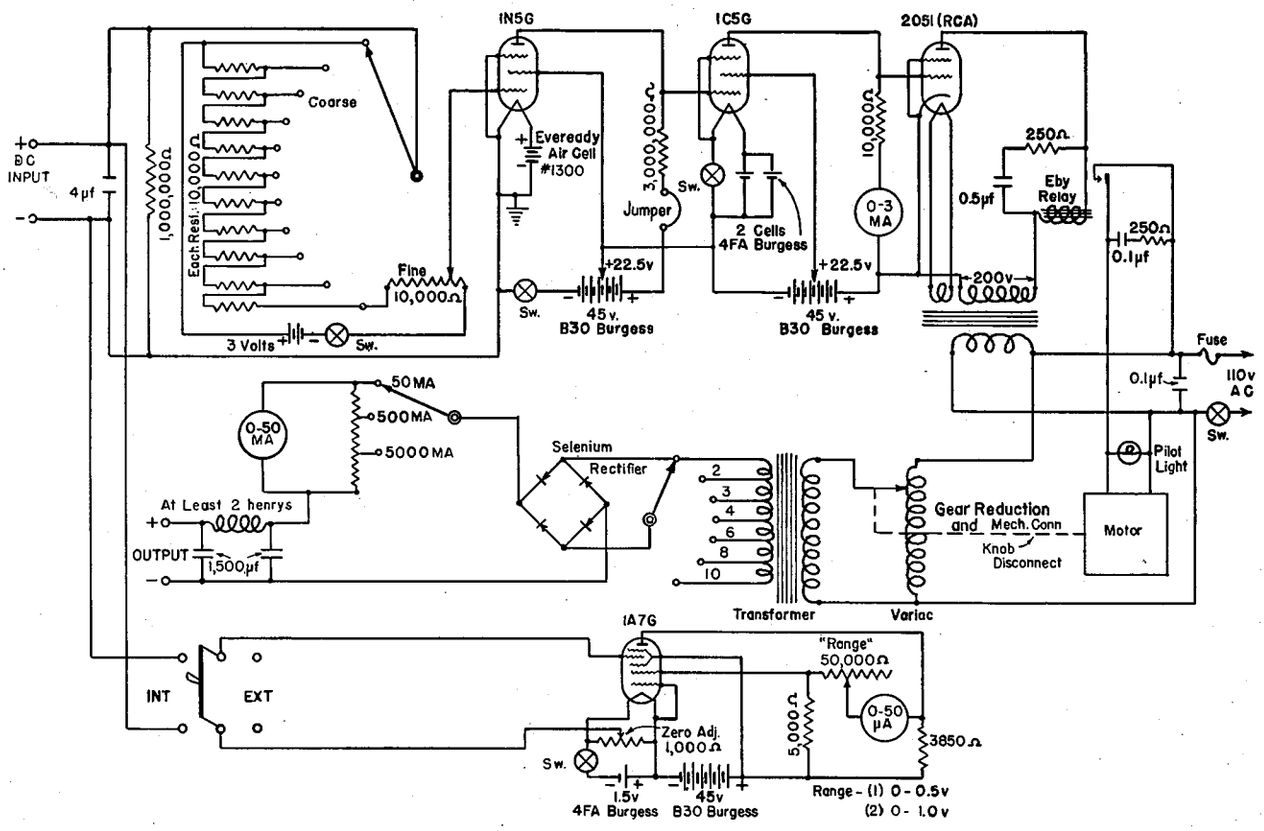

Figure 2. Circuit of Apparatus or Automatic Graded Cathode Potential Electrodeposition

Relay H. H. Eby Co., Philadelphia, Type ER12, 10,000 ohms. Variac, General Radio Co., Cambridge, Mass., Type 200B. Motor, 1/50 h.p. Induction motor with 1200 to 1800 r.p.m., gear reduction to turn Variac about 0.5 r.p.m. Rectifier, I.T. and T. selenium rectifier, Type 4B1C4

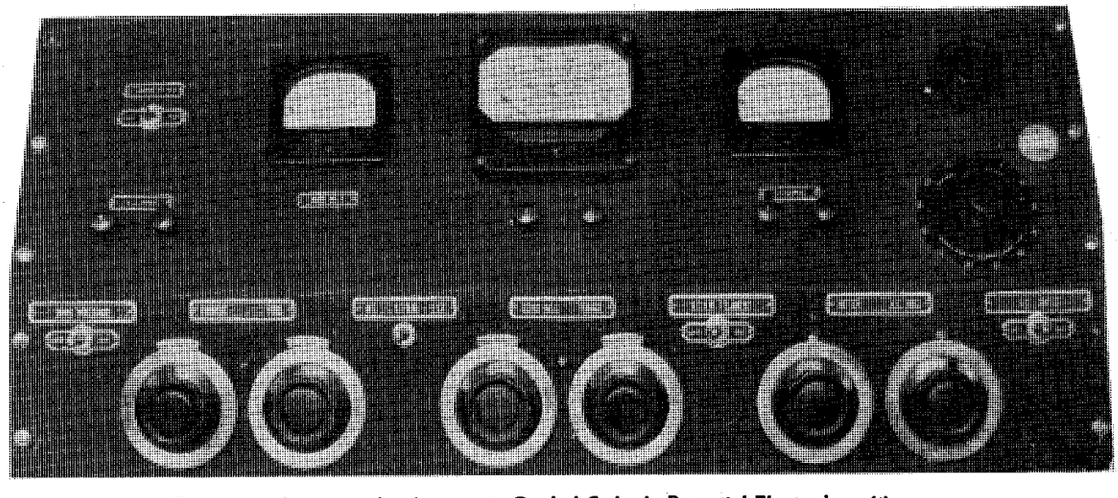

Figure 3. Apparatus for Automatic Graded Cathode Potential Electrodeposition

It was desired to have a control circuit which would respond to a change of 10 millivolts in the cathode-calomel voltage. Numerous attempts were made to design a line-operated amplifier of sufficient sensitivity. It appeared impossible to stabilize the filament supply when operated from the alternating current line voltage and it was necessary to resort to battery operation. (Numerous attempts to design a reasonably simple, line-operated amplifier are discussed by Parker, *2*.) The vacuum tubes selected were chosen from the low filament current tubes recently made available; power required is so low that the batteries last over 6 months in continuous operation.

The cathode-calomel voltage is applied so as to buck the grid bias of the first tube, a 1N5G; as the cathode-calomel voltage increases the cathode-grid voltage of the 1N5G becomes less negative, allowing more current to flow in its plate circuit. This increase of the plate current causes the grid of the second tube, a 1C5G, to become more negative and the plate current of this tube decreases, in turn causing the grid voltage of the third tube, a gas-filled tube, Type 2051, to become more positive. If the grid voltage of this tube becomes more positive (less) than −2.0 volts, the critical value for firing at the plate voltage used, it passes current sufficient to close the relay.

The grid bias voltage of the first tube is secured from a 3-volt battery with a potential divider with coarse and fine adjustments. The total resistance of the potential divider is 110,000 ohms in steps of 10,000 ohms, the coarse settings being fixed 10,000-ohm resistors and the fine adjustment a variable 10,000-resistor. The coarse setting thus changes in steps of about 0.27 volt and the fine adjustment permits setting to about 0.005 volt.

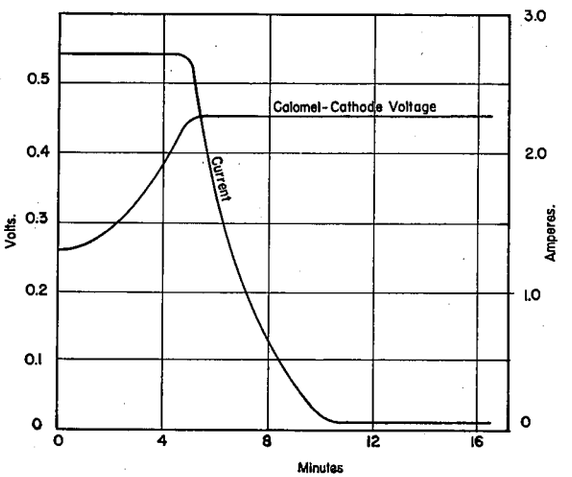

Figure 4. Course of Cathode-Calomel Voltage and Electrolyzing Current during Deposition of Copper in Presence of Tin

The cathode-calomel voltage (C.C.P.), the bias voltage (B.P.), and the grid voltage (G.P.), which is just sufficient to activate the relay, are related by: B.P. − C.C.P. = G.P. Thus for any calomel-cathode voltage there is a corresponding bias voltage which causes the relay to close. The bias setting may be calibrated in terms of the input voltage which just closes the relay, by impressing a known voltage on the input terminals and adjusting the bias until the relay just closes. The calibration is essentially linear and usually holds for about 2 weeks, after which the unit must be recalibrated. The use of the vacuum tube voltmeter makes such readjustments a simple matter.

In the separation of copper from tin, the calomel-cathode voltage (0.1 *N* calomel) must be limited to 0.45 volt. This corresponds to a certain bias setting—for example, coarse reading 8, fine 27.0. With the bias so adjusted any voltage greater than 0.45 volt applied to the D.C. input causes the relay to close. The electrolyzing current is then reduced until the calomel-cathode voltage falls below 0.45 volt, at which point the relay opens.

The 2051 tube which drives the relay is a gas-filled tetrode which passes a comparatively high current, about 9 milliamperes, once its grid voltage becomes less than −2.0 volts. Once the plate current has started, its magnitude is determined by the anode supply voltage and the impedance of the anode circuit and is practically independent of the grid voltage. By operating the 2051 on alternating current it is possible to have the tube turn off when the grid voltage becomes only slightly more negative than −2.0 volts. During the negative half cycle of the alternating current voltage applied to the plate, the plate current is zero, since the plate is negative with respect to the cathode. As long as the grid voltage is less negative than the critical value of −2.0 volts, the tube will conduct on positive half cycles. However, if the grid is more negative than the critical value, conduction will be prevented on positive half cycles. In other words, a change in grid potential can cause the 2051 tube not only to close but to open the relay.

A milliammeter (left-hand meter, Figure 3) was placed in the plate circuit of the second tube as an indication of approach to the point where the relay closes. This is convenient in showing that the amplifier is functioning and is a somewhat more sensitive indicator than the vacuum tube voltmeter of the changes in the cathode-calomel voltage.

Table I. Standardization of Copper and Tin Solutions

Copper Solution Taken *Grams*	Copper Found *Grams*		Concentration of Copper *G./g. of solution*
36.313	0.7560		0.020819
48.194	1.0033		0.020819
48.747	1.0146		0.020814
		Av	0.020818
Tin Solution Taken	**Tin Found**		**Concentration of Tin**
21.982	0.4243		0.019278
29.547	0.5701		0.019295
30.706	0.5913		0.019261
30.405	0.5852		0.019246
38.065	0.7335		0.019270
		Av.	0.019270

VACUUM TUBE VOLTMETER

For convenience in measuring the cathode-calomel voltage, a vacuum tube voltmeter was incorporated in the apparatus. The recent design of Garman and Droz (*1*) was used, employing a single, battery-operated tube and making use of a bridge-type circuit. Because of the low power consumption (0.3 watt) the inconvenience and cost of frequent battery replacement are reduced to a minimum and the added advantage is secured of greater stability and greater simplicity than with line operation. The circuit is shown in Figure 2.

The vacuum tube voltmeter was placed in the center of the apparatus and shielded by enclosure in a separate metal box.

The zero and range adjustment controls, meter, and filament switch were brought to the center of the front panel, as will be seen from a close inspection of Figure 3. In order to use the vacuum tube voltmeter for other purposes if desired, input terminals were placed on the panel (just below the meter) and a switch provided so that the voltmeter could be made to read the cathode-calomel voltage (int.) by direct connection within the apparatus with the D.C. input, or to read some other voltage applied to the voltmeter input terminals (ext.).

The vacuum tube voltmeter is calibrated by first shorting the input terminals and varying the zero adjustment to bring the meter to read zero. The desired voltage to cause full-scale reading is then applied and the range adjusted until the meter reads full scale. The zero is then checked and adjustment made if necessary. The full-scale setting is then checked and adjustment made if needed. The voltmeter may be calibrated over any range up to 1 volt—for example, 0 to 0.5 volt or 0 to 1.0 volt.

AUXILIARY EQUIPMENT

In graded cathode potential electrodepositions, vigorous stirring is essential. This is most conveniently accomplished with a rotating platinum anode driven at about 800 r.p.m. It was found that electrical contact to the rotating anode could be made conveniently by a carbon brush bearing on the flat upper surface of the pulley attached to the chuck holding the electrode; some minor variation of a few milliamperes in the electrolyzing current occurred because of the unevenness of this contact, but this had no effect on the operation of the apparatus.

The conventional form of calomel electrode may be used, 0.1 *N*, 1 *N*, or saturated, the appropriate change in the limited potential used being made on substituting one for another. The calomel cell must be placed with its contact tip on the outer side of the cathode and the tip should not extend below the lower edge of the cathode, so as to be as far away from the lines of flow of electrical current as possible.

The electrode assembly should be designed so that the beaker can be lowered away and the electrodes washed quickly following the electrolysis.

OPERATION

The filament voltage, bias voltage, and vacuum tube voltmeter filament are turned on and the apparatus is given a 20-minute warming up period before starting the electrodeposition Connections from the D.C. output are made to the cathode and anode and from the D.C. input to the cathode and calomel cell. In the case of copper and metals higher than copper in the electromotive series, the calomel cell is connected to the positive terminal. The bias controls are set for the limited potential wanted. The stirring motor is started and the electrolysis is begun by turning the alternating current switch on, setting the Variac to full value, and turning the voltage regulator to give a suitable current.

It is best then to test the D.C. input circuit by breaking contact at the calomel cell junction. The reading of the vacuum tube voltmeter should change on breaking the contact or upon altering the size of the electrolyzing current. If a variation is not observed, the other contacts should be examined and the calomel cell inspected for air bubbles. If the circuit is closed the electrolysis can proceed without further attention from the operator.

The electrolysis is usually complete in 20 to 40 minutes, by which time the current will have been reduced to 20 milliamperes or less. In some cases the current must not be allowed to fall below a certain value, below which the metal may dissolve more rapidly than it is being plated out. The solution is then removed, the electrodes washed without interrupting the current, and the determination concluded in the usual manner.

Table II. Separation and Determination of Copper and Tin

Copper Taken				Tin Taken			
Solution	Copper content	Copper Found	Copper Error	Solution	Tin content	Tin Found	Tin Error
Grams	*Gram*	*Gram*	*Mg.*	*Grams*	*Gram*	*Gram*	*Mg.*
13.819	0.2877	0.2876	−0.1	25.5	0.48	Not determined	
22.700	0.4726	0.4721	−0.5	25.5	0.48	Not determined	
22.902	0.4768	0.4763	−0.5	25.5	0.48	Not determined	
6.332	0.1318	0.1318	0.0	42.420	0.8175	0.8169	−0.6
12.701	0.2644	0.2649	−0.5	25.872	0.4986	0.4992	+0.6
16.620	0.3460	0.3467	+0.7	26.527	0.5112	0.5121	+0.9
16.997	0.3539	0.3539	0.0	27.749	0.5347	0.5354	+0.7
16.619	0.3460	0.3458	−0.2	26.401	0.5088	0.5078	−1.0
28.104	0.5851	0.5856	+0.5	15.230	0.2934	0.2942	+0.8
30.820	0.6417	0.6416	−0.1	16.415	0.3163	0.3173	+1.0

APPLICATION TO SEPARATION OF COPPER FROM TIN

The apparatus was tested on the separation of copper from tin. The electrode potentials of these metals are +0.345 and −0.136, respectively, and a separation of copper from appreciable amounts of tin by the ordinary electrodeposition process is impossible. The deposition was carried out from a hydrochloric acid solution containing hydroxylammonium chloride to prevent the liberation of chlorine at the anode, a procedure first described by Schoch and Brown (*4*).

Standard solutions of copper and tin were prepared as follows:

Electrolytic copper prepared by electrolysis of C.P. copper sulfate was dissolved in dilute nitric acid and converted to copper sulfate by evaporation with a slight excess of sulfuric acid. The gray, anhydrous copper sulfate remaining after fuming was dissolved carefully and diluted. The copper in this solution was determined electrolytically. A weight buret was used to measure out the solution. To each determination were added 3 grams of ammonium nitrate and 3 ml. of nitric acid. The electrolysis was carried out in the usual way and continued sufficiently long to ensure the deposition of all copper. The results are given in Table I.

Pure tin was dissolved in hot, concentrated hydrochloric acid in contact with metallic platinum, a reflux condenser being employed to prevent the loss of tin by volatilization. The solution was diluted carefully and the tin determined electrolytically. The solution was measured out with a weight buret, diluted to 250 ml., and treated with 10 grams of hydroxylammonium chloride. The tin was then deposited on a copper-plated platinum electrode, using a current of 1.5 amperes. Just before discontinuing the electrolysis the solution was neutralized with ammonia to avoid any solvent action of hydrochloric acid on the tin during the washing process. Following the deposition the solution was checked for the complete removal of tin. The results are given in Table I. This solution contained about 5 ml. of free, concentrated hydrochloric acid per 25 ml. It was found that if the solution was not diluted to about 250 ml. the tin deposited in part as large crystals at the top and bottom of the electrode.

Quantities of these solutions, delivered from a weight buret, were mixed and to the resulting solution were added 10 ml. of concentrated hydrochloric acid and 2 grams of hydroxylammonium chloride. The solution was then diluted to 150 ml. and the electrolysis begun at a current of 2 to 4 amperes. The apparatus was set to limit the cathode-calomel voltage to 0.45 volt (0.1 *N* calomel). The electrolysis was allowed to continue until the current had been decreased to about 0.020 ampere.

The course of the current and the cathode-calomel voltage during a typical deposition of copper are shown in Figure 4, the quantities of copper and tin present in the particular determination from which the data was obtained being, respectively, 0.3222 and 0.5190 gram. The action of the apparatus is clearly apparent. Once the critical potential, as set by the bias controls, is reached the calomel-cathode voltage is held constant and the current decreased to a residual value approaching zero. The electrolysis was generally continued until the residual current was about 20 milliamperes, the time required being from 20 to 40 minutes, depending on the amount of copper present.

Following the deposition of copper, about 8 grams of hydroxylammonium chloride were added, the solution was diluted to about 250 ml., and the tin deposited on a copper-clad platinum cathode.

The results of a series of separations of copper from tin are given in Table II. The separation is very successful as long as a large amount of tin is present, as in the analyses reported in Table II. When the amount of tin is less than that equivalent to the copper present the separation becomes erratic, low results being frequently obtained for copper. This peculiar behavior resides in the electrochemistry involved, however, and not in the action of the apparatus described, since similar erratic results were obtained on low-tin mixtures by the conventional, manual method of carrying out the graded cathode potential electrodeposition. Additional tin can be added when necessary, as, for example, in the direct determination of copper in bronze

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