ELECTROCHEMICAL ANALYSIS WITH GRADED CATHODE POTENTIAL CONTROL

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HARVEY DIEHL

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PREFACE

In this booklet will be found an introduction to the theory and practice of effecting the separation of certain metals by electrodeposition, using the so-called *graded cathode potential* method. An apparatus for carrying out such separations automatically is described. The literature on the subject as it is related to the metals—silver, copper, bismuth, antimony, lead, tin, nickel, and cadmium—is reviewed and finally typical procedures for the determination of the various metals in their alloys are given.

A complete discussion of the electrochemical determination of the various metals has not been attempted; this is cared for adequately in the classical books by E. F. Smith, by Classen and Danneel, and by Fischer, and especially by the more recent three-volume work, *Electrochemistry and Electrochemical Analysis*, by H. J. S. Sand. Sand, who devised the graded cathode potential method back in 1906, was pleased when recent years brought renewed interest to his method and it is unforunate he did not survive to see the increased use being made of his method as automatic apparatus has been made available to relieve the tedium of carrying it out.

The author wishes to express his appreciation to the G. Frederick Smith Chemical Company for their generous financial aid to his work on the apparatus described in this booklet.

HARVEY DIEHL.

Ames, Iowa
June, 1947

HENRY S. J. SAND
1873-1944

INVENTOR OF THE GRADED CATHODE
POTENTIAL METHOD OF ANALYSIS

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ELECTROCHEMICAL ANALYSIS WITH GRADED CATHODE POTENTIAL CONTROL

INTRODUCTION

In the usual method of chemical analysis by electrodeposition a voltage is applied to the cathode and anode and the electrolysis allowed to continue without further attention, except perhaps to occasionally increase the applied voltage to maintain the current at about the same value. Such a process, which is designated as a *constant current electrolysis,* is satisfactory for the deposition of a single metal when present alone in solution or at best for the separation of one metal from another when the first is below and the second above hydrogen in the electromotive series. Following the deposition of the first metal, hydrogen is evolved at the cathode, and as long as the solution remains acid the second metal is not deposited. The separation of copper from nickel and zinc by deposition from a sulfuric acid solution is an example of this.

Such a method fails, however, if the second metal lies only slightly above the other in the electromotive series, for example, copper from tin, for here the second metal can also be deposited from acid solution and in fact begins to deposit before the last of the first metal has been deposited. To effect the separation of such a mixture, it is necessary to employ a *graded cathode potential electrolysis* in which, by means of an auxiliary, reference electrode, the potential of the cathode is measured and during the electrolysis limited to a certain value by decreasing the voltage applied to the cathode and anode. Necessarily the technique of doing this is more complicated than that of the constant current method. Continuous attention is required for a considerable period if the cathode potential is to be held at a constant value and the tediousness of this manual control quickly compels the operator to seek some other method. In recent years automatic apparatus for effecting the cathode control have been described so that graded cathode potential methods should now find wider acceptance.

THE GENERAL TECHNIQUE OF GRADED CATHODE POTENTIAL ELECTROLYSIS

The electrical potential applied to a cell to cause electrolysis, that is, the potential indicated by the voltmeter, V, of Figure 1, consists of several potentials:

$$V = (E_c + \omega_c) - (E_a + \omega_a) + IR$$

in which E_c is the reversible, single electrode potential between the cathode and the solution; ω_c is the cathode polarization (cathode overvoltage); E_a and ω_a are the corresponding terms at the anode; and IR is the potential drop between the cathode and the anode, R being the resistance of the electrolyte between the cathode and the anode. During an electrolysis the term $(E_a + \omega_a)$ remains about constant, the reaction at the anode usually being the evolution of oxygen and the conditions governing it being largely unchanged. The remaining terms, however, all vary. Because the reaction occurring at the cathode is determined by the potential between the cathode and the solution, that is, the term $(E_c + \omega_c)$, it is necessary to isolate and follow this term separately, if one of several competing reactions at the cathode is to be made to occur exclusively. This can be done by placing a reference half cell (calomel electrode) in the solution and measuring the potential between it and the cathode.

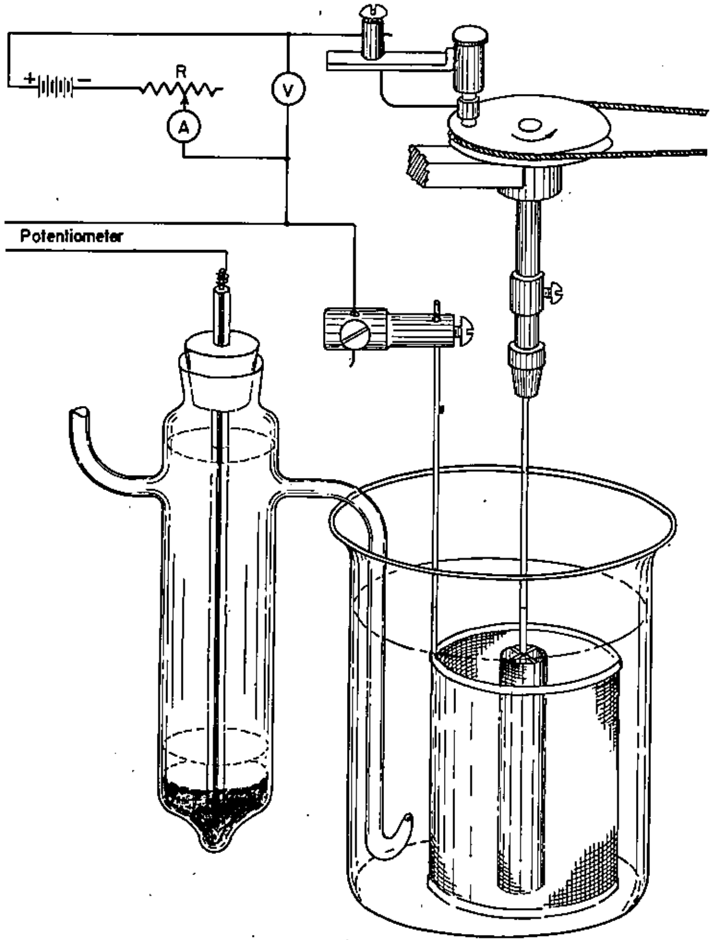

FIGURE 1. Circuit and Apparatus for Graded Cathode Potential Electrodeposition.

The potential between the cathode and the reference half cell must, of course, be measured with a potentiometer or vacuum tube voltmeter in order that so little current will be drawn from the reference cell that its potential will not be altered, and certain precautions must be observed in placing the reference electrode in the solution. The potential so obtained is the difference of the single electrode potentials of the reference cell and of the cathode:

$$E_{\text{Cath.-Ref. Half Cell}} = E_{\text{Ref. Half Cell}} - (E_c + \omega_c)$$

Knowing the potential of the reference half cell, the electrode potential of the cathode can be easily referred to the hydrogen scale.

The reversible cathode potential, E_c, is determined by the metal of the electrode and the concentration of its ions in solution, as given by the Nernst equation:

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

E° being the standard reduction potential of the metal (see Electromotive Series, Table I), R the gas constant, T the absolute temperature, n the number of electrons involved in the reduction, and F the Faraday (96,500 coulombs). As the metal is deposited the logarithmic term becomes progressively smaller, moving the cathode potential toward the negative end of the electromotive series. Thus, for example, a copper electrode dipping into solutions 1*M*, 0.01 *M*, and 0.0001 *M* in cupric ions would have a potential toward the solution (on the hydrogen scale) of

$$E_{Cu} = +0.345 + \frac{0.059}{2} \log 1 = +0.345 \text{ v.}$$

$$E_{Cu} = +0.345 + \frac{0.059}{2} \log 10^{-2} = +0.286 \text{ v.}$$

$$E_{Cu} = +0.345 + \frac{0.059}{2} \log 10^{-4} = +0.227 \text{ v.}$$

TABLE I. ELECTROMOTIVE SERIES.
STANDARD REDUCTION POTENTIALS, 25°

Reaction	E° Volts
$Hg^{++} + 2e^- = Hg^\circ$	+0.7986
$Ag^+ + e^- = Ag^\circ$	+0.7995
$Cu^{++} + 2e^- = Cu^\circ$	+0.3448
$BiO^+ + 2H^+ + 3e^- = Bi^\circ + H_2O$	+ .32
$HAsO_2 + 3H^+ + 3e^- = As^\circ + 2H_2O$	+0.2475
$SbO^+ + 2H^+ + 3e^- = Sb^\circ + H_2O$	+ .212
$H^+ + e^- = \frac{1}{2}H_2$	0.000
$Pb^{++} + 2e^- = Pb^\circ$	− .126
$Sn^{++} + 2e^- = Sn^\circ$	− .136
$Ni^{++} + 2e^- = Ni^\circ$	−0.250
$Co^{++} + 2e^- = Co^\circ$	− .277
$Cd^{++} + 2e^- = Cd^\circ$	−0.4020
$Fe^{++} + 2e^- = Fe^\circ$	− .440
$Cr^{+++} + 3e^- = Cr^\circ$	− .71
$Zn^{++} + 2e^- = Zn^\circ$	−0.7620
$Mn^{++} + 2e^- = Mn^\circ$	−1.05

respectively. When referred to the saturated calomel electrode ($E^\circ = +0.246$), 0.099 v., 0.040 v., and —0.019 v. respectively. These various potentials are perhaps more readily understood from the graphical representation of Figure 2.

Thus, every tenfold decrease in the concentration of a univalent metal ion shifts the cathode potential 0.059 volt more negative; and similarly, for a bivalent metal 0.0295 volt more negative, and for a trivalent metal 0.0197 volt, or in general $\frac{0.059}{n}$ volt more negative for the deposition of a metal from an ion carrying an n+ charge.

Neglecting for the time being the cathode polarization term, ω_c, there is thus provided a means of following the change in the concentration of the metal ion during the electrolysis and, by controlling the cathode potential, of effecting the separation of one metal from another lying somewhat higher in the electromotive series. In order to prevent the cathode potential from exceeding a certain value it is simply necessary to decrease the potential applied to the cathode and anode. This may be done conveniently by increasing the resistance R. Thus, in Figure 3 are plotted the cathode-reference cell potential, E, and the electrolyzing current, I, against time for the deposition of copper from a solution containing about 0.4 g. of copper, 0.2 g. of tin and 15 per cent of sulfuric acid. The cathode potential became

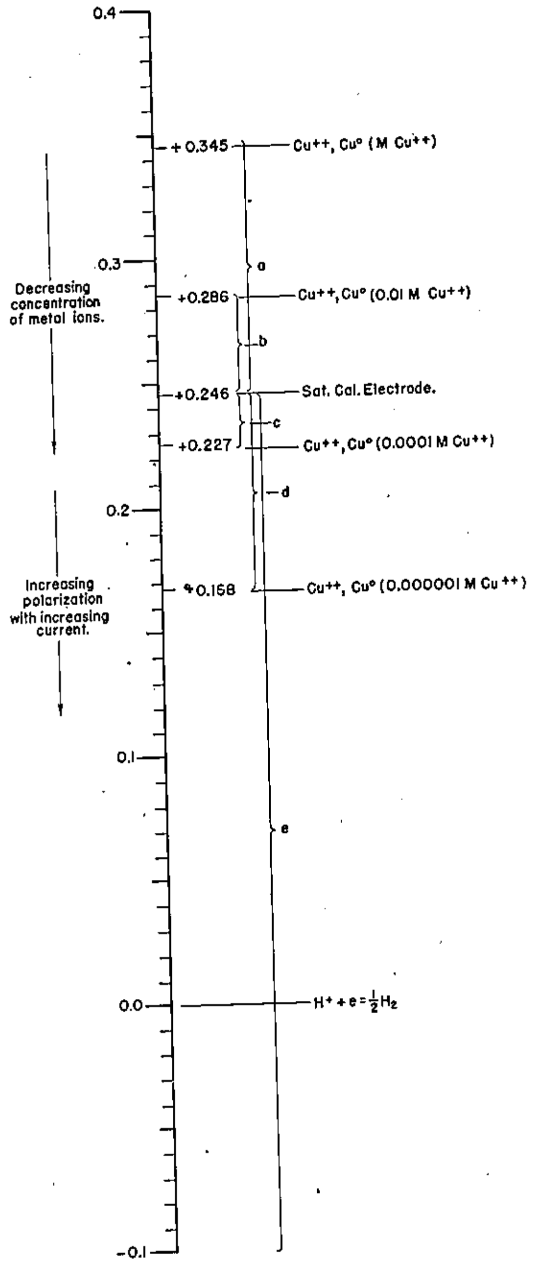

FIGURE 2. Potentials of the Cupric-Copper System at Various Concentration of Cupric Ion. a,b,c and d: Potentials Toward Saturated Calomel Electrode. e: The Limited Cathode Potential for Separation of Copper from Tin in Sulfate Solution.

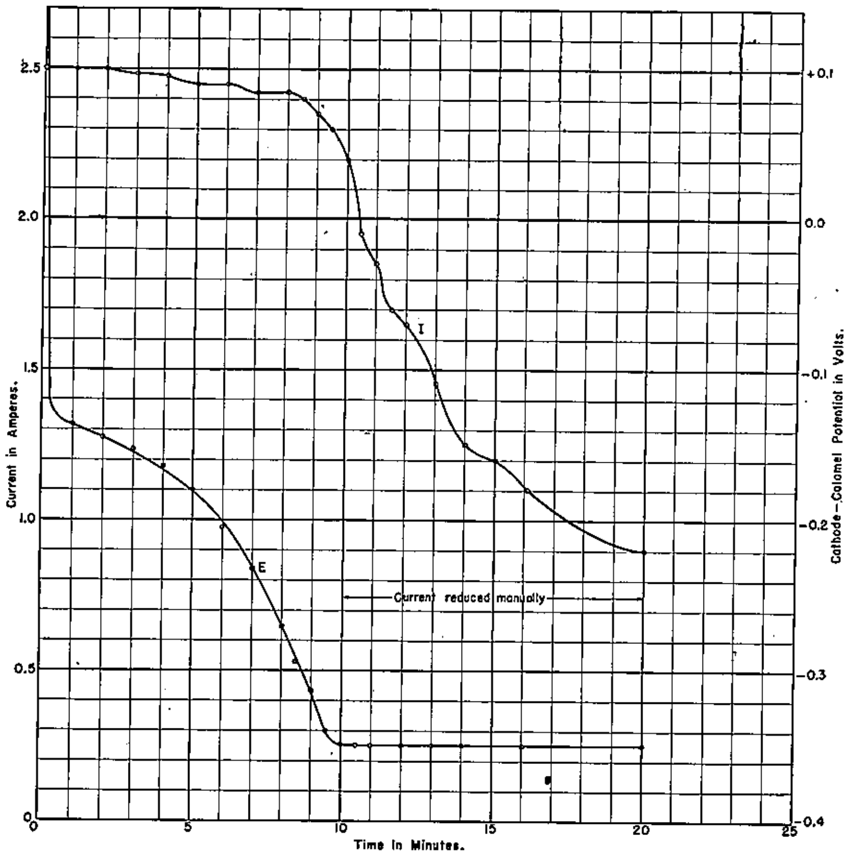

FIGURE 3. Course of Current and Cathode-Saturated Calomel Electrode Potential in the Separation of Copper from Tin in Sulfate Solution.

more negative rapidly at the beginning of the electrolysis as the platinum electrode was covered with copper and as the copper was deposited. By the time the cathode potential had fallen to —0.35 volt toward the saturated calomel electrode the applied voltage had decreased, causing a decrease in the current. The cathode was not allowed to become more than 0.35 volt negative to the calomel electrode by reducing the applied potential (that is, to the cathode and anode) by increasing the resistance R. In this manner the copper was separated from the tin. In the analysis from which the data of Figure 3 was taken the amount of copper taken was 0.3805 g., the copper found 0.3802 g.

The course of the cathode-calomel potential beyond the point where it was no longer allowed to fall is not a smooth straight line as indicated but is actually a jagged, saw-tooth line with the peaks at —0.35 volt. The cathode polarization (the extra potential above the reversible potential as calculated by the Nernst equation owing to the current flowing) is a function of the current and when the current is decreased the polarization decreases. That is, the cathode potential is shifted in the positive direction. As more copper is plated out, the concentration of the copper decreases and the cathode potential becomes more negative according to the logarithmic term of the Nernst equation. When the cathode potential reaches —0.35 volt the current is again decreased, the cathode potential is momentarily made more positive, then gradually becomes more negative again, and so on. Ultimately, the copper is all plated out and the electrolysis is discontinued. The current never falls completely to zero owing to the cyclic oxidation and reduction of stannous and stannic ions at the anode and cathode. Even with copper alone the current reaches a minimum value, probably owing to an equilibrium between the rate at which copper is being plated out and is being redissolved by the acid and the oxygen stirred into the solution from the anode.

Manual control of this process is tedious. It is necessary to read the potentiometer and adjust R, read the potentiometer and adjust R, and so on. In the apparatus described subsequently a vacuum tube voltmeter is substituted for the potentiometer; the vacuum tube voltmeter is direct reading and may be left connected continuously to the cathode and reference cell and this eliminates the key tapping and adjustment of the potentiometer scales. An electronic device is described for automatically controlling the applied voltage. Inasmuch as the automatic device operates continuously and almost instantaneously considerably higher currents may be used at the beginning of the electrolysis and the time required reduced.

AUTOMATIC CATHODE POTENTIAL CONTROL. THE DIEHL APPARATUS

The apparatus designed by Diehl[1] to carry out the graded cathode potential separation automatically, consists of three main units:

1. A direct current output unit by which a direct current output of low voltage can be obtained from the 110-volt alternating current main to perform the electrolysis.

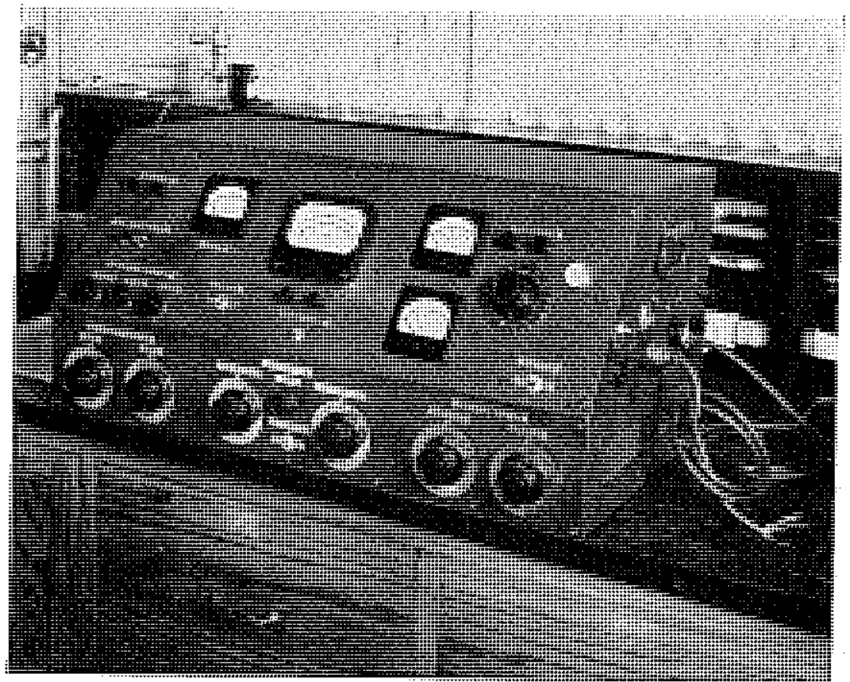

FIGURE 4. Diehl Apparatus for Automatic Graded Cathode Potential Electrodeposition.

2. A control circuit consisting of a potentiometer, a vacuum tube amplifier, a relay, and a motor-driven Variac by which the cathode-reference cell potential is made to govern the electrolyzing current.

3. A vacuum tube voltmeter for convenience in measuring the cathode-reference cell potential.

The appearance and circuit of the apparatus are shown in Figures 4, 5, and 6.

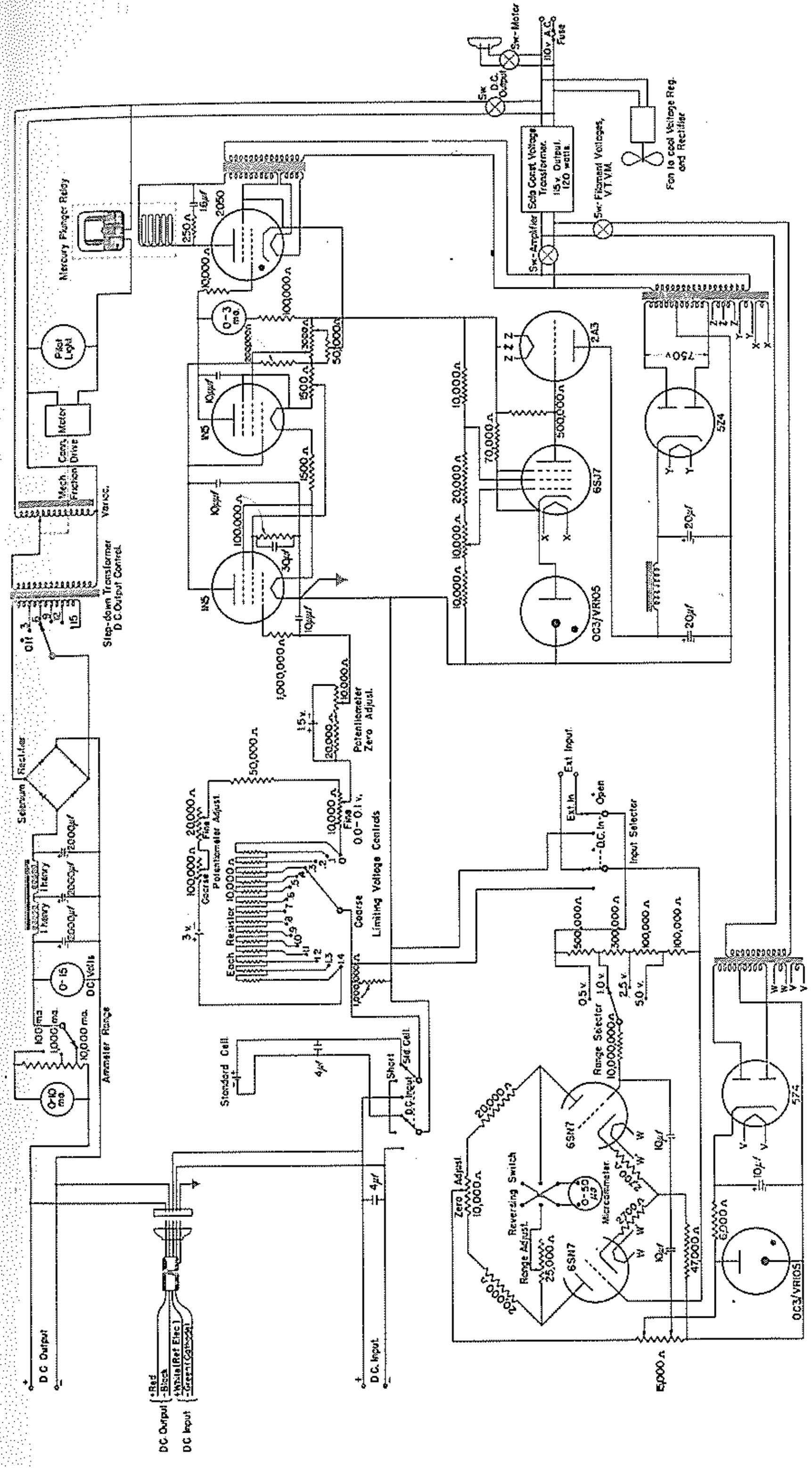

FIGURE 5. Circuit of Diehl Apparatus for Automatic Graded Cathode Potential Electrodeposition.

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[1] This apparatus was first described by Caldwell, Parker and Diehl, *Ind. Eng. Chem., Anal. Ed.*, 16, 532 (1944); the apparatus to be described is a greatly improved version of the original apparatus.

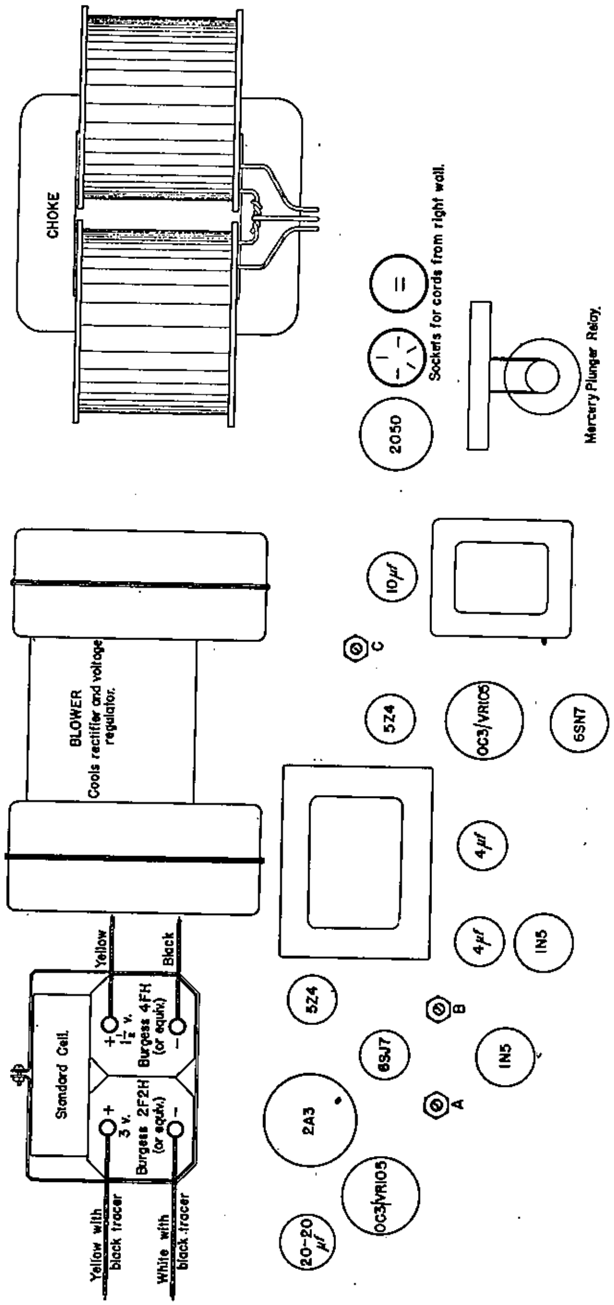

FIGURE 6. Chassis Layout of Diehl Apparatus.

D.C. OUTPUT CIRCUIT

The direct current needed for the electrolysis 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, an electric wave filter, a voltmeter, and a milliammeter-shunt combination.

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-reference cell potential. The Variac is connected to the motor by a friction drive which permits sufficient slippage so that the Variac may be set by hand by turning the knob on the panel at any time.

The secondary of the step-down transformer has taps to provide voltages of 3, 6, 9, 12, and 15 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 20 volts.

The rectifier is followed by a filter consisting of two inductances of about one henry each and three capacitances of 2,000 microfarads each arranged in parallel before and after each choke. The purpose of the filter is to by-pass any residual alternating current remaining and to smooth out the 120-cycle pulsating direct current ripple which otherwise adversely affects the electrodeposition and the control circuit amplifier.

The voltmeter reads the voltage applied to the electrolysis cell, that is, the voltage applied to the cathode and anode.

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 0.1 ampere, 0 to 1.0 ampere, and 0 to 10.0 amperes, by changing the position of the range selector dial on the lower right front panel of the instrument.

The direct current output is brought to terminals on the front panel and also out through a four-wire cable connected on the right hand side of the instrument; the latter is somewhat more convenient in making the four connections to the electrolysis cell necessary in a controlled cathode potential electrolysis.

CONTROL CIRCUIT

The cathode-reference cell potential is opposed, that is, connected positive to positive, by the potential of a semiprecision potentiometer and the difference of the two potentials 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. In this manner a slight difference between the input potential (cathode-reference cell potential) and that of the potentiometer actuates the control circuit to decrease the electrolyzing current.

The potentiometer is identical in design to those commonly used in the laboratory to measure potential, with the exception that the galvanometer is replaced by the vacuum tube amplifier and no tapping key is used. In parallel with the motor which drives the Variac is a pilot light which lights when the relay closes. The amplifier is set to close the relay when the input potential just slightly exceeds the potential of the potentiometer; the amplifier thus functions as a galvanometer, the pilot light being on when the input potential exceeds the potential of the potentiometer, and off when it is less, balance being indicated when the pilot light just comes on. Since the electronic amplifier draws so little current that it cannot polarize the electrodes it may be left connected to the circuit at all times.

The potentiometer itself consists of a 3-volt battery, coarse and fine resistances which are used to adjust the working current, and a slide wire which consists of a series of fixed resistors of exactly 10,000 ohms providing steps of 0.1 volt and a slide wire proper of 10,000 ohms resistance giving a continuance fine adjustment from zero to 0.1 volt. A double pole, triple position selector switch is provided so that the potential applied may be either the cathode-reference cell potential, the standard cell used for calibrating the potentiometer slide wire, or a direct short used in initially setting the amplifier. The operation of calibrating the slide wire to read exactly the values on the dials are the same as with the ordinary laboratory potentiometer with the exception that the amplifier must first be set to indicate zero potential. This initial setting of the amplifier is accomplished by setting the potentiometer on zero, shorting the input terminals by means of the selector switch, and adjusting the grid biasing potential of the first tube of the amplifier until the relay just closes as indicated by the pilot light. The grid biasing potential is derived from a potential divider supplied by a 1.5 volt dry cell.

The various potentials involved can be seen more readily by examining Figure 7 which is an enlargement of the portion of Figure 5 involved in this discussion. The potential E_{grid} between the filament and grid of the 1N5 tube needed to just close the relay is about 1.2 volts and with E_{in} and E_{pot} both equal to zero, this potential is just supplied by $E_{zero\ adj.}$. If E_{pot} is made some value greater than zero, say 0.4000 volt, E_{in} will have to be increased to 0.4000 volt to cause the relay to close. Thus if it is desired to limit the cathode-reference cell potential to 0.4000 volt, the potentiometer is set at this value and then whenever the cathode-reference cell potential exceeds this value the amplifier will close the relay and the motor will turn the Variac decreasing the electrolyzing current. As the cathode-reference cell potential increases the filament-grid potential, E_{grid}, of the 1N5 tube becomes smaller allowing more current to flow in the plate circuit. This increase of the plate current causes the grid of the second tube, also a 1N5, to become more negative and the plate current of this tube decreases, in turn causing the grid potential of the third tube, a gas-filled tetrode, Type 2050, to become more positive. If the grid potential 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.

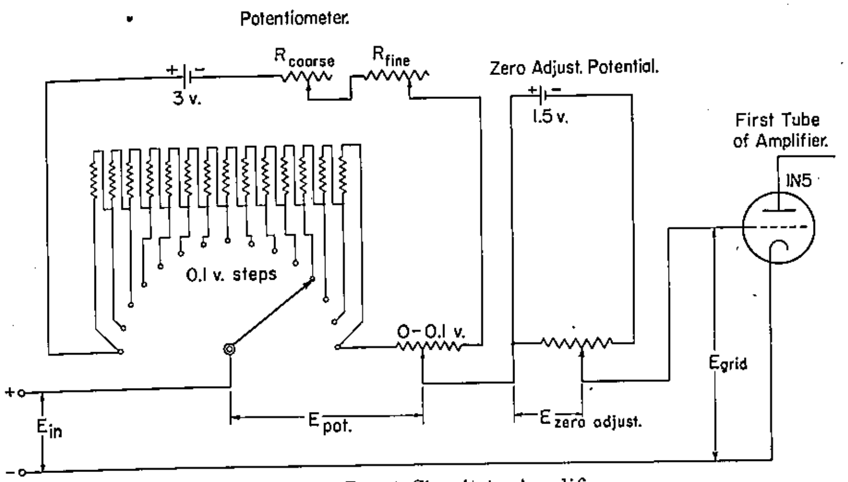

FIGURE 7. Input Circuit to Amplifier.

E_{in} may be the cathode-reference cell potential, standard cell or short depending on the position of the selector switch (not shown). E_{pot} is selected on the coarse and fine dials on the lower left hand side of the panel. $E_{zero\ adj.}$ is about 1.25 volts and changes slightly with the life of the 1N5 tube.

The current passed by the 2050 tube is comparatively high, about 9 milliamperes, once its grid potential becomes less than -2.0 volts. Once the plate current has started, its magnitude is determined by the plate supply potential and the impedance of the plate circuit and is practically independent of the grid potential. By operating the 2050 tube on alternating current it is possible to have the tube turn off when the grid potential becomes only slightly more negative than -2.0 volts. During the negative half cycle of the alternating current potential applied to the plate, the plate current is zero; since the plate is negative with respect to the filament. As long as the grid potential 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 2050 tube not only to close but to open the relay.

A milliammeter (left-hand meter, Figure 4) is 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 cathode-reference cell potential.

VACUUM TUBE VOLTMETER

For convenience in reading the cathode-reference cell potential a vacuum tube voltmeter is incorporated in the apparatus. The vacuum tube voltmeter is line operated, having its own d.c. power supply (rectifier and voltage regulator tubes). It is based on a bridge type circuit employing a single duplex tetrode for amplification. The circuit is shown in the lower left hand corner of Figure 5.

The vacuum tube voltmeter is placed in the center of the apparatus. The zero adjustment control, range selector switch, meter, and filament switch are brought to the center of the front panel, as will be seen from a close inspection of Figure 4. In order to use the vacuum tube voltmeter for other purposes if desired, input terminals are placed on the panel (just below the meter) and a selector switch provided so that the voltmeter could be made to read the cathode-reference cell potential (D.C. IN) by direct connection within the apparatus with d.c. input, or to read some other potential applied to the voltmeter input terminals (EXTernal).

The zero adjustment is made with the selector switch on OPEN. A voltage divider of precision resistors, placed in the input circuit of the vacuum tube voltmeter, enables the meter to read the ranges 0 to 0.5 volt, 0 to 1.0 volt, 0 to 2.5 volts, and 0 to 5.0 volts. The calibration can be checked against the standard cell on the three high ranges, red marks being provided on the scale. Calibration on one scale holds for the others, however. Occasionally a calibration adjustment may be necessary, for example when installing a new tube; this is accomplished by varying resistance in series with the microammeter, the shaft of this resistance being located within the instrument directly in back of the tubes of the voltmeter circuit (C in Figure 6).

The reversing switch on the meter is convenient in that the polarity of the cathode and the reference cell sometimes changes during an electrolysis.

AUXILIARY EQUIPMENT

In graded cathode potential electrodepositions, vigorous stirring is essential. The most satisfactory combination of electrodes and stirring apparatus consists of two stationary concentric platinum gauzes with the shaft of the stirrer passing through the axis of the electrodes and bending back up between the electrodes in the form of a W. The stirring apparatus furnished with the Diehl apparatus is shown in Figure 8. The bakelite block serves as a beaker cover, electrode holder, and bearing for the shaft of the glass stirring rod. The electrode holder is designed for American Platinum Works, Model 77a, gauze electrodes, inner electrode (anode) ⅞ in. dia., outer electrode (cathode) 1⅝ in. dia., stem dia. 0.065 in., 45 mesh, 5 in. tall.

The conventional form of calomel electrode may be used, 0.1 *N*, 1 *N*, or saturated, the appropriate change in the limited cathode potential used being made on substituting one for another. An agar-salt bridge for making the connection to the solution is preferred but a straight salt bridge may be used if provision is made for flushing out the arm occasionally. The flushing arrangement should be such that only saturated potassium chloride is flushed into the solution and not saturated potassium chloride solution also saturated with calomel, as a considerable quantity of mercurous chloride dissolves in a saturated potassium chloride solution and the mercury is deposited on the cathode, radically altering the cathode potential.

The commercial types of calomel reference electrode, in which the electrical contact is made through a minute hole or ungreased ground glass joint, are very satisfactory, the higher internal resistance of these cells being no impediment to the vacuum tube amplifier and voltmeter.

The reference electrode must be placed with its contact tip on the outer side of the cathode and at about its middle, so as to be out of the lines of flow of electrical current.

OPERATION

Connect the terminal marked GROUND, on the right hand side of the instrument, to a convenient plumbing pipe making sure that good electrical contact is established, preferably by soldering the connection wire to the pipe.

Turn Output Voltage Selector Switch to OFF and plug the line cord from A.C. INPUT into a 110-v. a.c. line. The blower used to

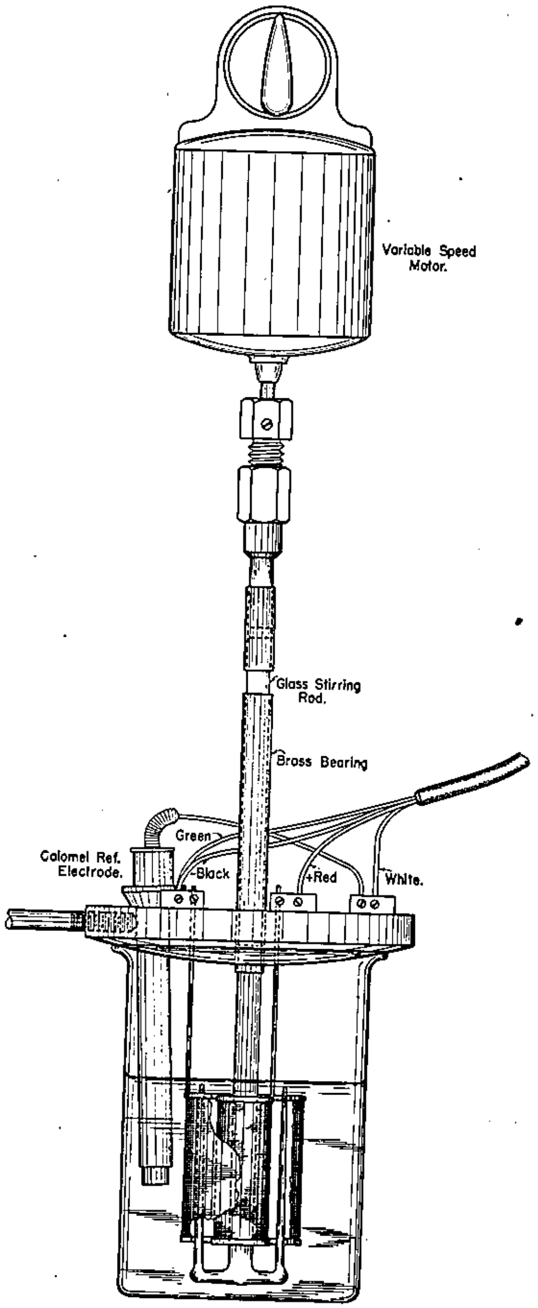

FIGURE 8. Electrode Holder and Stirring Device.

cool the rectifier and voltage regulator is turned on as soon as the line cord is plugged in; air will issue from the opening in the back.

Turn on the switches marked V.T.V.M. (vacuum tube voltmeter) FILAMENT VOLTAGES, AMPLIFIER, and D.C. OUTPUT. The center meter (meter of the vacuum tube voltmeter) will make an initial excursion and settle back to approximately zero; the meter marked PLATE No. 2 will read some value greater than zero, indicating that the amplifier is working. Allow five minutes for the tubes to establish equilibrium and then calibrate the vacuum tube voltmeter and the potentiometer. If the calibrations are made immediately they should be checked after a five- or ten-minute interval.

Voltmeter Calibration. Turn V.T.V.M. INPUT SELECTOR Switch to OPEN and vary V.T.V.M. ZERO adjust knob until the meter reads exactly zero. Turn V.T.V.M. INPUT SELECTOR Switch to D.C. IN and V.T.V.M. RANGE SELECTOR Switch to 1.0-volt range. Throw V.T.V.M. reversing switch to left. Move Amplifier Selector Switch to STD. CELL. The vacuum tube voltmeter should read the voltage of the standard cell, 1.0185 volts, indicated by the red line on the scale. If it does not it can be made to do so by varying the Range Adjust resistance inside the apparatus; this resistance has a slotted shaft extending through the chassis approximately in the center of the apparatus and is designated C in the chassis layout shown in Figure 6. The voltmeter is now ready to read on any of the four ranges, 0 to 0.5 volt, 0 to 1.0 volt, 0 to 2.5 volts, and 0 to 5.0 volts. If the V.T.V.M. INPUT SELECTOR Switch is on the D.C. IN position the voltage measured is that impressed on the D.C. INPUT terminals (in which case the vacuum tube voltmeter is in parallel with the amplifier). If the V.T.V.M. INPUT SELECTOR Switch is in the EXTernal IN position the voltage measured is that impressed on the EXT. INPUT terminals; this would be the case when the vacuum tube voltmeter is used as a titrimeter.

Check the zero setting of the vacuum tube voltmeter occasionally during use.

Potentiometer Calibration. Throw the Amplifier Selector Switch to SHORT (center position). Turn the LIMITING VOLTAGE CONTROLS, both COARSE and FINE, to zero. Vary the POTENTIOMETER ZERO ADJUST knob until the relay just closes as indicated by the pilot light coming on (the Variac will begin to turn at the same time and the milliammeter marked Plate No. 2 will reach a minimum value moving left).

Turn the LIMITING VOLTAGE CONTROLS to read the voltage of the standard cell, 1.0185 volts, and throw Amplifier Selector Switch to STD. CELL. Vary the Potentiometer Adjustment knobs COARSE and FINE until the relay just closes, that is, the pilot light just comes on. This operation adjusts the working current in the potentiometer circuit to such a value that each step on the LIMITING VOLTAGE CONTROL COARSE dial is exactly 0.1 volt and the full scale of the FINE dial is exactly 0.1 volt.

Recheck zero.

Controlled Cathode Potential Electrodeposition. Connect the anode, cathode, and reference cell to the instrument either by *(a)* individual wires or *(b)* the shielded four-wire cable. If method *(a)* is used, connect the anode and cathode to D.C. OUTPUT terminals + and — respectively, and connect the cathode and reference cell to D.C. INPUT terminals, using four wires in all from the cell. Connect the cathode to the negative terminal and the reference cell to the positive. In some cases the cathode may be positive to the reference cell in which case the reversing switch of the vacuum tube voltmeter will have to be thrown to the right.

If method *(b)* is used to connect the cell to the instrument plug the four-wire cable into the socket on the right side of the instrument, connect the red wire to the anode, the black and green wires to the cathode and the white wire to the reference cell. If the cathode happens to be positive to the reference cell throw the reversing switch of the vacuum tube voltmeter to the left.

Bring the solution to he electrolyzed up around the electrodes, placing the tip of the reference electrode outside the cathode but as close to it as possible and at about its middle. Start the stirring motor. With the potentiometer and vacuum tube voltmeter calibrated as described above, the electrolysis may be started. Set the AMPLIFIER SELECTOR Switch on D.C. INPUT and the V.T.V.M. INPUT SELECTOR Switch on D.C. IN. Set the Limiting Voltage Controls, COARSE and FINE, to the limiting cathode potential desired. Turn the AMMETER RANGE Switch to 10,000 MAMP. (10 amperes full scale), and turn on the D.C. OUTPUT Switch. Adjust the current to a suitable value by turning the VOLTAGE SELECTOR dial and the VARIAC.

With good stirring a current of 8 amps. may safely be used at the beginning of the electrolysis. The size of this current will remain constant for several minutes, depending on the size of the sample taken, and on other factors. The cathode-reference cell potential will gradually increase (cathode becoming more negative) as shown by the vacuum tube voltmeter. When the cathode-reference cell voltage reaches the limiting value set on the controls, the relay will close, as indicated by the pilot light, and the Variac will begin to turn, decreasing the electrolyzing current. This operation is intermittent, the cathode voltage increasing owing to the decrease in the metal ion concentration as the deposition occurs and decreasing each time the control operates to decrease the electrolyzing current owing to the dependence of the cathode overvoltage on the current.

When the current has been reduced to a value less than 1.0 ampere the ammeter range may be changed to the 1,000 MAMP. range and again later it may be changed to the 100 MAMP. range.

Discontinue the electrolysis after the current has been reduced to 10 to 30 milliamperes. Remove electrolyte and simultaneously wash the electrodes without interrupting the current.

At the conclusion of the work turn off the vacuum tube voltmeter, amplifier, and d.c. output. Disconnect the a.c. line cord (necessary in order to turn off blower).

Miscellaneous Notes on Operation. In method *(a)* above of connecting the apparatus to the electrolysis cell four wires from the cell must be used. A jumper from the negative terminal of the D.C. INPUT to the negative terminal of the D.C. OUTPUT is not satisfactory because the vacuum tube voltmeter will then read and the amplifier respond to the IR drop through the wire connecting the D.C. OUTPUT to the cathode in addition to the cathode reference cell potential.

The voltmeter in the output circuit has no essential function in the operation of the apparatus. It measures the voltage applied to the cathode and the anode, a knowledge of which is occasionally useful.

OTHER APPARATUS FOR AUTOMATIC CATHODE POTENTIAL CONTROL

Besides the Diehl apparatus described in the preceding pages two other devices have been described for the automatic control of the cathode potential during an electrolysis.

The circuit of Hickling[1] is particularly ingenious, being all electronic in nature. Unfortunately the direct current output is limited to the plate current of a vacuum tube or two such tubes in parallel and at most is only one or two tenths of an ampere so that from a practical standpoint the device requires further modification.

A second circuit described by Lingane[2] has apparently never been placed on the market in satisfactory commercial form. It is a partly mechanical device in which the off-balance between the cathode calomel potential and the limiting potential set on a potentiometer actuates a contact galvanometer which operating through relays causes a reversible synchronous motor to turn a variable resistance in the direct current electrolyzing circuit. An external source of direct current is required.

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[1] Hickling, *Trans. Faraday Soc.*, 38, 27 (1942).
[2] Lingane, *Ind. Eng. Chem., Anal. Ed.*, 17, 332 (1945).

POLARIZATION

When a current is flowing the potential of the cathode departs from the equilibrium potential by a value which depends on the size of the current. With increasing current the cathode potential is made more negative, thus acting in the same direction as a decrease in the concentration of the metal ion. Indeed, polarization may be due in part to a depletion of metal ions in the layer of solution immediately surrounding the cathode but other factors are also involved. Practically all of the theoretical and experimental studies by electrochemists on polarization have dealt with the polarization of hydrogen and of oxygen, in which cases the polarization is known as *overvoltage.*

The polarization where a gas is liberated, that is overvoltage, is considerably greater than that of a metal on metal. Since polarization depends on the area of the electrode as well as the size of the current, polarization is reported as a function of the current density, usually in amperes per square centimeter. Thus, whereas the overvoltage of hydrogen on various metals approaches one volt at a current density of 0.05 amp. per sq. cm., the polarization of copper on copper is about 0.2 volt at the same current density.

The polarization of copper on copper was determined during the deposition of copper from a hydrochloric acid solution by turning off the current at various stages of the electrolysis. The stirring was continued and the cathode-calomel potential measured. Assuming this to be the reversible cathode potential, true probably to within a few millivolts, the polarization of copper on copper was calculated. The results are shown in Table II:

TABLE II. POLARIZATION DURING THE ELECTRODEPOSITION OF COPPER

Current Amp.	Cathode-Calomel Voltage		Polarization Volt
	Current On	Current Off	
4.4	0.339	0.152	0.187
1.6	.388	.250	.138
1.0	.388	.263	.125
0.50	.388	.288	.100
0.17	.388	.320	.068

In a somewhat more elegant experiment a fourth electrode, a platinum wire covered with copper deposited from a hydrochloric acid solution, was dipped into the electrolysis cell. The electrolyte used was a hydrochloric acid solution containing hydroxylammonium chloride into which was dipped the platinum gauze cathode and anode (through which was passed the electrolyzing current, I), a saturated calomel electrode, and a copper covered platinum wire.

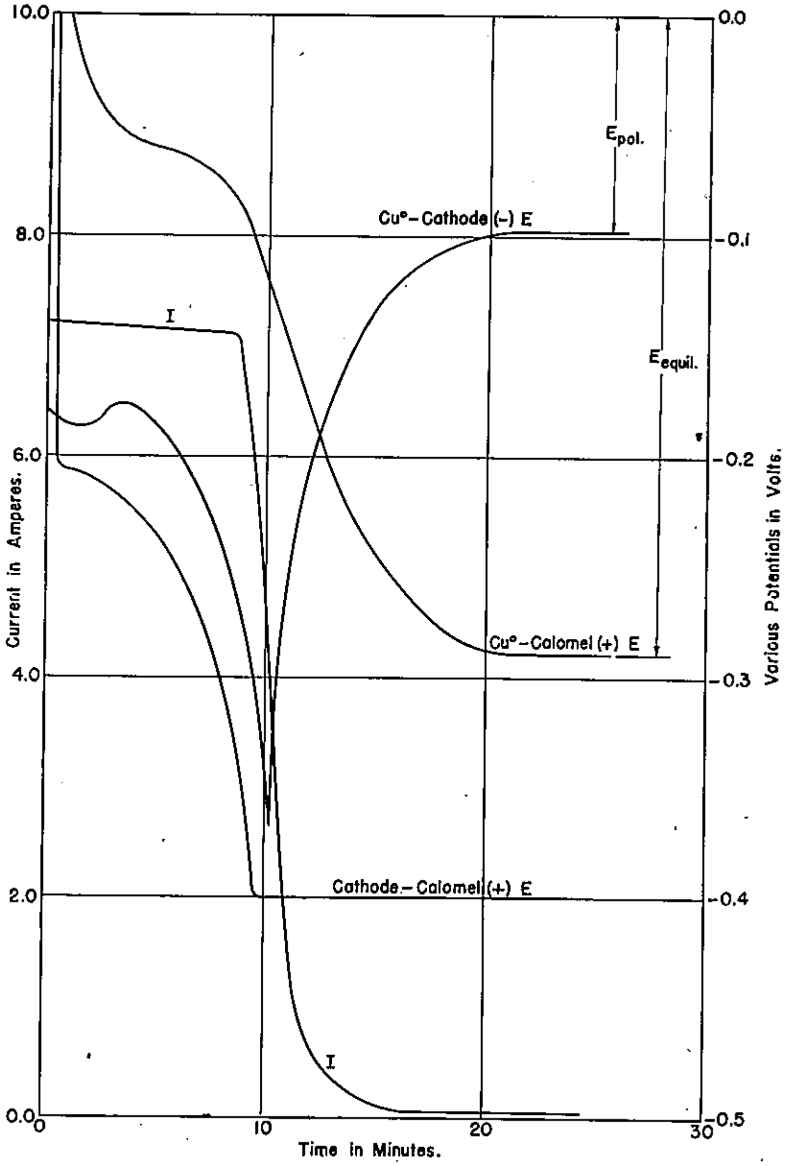

FIGURE 9. Various Potentials and Current During the Deposition of Copper from a Hydrochloric Acid Solution.

During the deposition three potentials were measured simultaneously and continuously with vacuum tube voltmeters: the cathode-calomel reference cell potential, the copper-reference cell potential, and the copper-cathode potential. The course of these potentials during the electrodeposition is plotted in Figure 9. The cathode-calomel potential fell quickly as the platinum became covered with copper, then more gradually as the copper was plated out, finally falling to a value of —0.40 volt after which it was held constant by decreasing the potential applied to the cathode and anode. The copper-calomel and copper-cathode potentials are of no great significance during the early part of the deposition although they do reflect the reduction of the cupric ion to the chlorocuprous ion and the depletion of copper ions as the deposition progressed. Toward the end of the deposition the copper electrode indicates the equilibrium potential of copper toward a solution of chlorocuprous ions to within a few millivolts. The copper-calomel potential is thus the equilibrium potential and the copper-cathode potential the polarization. The sum of the two is the cathode-calomel potential.

It thus appears that in calculating the cathode potential to which to limit an electrolysis to effect the separation of one metal from another, a simple calculation of the equilibrium potential from the Nernst equation is not sufficient. To the equilibrium potential must be added the polarization potential. Since the latter depends on the rate of stirring and on the current as well as on the nature of the metal surface, it is apparent that the limiting potential must be established more or less empirically.

The variation of the polarization potential with the nature of the metal surface also introduces another factor. In an ammoniacal solution, the polarization of copper on platinum is lower than that of copper on silver. In the separation of silver from copper by deposition from ammoniacal solution (p. 32), if the silver is plated on a platinum electrode and toward the end of the electrolysis the level of the solution is raised, copper will plate on the bare platinum exposed and the results for silver become high. This error can be eliminated by plating the gauze with silver prior to the electrolysis.

THE BROWN ELECTRODE

In a variation in the controlled cathode potential technique, proposed by D. J. Brown,[1] the calomel reference electrode is replaced by a wire of the metal being plated on the cathode. The potential between the cathode and wire, or Brown electrode, is then measured and during the deposition the current is regulated to maintain the cathode 0.1 to 0.2 volts negative to the wire by suitably regulating the potential applied to the cathode and anode. The Brown electrode and cathode are weighed together, any metal having dissolved from the Brown electrode being deposited on the cathode and the net gain in weight then giving the amount of metal derived from the solution analyzed. The electrolyzing current is maintained until it reaches a suitably low residual value.

When no wire of the metal is available, then a platinum wire, or for tin a copper wire, is placed in parallel with the cathode and the current broken a moment before the wire is used as an auxiliary electrode. In each case where platinum wire is used in parallel a low potential difference must be used until the wire is covered with the deposited metal.

Brown applied this method to the separation of copper from tin (—0.20 v.), of bismuth from lead (—0.10 v.), of antimony from tin (—0.15 v). and of tin from cadmium (—0.10 v.), all of the separations being made from a hydrochloric acid solution containing hydroxylammonium chloride. The results were excellent.

The theory underlying the Brown electrode is readily understood from the discussion in the preceding section on polarization and the accompanying Figure 9. The Brown electrode-cathode potential is the polarization potential, E_p. Since this becomes constant toward the end of the electrolysis it can be used to control the deposition as well as the customary reference electrode. Obviously, however, the limiting Brown potential will also depend on those factors affecting the polarization, the particular metal involved, the rate of stirring, and the temperature.

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[1] Brown, *J. Amer. Chem. Soc.*, 48, 582 (1926).

ANODIC REOXIDATION

In the deposition of metals having more than one positive valence, the electrochemistry involved in the electrolysis may be fairly complex. The deposition of copper is a case in point, the electrochemistry having been worked out in detail by Diehl and Brouns.[1]

In a hydrochloric acid solution the reactions and corresponding electrode potentials of copper are

$$Cu^{++} + e^- + 3\,Cl^- = CuCl_3^= \qquad E^\circ = +0.51$$
$$Cu^{++} + 2\,e^- = Cu^\circ \qquad E^\circ = +0.3448$$
$$CuCl_3^= + e^- = Cu^\circ + 3\,Cl^- \qquad E^\circ = +0.178$$

The great alteration of these potentials from the corresponding potentials in a sulfate solution is due to the great stability of the chlorocuprous ion, $CuCl_3^=$. It is apparent from these potentials that in a solution of cupric ion containing hydrochloric acid the reduction at the cathode will take place stepwise. The cupric ion (a complex ion of cupric and chloride forms to only a very slight extent) is reduced first to the chlorocuprous ion, $CuCl_3^=$, and the latter is then reduced to metallic copper. Moreover, the first reaction takes place completely before the third one begins, as is evidenced by the disappearance of the blue color before any copper appears on the platinum electrode. At the anode the chlorocuprous ion is reoxidized to the cupric ion. The cupric ion also reacts with the copper deposited on the cathode to dissolve it

$$Cu^{++} + Cu^\circ + 6\,Cl^- = 2\,CuCl_3^= \qquad K = 4 \times 10^5$$

This reaction takes place very rapidly.

Although such anodic reoxidation and resolution of deposited metals has been investigated thoroughly in the case of copper, it should occur with any metal having two or more positive valences, tin and antimony certainly, and possibly with mercury, bismuth, lead, nickel, and cobalt.

From a practical viewpoint it is of considerable importance that any anodic reoxidation of cuprous copper be kept at a minimum both to insure the quantitative deposition of the copper at the cathode and to obtain as high a current efficiency as possible to minimize the time required for the deposition. The ways of reducing or eliminating the anodic oxidation of the chlorocuprous ion are: *(1)* the use of a reducing agent which will be oxidized in preference to the chlorocuprous ion; *(2)* increasing the initial cathode voltage to a value sufficient to

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[1] Diehl and Brouns, *Iowa State College J. Sci.*, 20, 155 (1945).

instantly reduce to metallic copper more than half of the chlorocuprous ions formed before the latter have been stirred away from the immediate vicinity of the cathode: *(3)* isolation of the anode by means of a membrane or porous cup; *(4)* reduction of the anode potential to a value which will not oxidize the chlorocuprous ion.

(1). Use of Reducing Agents. In the case of copper the addition of stannous chloride to the solution will insure the quantitative deposition of copper owing to the fact that the stannous ion is more readily oxidized at the anode than the chlorocuprous ion. Obviously, however, if the tin is to be determined subsequently, this is not an entirely desirable procedure. Extra weighings are involved and the tin determination made by difference from the total must necessarily be somewhat less accurate. Titanous chloride works very well for the purpose and permits the determination of tin. A convenient way to obtain the titanous chloride is to dissolve titanium hydride in hydrochloric acid. The direct addition of the titanium hydride to the hydrochloric acid solution of the copper reduces the copper to the metal.

Hydroxylammonium chloride and hydrazonium chloride were found to be too weak to reduce the copper. Hypophosphorous acid was very effective but the results obtained for copper were high. The deposits blackened badly on exposure to air and were obviously impure. Phosphine was evolved toward the end of the deposition and although it was found that ammonium nitrate prevented the evolution of phosphine it is believed that some reduced form of phosphorus was present in the deposit.

Preferably, of course, the reducing agent should be strong enough to reduce the copper to the chlorocuprous ion immediately so that a smaller quantity of electricity and a shorter time will be required to deposit the copper. Sufficient reducing agent should be added to reduce the copper to the cuprous state and also to furnish material for the anode reaction throughout the electrolysis. Stannous chloride and titanous ion fill the requirements admirably.

(2). Application of a High Initial Cathode Voltage. This is probably the easiest way of initiating the deposition of copper and of maintaining the deposition. A consideration of the electrode potentials given above shows that with respect to the ease of reduction the cupric ion is reduced first to the chlorocuprous ion and that the latter is further reduced to the metal only at a much higher potential, 0.178 volt. If the cathode potential is sufficiently high some of the cupric ion in addition to being reduced to the chlorocuprous ion will be reduced directly to the metal and indeed if the cathode potential is sufficiently high some of the chlorocuprous ions will be reduced to the metal. Obviously if more than half of the copper has been reduced directly to the metal the deposition will ultimately be complete in spite of any anodic reoxidation which may occur.

In practice the cathode potential must be negative to a saturated calomel electrode by about 0.22 volt for the deposition of copper to begin and about 0.3 volt for the deposition to continue rapidly. These potentials cannot be calculated exactly owing to the polarization (copper on copper) which amounts to about 0.2 volt at the highest current employed, although they can be calculated approximately from the standard electrode potential and the concentration. Thus, if the concentration of copper in the solution is about 0.1 *M*, the concentration of chlorocuprous ion in the layer surrounding the cathode may also be taken as this same concentration, and assuming the chloride concentration to be 1 *M*, the copper should be deposited at a cathode potential of $+0.178 - 0.06 = +0.12$ volt on the hydrogen scale or -0.13 volt toward the saturated calomel electrode. Allowing 0.2 volts for polarization this would mean a cathode potential of -0.33 for the deposition, a value which experiment has shown will cause the deposition to proceed rapidly.

As a matter of fact, with adequate stirring there appears to be no reason why the current cannot be lifted to a sufficiently high value, 10 amperes or more if necessary, so long as the cathode potential does not exceed $-.40$ volt toward the calomel electrode.

(3). Use of a Porous Membrane. The use of a porous membrane in analytical work to isolate the anode from the solution from which a metal is being deposited is not new. Sand[2] employed a parchment membrane for the purpose, flushing the entire anolyte into the catholyte toward the end of the electrolysis. More recently Clarke, Wooten, and Luke[3] used porous alundum thimbles in the design of an apparatus for internal electrolysis. The latter type of diaphragm was also used by Diehl and Brouns.[1] Their apparatus is shown in Figure 10.

The alundum thimble, 2×19 cm. in size, was of medium porosity, model RA-84 of the Norton Company. With a 25-cm. head of water, about 2 ml. per minute of water diffused through the thimble. The thimble was connected to a reservoir containing the anolyte, a solution containing 5 ml. of hydrochloric acid and 4 g. of hydroxylammonium chloride per 100 ml. The platinum gauze anode was placed inside the thimble with a platinum wire leading out through the top

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[2] Sand, *J. Chem. Soc.*, 93, 1572 (1908).

[3] Clarke, Wooten and Luke, *Ind. Eng. Chem., Anal. Ed.*, 8, 411 (1936).

of the reservoir to the electrical contact. A platinum gauze cathode was placed symmetrically around this anode and a good paddle stirrer was placed below the electrodes. The catholyte contained about 10 ml. of hydrochloric acid in 150 ml. of solution and hydroxylammonium chloride was added in only a few of the determinations made. The volume of solution increased to over 200 ml. during the course of an analysis owing to the passage of anolyte through the alundum shell

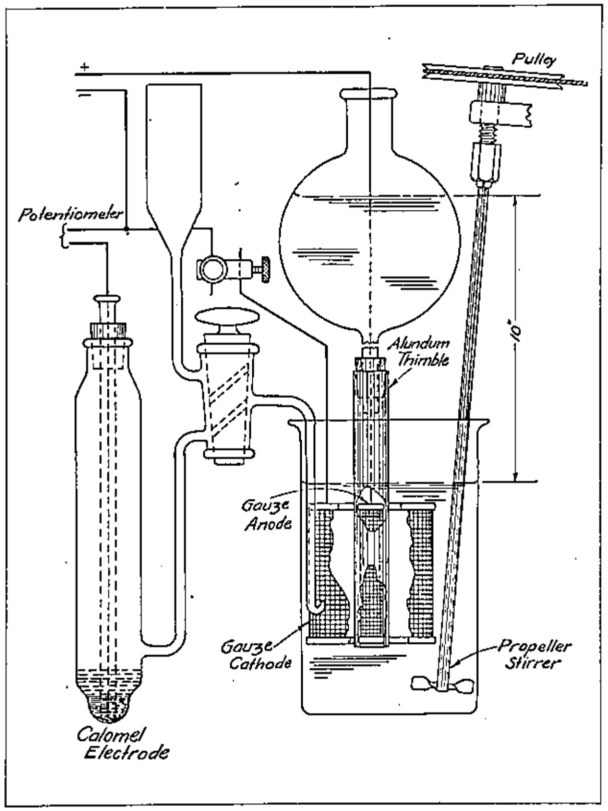

FIGURE 10. Electrodeposition Apparatus Using a Diaphragm with Continuous Flushing.

because of the 25 cm. head. In all cases the solution first became colorless, indicating reduction to the cuprous state, and then the copper was deposited at the cathode. About 3 or 4 minutes elapsed before the copper began to plate. The deposition was complete within 30 minutes. The deposition of the copper was quantitative but the deposits had a great tendency to darken on exposure to air. The separation of copper from tin, however, was not satisfactory either

at a limited potential of —0.40 volt or at the lower value of —0.35 volt. The difficulty obviously lay in the ineffectiveness of the stirring which was largely up and down parallel to the gauze electrode rather than through the mesh of the electrode.

In order to improve the stirring efficiency, the apparatus of Figure 11 was designed. The lead to the anode was brought in through the bottom of the beaker thus permitting the use of a stirrer which

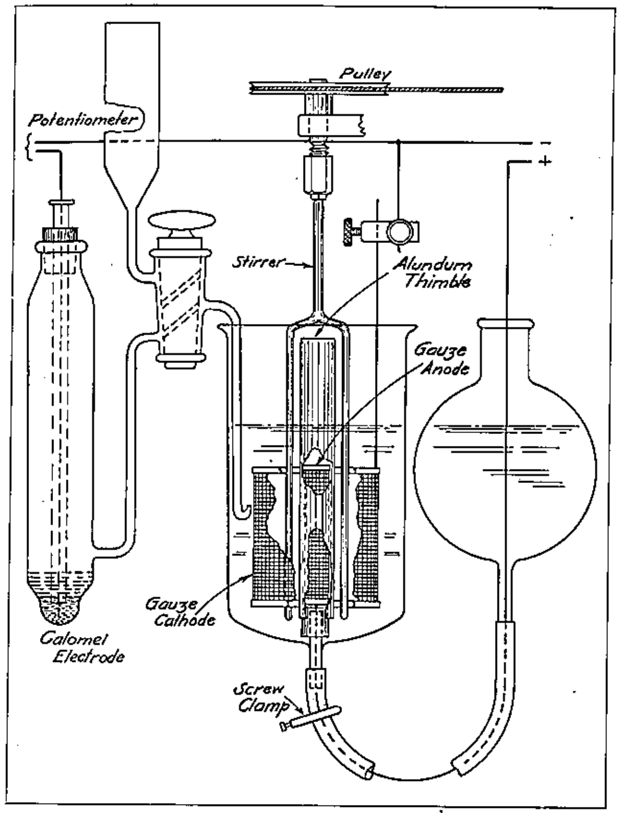

FIGURE 11. Electrodeposition Apparatus Using a Diaphragm with Intermittent Flushing.

straddled the membrane. A length of glass tubing was sealed into the bottom of a 300-ml. tall form beaker in such a way that a cylindrical porous thimble (open at both ends) could be mounted on a rubber stopper. A reservoir containing the anolyte was attached and electrical contact to the anode was made through the reservoir. The beaker was raised into position around the cathode and stirrer. The stirring efficiency obtained with this apparatus was exceptionally high but was obtained at the expense of the continuous flushing of the anode compartment obtained in the apparatus of Figure 10. It was soon found that considerable copper was lost through the diaphragm, even though the anode compartment was frequently flushed out by raising the reservoir and causing the thimble to overflow. Trouble was also experienced in the depletion of the depolarizer in the relatively small volume of the anolyte and the subsequent attack of the anode leading to deposition of platinum on the cathode. The results obtained with this apparatus were erratic in character and generally low although the separation of copper from tin was satisfactory.

Work with a diaphragm was given up because it was felt that that apparatus was getting needlessly complex. A simple diaphragm apparatus which would permit continuous flushing of the anolyte into the catholyte and allow vigorous stirring would, however, be advantageous in speeding up the electrolysis since a very high current efficiency, at least 95 per cent, can be obtained.

(4). Reduction of Anode Potential by Choice of Anode Material. Lingane[4] used a silver anode to prevent the anodic oxidation of bismuth in an acid tartrate solution, using enough chloride to obtain a layer of silver chloride on the anode. He pointed out that the oxidation potential of the silver chloride electrode is about a volt less positive than that of the platinum-oxygen electrode.

The standard electrode potential of the silver-silver chloride electrode is $+0.22$ volt, so that it is apparent that oxidation of the chlorocuprous ion will not occur because the potential of the couple $Cu^{++}, CuCl_3^{=}$ is $+0.51$ volt. In as much as an amount of silver chloride will be formed equivalent to the metal deposited and as the amount of copper is large, 0.3 to 1.0 g., it is apparent that a large surface area of silver is needed. In work by Diehl and Brouns[1] a cylindrical silver foil 4.5 cm. in height and 6.5 cm. in diameter was used as anode, being placed concentrically about the usual platinum cathode. Vigorous stirring was supplied by a rotating platinum gauze placed at the center. The electrolyte was prepared by dissolving 0.5 g. of copper in 10 ml. of hydrochloric acid with the addition of a little nitric acid. After dilution the copper was reduced by the addition of hydroxylammonium chloride and careful neutralization with ammonia. The precipitate of cuprous hydroxide was then dissolved in hydrochloric acid and 10 ml. of hydrochloric acid in excess added. It was observed that the deposition of copper began at a lower applied voltage (cathode-anode voltage) than with the usual platinum anode and that no reoxidation of copper occurred as indicated by the absence of any blue color. Some silver was found in the copper deposit, however, and the silver chloride formed flaked off the anode and either settled to the bottom or became lodged in the mesh of the platinum cathode. The tendency of the silver chloride to fall from the electrode could not be overcome by thorough preliminary cleaning or by modifying the rate of stirring.

The solubility of silver chloride in hydrochloric acid of the concentration used, coupled with the large amount of silver chloride formed, alters the problem considerably from that of Lingane who worked in solutions containing only a small amount of chloride and relatively little metal.

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[4] Lingane, *Ind. Eng. Chem., Anal. Ed.*, 16, 149 (1944).

SILVER

$$\begin{array}{ll} Ag^+ + e^- = Ag^0 & E^\circ = +0.799 \\ Ag(NH_3)_2^+ + e^- = Ag^\circ + 2NH_3 & E^\circ = +0.374 \end{array}$$

Silver may be deposited from an ammoniacal or alkaline cyanide solution. It tends to form large, loose crystals when deposited from nitric acid solution so that such a solution is not satisfactory for the quantitative determination of more than small amounts of silver. The deposits from ammonia or cyanide solutions are bright, smooth, and adherent.

The separation of silver from copper may be effected in ammoniacal or alkaline cyanide solutions. Miller[1] applied the deposition from ammoniacal solutions to the determination of silver in silver-copper alloys, arbitrarily limiting the current to 0.4 ampere throughout the electrolysis. Miller found that some metallic silver appeared in the solution and that the addition of hydrogen peroxide toward the end of the electrolysis effected the resolution of the silver and insured its ultimate deposition on the cathode. Miller used a platinum gauze cathode of about 100 sq. cm. area and a spiral-shaped platinum wire anode. By stirring the solution adequately he found that only silver was deposited. Although Miller states that with sufficient stirring the current may be safely doubled, the permissible current will depend on the sizes of the electrodes employed and the manner of stirring.

If attention is paid to the cathode potential the current may be greatly increased, any suitable electrode pair used,[2] and the time of electrolysis materially decreased. Calculation, based on the standard reduction potential of the diammine silver ion given above and the following potentials of the various copper ions involved

$$\begin{array}{ll} Cu(NH_3)_4^{++} + e^- = Cu(NH_3)_2^+ + 2NH_3 & E^\circ = +0.00 \\ Cu(NH_3)_4^{++} + 2e^- = Cu^\circ + 4NH_3 & E^\circ = +0.05 \\ Cu(NH_3)^+ + e^- = Cu^\circ + 2NH_3 & E^\circ = -0.11 \end{array}$$

indicates that the silver concentration can be reduced to about $7.6x10^{-7}$ before copper should plate. This assumes that the diammino cuprous ion concentration is one molar and in practice it would be much less, favoring the separation even more. It assumes also that the ammonia concentration is one molar and that the polarization of silver on silver is negligible. The first assumption is not bad since the amount of excess ammonia added in the Miller procedure approximates one molar. The polarization, however, toward the end of the electrolysis is of the order of 0.1 volt which would indicate that the separation would be less effective by a concentration factor of ten or so.

Experience proved that the separation was actually very satisfactory, as Miller indicated, but by employing the graded cathode potential method currents as high as 2.5 amp. could be used. The cathode potential was limited to —0.1 volt toward the saturated calomel electrode during the early part of the electrolysis and raised to —0.20 toward the end. As Miller reported, a suspension of metallic silver appeared in the solution during the electrolysis and it was necessary to add hydrogen peroxide to redissolve this silver before completing the deposition. The formation of this metallic silver probably is caused by the reduction of the diammino silver ion by the diammino cuprous ion, also formed by reduction at the cathode. The addition of hydrogen peroxide causes the cathode potential to drop to about —0.11 volt after which the cathode potential rises as the peroxide is decomposed. The standard reduction potential of hydrogen peroxide is +0.87 so that the hydrogen peroxide is oxidized before or at least concommitantly with the deposition of the silver and nothing is gained by adding it at the beginning of the electrolysis. The presence of a large amount of nitrate materially reduced the amount of silver formed and even made unnesessary the addition of hydrogen peroxide.

In certain determinations in which the cathode-calomel potential was above —0.20 volt, when the hydrogen peroxide was added to redissolve the precipitated silver the upper rim and stem of the bare platinum electrode became immersed in the solution and on this bright platinum copper deposited even though not all of the silver had been removed from the solution. It appeared that the polarization of copper on platinum is less than that of copper on silver. It was therefore necessary to plate the platinum cathode completely with silver before beginning the electrolysis. If the entire deposition is carried out at a cathode-saturated calomel potential less than —0.2 volt this is not necessary.

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[1] Miller, *Ind. Eng. Chem., Anal. Ed.*, 8, 431 (1936).

[2] Rhees and Diehl, unpublished work.

COPPER

$$Cu^{++} + 2e^- = Cu^\circ \qquad E^\circ = +0.3448$$
$$CuCl_3^= + e^- = Cu^\circ + 3Cl^- \qquad E^\circ = +0.178$$
$$Cu(NH_3)_2^+ + e^- = Cu^\circ + 2NH_3 \qquad E^\circ = -0.11$$

The first of these potentials is applicable to sulfate, nitrate, and perchlorate solutions in which no complex ions of copper are present. Deposition from solutions containing chloride or free ammonia proceed stepwise, the cupric ions being reduced to the complex cuprous ions and the latter then reduced to the metal.

Deposition from a Sulfate-Nitrate Solution. Copper is most commonly deposited from a sulfate-nitrate solution, the solution containing about 2 ml. of concentrated sulfuric acid and 1 ml. of nitric acid per 200 ml. of solution. The presence of ammonium nitrate, about 1 g., has a beneficial effect on the character of the deposit, acting probably as a cathodic depolarizer preventing the evolution of hydrogen. The determination of copper in brass and bronze is always made after the removal of tin and lead, and because the zinc and traces of iron, manganese, and aluminum remaining do not interfere with the deposition of copper from acid solution, the electrodeposition is made without controlling the cathode potential.

The standard potential of copper in a sulfate, nitrate, or perchlorate solution, in which no complex ions are present, is

$$Cu^{++} + 2e^- = Cu^\circ \qquad E^\circ = +0.3448$$

Assuming $[Cu^{++}] = 10^{-6}$ as representing a negligible amount of copper remaining in solution at the end of an electrodeposition, a cathode voltage of

$$E = +0.3448 + \frac{0.059}{2} \log 10^{-6} = +0.171$$

(on the hydrogen scale) should ensure quantitative deposition. Toward the mercurous sulfate saturated potassium sulfate half cell, $E^\circ = 0.65$, this would be a voltage of -0.48.

Deposition from an acid, sulfate-nitrate solution without control of the cathode potential effects the separation of copper from nickel, and the metals above it in the electromotive series, such as cobalt, cadmium, zinc, manganese, aluminum, and the alkali, and alkaline earth metals. The separation of copper from these metals succeeds because the deposition of hydrogen follows the deposition of the copper and continues as long as the solution remains acid. On continued electrolysis of a nitrate solution the solution may become alkaline owing to the reduction of nitrate to ammonia and then other metals may deposit and the copper redissolve owing to oxidation by air and the stability of the cupric ammonia complex.

Deposition from a Chloride Solution. It is impossible to deposit copper in good condition from a simple solution of cupric chloride acidified with hydrochloric acid, but in the presence of suitable reducing agents copper can be deposited in excellent form. This was first studied by Schoch and Brown[1] who added hydroxylammonium chloride to the solution to prevent the evolution of chlorine at the anode since the evolution of chlorine would attack the platinum anode and being stirred into the solution have a deleterious effect on the copper deposited on the cathode. The situation is much more complex, however, than was originally supposed by Schoch and Brown[1] or by the later workers, Lassieur[2] and Torrance.[3] The electrochemistry was worked out in detail by Diehl and Brouns[4] in connection with the separation of copper from tin. Unlike the electrodeposition of copper from a sulfate-nitrate solution where the copper is deposited directly from the cupric state, the deposition of copper from a chloride solution is essentially a two-step process, the copper first being reduced to the cuprous state. This reduction takes place almost completely before the deposition of metallic copper begins as is evidenced by the almost complete disappearance of the blue color of the cupric ion. This phenomenon is due to the formation of the very stable complex ions $CuCl_2^-$ and $CuCl_3^=$. The standard electrode potential of the couples Cu^{++}, Cu^+ ($E^\circ = +0.167$), and Cu^+, Cu° ($E^\circ = +0.522$) do not apply in this case since they were determined in sulfate and perchlorate solutions in which no complex ion formation is involved.

According to Bodländer and Storbeck[5] the $CuCl_2^-$ ion is present in solutions of chloride concentration up to 0.4 *M* and the $CuCl_3^=$ ion above 0.4 *M*. From various data which he assembled Latimer[6] has calculated the constant for the dissociation

$$CuCl_2^- = Cu^+ + 2Cl^- \qquad K = 2.9 \times 10^{-6}$$

from which in turn he calculated the normal electrode potential for the reaction

$$CuCl_2^- + e^- = Cu^\circ + 2Cl^- \qquad E^\circ = +0.19$$

Inasmuch as the determination of copper from a chloride solution is made from a chloride concentration of about one molar, a more satis-

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[1] Schoch and Brown, *Trans. Amer. Electrochem. Soc.*, 22, 265 (1913); *J. Amer. Chem. Soc.* 38, 1660 (1916).

[2] Lassieur, *Bull. soc. chim.*, 39, 1167 (1926).

[3] Torrance, *Analyst*, 62, 719 (1937).

[4] Diehl and Brouns, *Iowa State College J. Sci.*, 20, 155 (1945).

[5] Bodländer and Storbeck, *Z. anorg. Chem.*, 31, 1 (1902).

[6] Latimer "Oxidation Potentials" Prentice Hall, New York, 1938, p. 171.

factory value was calculated by Diehl and Brouns[4] on the assumption that the complex ion present is $CuCl_3^{=}$. Using the data of Bodländer and Storbeck[5] for the solubility of cuprous chloride in 1 *M* potassium chloride and the solubility product of cuprous chloride, 1.85×10^{-7}, the constants were calculated for the reactions

$$CuCl_3^{=} = Cu^{+} + 3\,Cl^{-} \qquad K = 1.23 \times 10^{-6}$$
$$CuCl_3^{=} + e^{-} = Cu^{\circ} + 3\,Cl^{-} \qquad E^{\circ} = +0.178$$

Using the couples Cu^{++}, Cu° ($E^{\circ} = +0.3448$) and $CuCl_2^{-}, Cu^{\circ}$ ($E^{\circ} = +0.19$) the standard potential was calculated for the reaction:

$$Cu^{++} + 2\,Cl^{-} + e^{-} = CuCl_2^{-} \qquad E^{\circ} = +0.50$$

and similarly

$$Cu^{++} + 3\,Cl^{-} + e^{-} = CuCl_3^{=} \qquad E^{\circ} = +0.51$$

Thus, it is readily apparent why the reduction of cupric chloride in chloride solutions goes stepwise with complete reduction to the cuprous state as the first step. This is the case irrespective of whether the complex ion present is $CuCl_2^{-}$ or $CuCl_3^{=}$ or both simultaneously as discussed in a more complicated treatment by Chang and Cha[7] of the solubility of cuprous chloride in hydrochloric acid solutions.

Adopting as a satisfactory value for the couple $CuCl_3^{=}, Cu^{\circ}$ $E^{\circ} = +0.178$ using a chloride concentration 1 *M* and using a concentration of 10^{-6} *M* as a sufficiently small value for the copper remaining in solution after the deposition, application of the Nernst equation yields the cathode potential at which complete deposition will occur:

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[Cl^{-}]^3}{[CuCl_3^{=}]}$$
$$= 0.178 - 0.059 \log \frac{1}{10^{-6}}$$
$$= 0.178 - 0.354 = -0.176$$

or referred to a saturated calomel electrode ($E^{\circ} = +0.2456$) a cathode voltage of -0.422. Experimentally it has been found that complete deposition can be secured at a cathode voltage somewhat less than this, e.g., at -0.39.

Anodic Reoxidation Involved in the Deposition of Copper from Chloride Solution. Schoch and Brown,[1] who first carried out the deposition of copper from a chloride solution, reported frequent trouble in the failure of copper to plate and attributed the difficulty to the introduction of an excess of nitric acid during the process of dissolving the metal. Diehl and Brouns[4] encountered the same difficulty; indeed, they found that occasionally the deposit, after having once formed, would redissolve. As the result of a careful study of the electrochemistry involved they explained the cause of the trouble and devised ways of overcoming the difficulty.

As explained above the deposition of copper from a chloride solution proceeds stepwise owing to the great stability of the chlorocuprous complex ion $CuCl_3^{=}$. The chlorocuprous ion can be not only reduced at the cathode but can also be oxidized at the anode. The cupric ions so formed, being stirred about, react with the metallic copper on the cathode to dissolve it:

$$Cu^{++} + Cu^{\circ} + 6\,Cl^{-} = 2\,CuCl_3^{=}$$

Thus, unless the reduction of the chlorocuprous ion at the cathode proceeds more rapidly than its oxidation at the anode the deposition can never be complete, or may not occur at all. If the copper is reduced completely to the cuprous state prior to the electrolysis, the deposition of the metallic copper from the colorless solution of the chlorocuprous ions begins immediately but even in this case the deposition of metallic copper may not be complete, the solution quickly becoming blue because of cupric ion formed and the deposit of metallic copper either redissolving or reaching a more or less equilibrium state.

By combining the standard electrode potentials of the couples $Cu^{++}, CuCl_3^{=}$ ($E^{\circ} = +0.51$) and $CuCl_3^{=}, Cu^{\circ}$ ($E^{\circ} = +0.178$) the equilibrium constant was calculated for the reaction

$$Cu^{++} + Cu^{\circ} + 6\,Cl^{-} = 2\,CuCl_3^{=} \qquad K = \frac{[CuCl_3^{=}]^2}{[Cu^{++}]\,[Cl^{-}]^6} = 4 \times 10^5$$

Obviously this reaction proceeds almost completely to the right. In addition, the rate at which the reaction occurs is startling. Indeed, the reaction is used for the preparation of cuprous chloride. Incidentally, the corresponding reaction in a sulfate, nitrate, or perchlorate solution proceeds hardly at all

$$Cu^{++} + Cu^{\circ} = 2\,Cu^{+} \qquad K = \frac{[Cu^{+}]^2}{[Cu^{++}]} = 1 \times 10^{-6}$$

Four ways exist of eliminating the anodic reoxidation of the copper and the solvent action of cupric ion on the metallic copper: *(1)* the addition of a reducing agent which will be oxidized in preference to the chlorocuprous ion, *(2)* increasing the initial cathode voltage to a value sufficient to instantly reduce to metallic copper more than half of the chlorocuprous ions formed before the latter have been stirred away from the immediate vicinity of the cathode, *(3)* isolation of the anode by means of a membrane or porous cup, and *(4)* reduction of the anode potential to a value which will not

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[7] Chang and Cha, *J. Chinese Chem. Soc.*, 2, 298 (1934).

oxidize the chlorocuprous ion. These methods were discussed in detail on p. 25. In the present case a combination of methods *(1)* and *(2)* is sufficient to insure the complete and rapid deposition of the copper. Stannous tin, either added as stannous chloride or perhaps present in the solution from the material being analyzed, serves well as the reducing agent. The standard potential of the couple Sn^{++++},Sn^{o}(1 *M* HCl) $E^{o} = +0.14$ is well above that of the couple $Cu^{++},CuCl_3^{=}$ $E^{o} = +0.51$ so that the stannous tin will be oxidized in preference to the chlorocuprous ion. On the other hand the reduction of stannic to stannous tin will occur more or less concurrently with the deposition of copper, depending on the concentrations, the couples involved being

Sn^{++++},Sn^{++}(1 *M* HCl) $E^{o} = +0.14$
$CuCl_3^{=},Cu^{o}$ $E^{o} = +0.178$

so that as long as tin is present stannous tin will be available to prevent the anodic oxidation of the chlorocuprous ion.

The effect of a high initial cathode potential is apparent from the values of the couples $Cu^{++},CuCl_3^{=}$ $E^{o} = +0.51$ and $CuCl_3^{=},Cu^{o}$ $E^{o} = +0.178$. If the cathode voltage exceeds +0.178 (on the hydrogen scale) or —0.068 toward a saturated calomel electrode the copper, at least in part, should undergo reduction all the way to the metal. In an actual determination where the initial concentration of the copper is more nearly 0.1 *M* than 1 *M* and where polarization is involved of the order of 0.15 v., the actual initial cathode voltage at which copper begins to deposit is about —0.22 toward the saturated calomel electrode. Below this, copper may not deposit at all and will be incomplete, in any case, owing to the anodic reoxidation phenomenon discussed above. Obviously if more than half of the copper reduced to the chlorocuprous ion is immediately reduced further to the metal, deposition will ultimately be complete irrespective of anodic reoxidation.

In the procedure given below for the direct determination of copper in bronze advantage is taken of both of these techniques of minimizing anodic reoxidation.

The Separation of Copper from Tin in Chloride Solution. The electrochemistry of tin and the values of the various tin couples are discussed on p. 47. The couples of importance in the separation of copper from tin are

Sn^{IV},Sn^{II} (1 *M* HCl) $E^{o} = +0.14$
Sn^{II},Sn^{o} (1 *M* HCl) $E^{o} = -0.19$

As calculated above the deposition of copper from a solution 1 *M* in chloride should be complete at a cathode voltage of —0.176 (—0.422

toward the saturated calomel electrode). Assuming the tin to have a concentration of 0.1 *M*, a value greater than would be encountered in analytical work, deposition of tin should begin at —0.22 (—0.47 toward the saturated calomel electrode) allowing ample potential difference to effect a clean cut separation of copper from tin. This has been confirmed experimentally; it has been found, indeed, that a complete deposition of copper can be secured at a cathode-calomel potential of —0.39 v. It should be noted that the value usually given for the couple Sn^{++},Sn^{o} $E^{o} = -0.136$ applies to sulfate and perchlorate solutions and not to the chloride solution being employed.

Procedure for the Direct Determination of Copper in Bronze. (Diehl and Brouns [4]). Weigh out accurately into a 300-ml. tall form beaker 0.5 to 1.0 g. of sample. Add 10 ml. of concentrated hydrochloric acid, heat, and cause the sample to dissolve by the dropwise addition of nitric acid. Avoid adding an excess of nitric acid. When the sample has dissolved, wash the cover glass and beaker, add 20 ml. of concentrated hydrochloric acid and 4 g. of hydroxylammonium chloride.

Dilute the solution to 225 to 250 ml. and electrolyze with vigorous stirring using a limited cathode potential of —0.40 v. against a saturated calomel electrode. The current should have an initial value of at least 8 amp. so that the initial cathode potential quickly reaches a value of at least —0.30 v. Copper may not deposit for several minutes after the electrolysis is started and the saturated calomel cell may be negative to the cathode at the start. Copper will begin to plate when the cathode becomes negative to the saturated calomel cell about 0.2 v. Flush out the calomel cell if it is not the type having an agar gel salt bridge and wash down the walls of the beaker once or twice during the electrolysis. Continue the electrolysis until the current has been decreased to about 0.03 amp. Complete the determination in the usual manner, removing the electrolyte before turning off the current. Wash the deposit of copper with water and then with alcohol and dry at a temperature not exceeding 100° for ten minutes.

As an alternative method of dissolving the sample to avoid the introduction of nitrate, the following modification, devised by Professor H. H. Willard, may be used. Weigh out accurately into a 300-ml. tall form beaker, 0.5 to 1.0 g. of sample. Add 10 ml. of concentrated hydrochloric acid and 5 ml. of water. Add, 1 ml. at a time, 5 ml. of 30 per cent hydrogen peroxide (Superoxol). Considerable heat is generated and if the peroxide is added too rapidly the action will become too violent; wait until the reaction moderates before adding the next portion. The acid-peroxide mixture will dissolve the sample only if the solution does not become too hot. It may be necessary to cool the mixture during the dissolution process by immersing the beaker in cold water. It can all be added within about 5 or 6 minutes. By this time the sample will have practically all dissolved. Boil gently until the excess of peroxide is decomposed, which will require about five minutes, and will be indicated by the absence of small bubbles. By this time solution will be complete. Add 25 ml. of water and 4 g. of hydroxylammonium chloride. Keep the solution just below the boiling point for 5 or 10 minutes, until the green color which becomes dark at first is much lighter, indicating considerable reduction to the cuprous state. Add 5 ml. of concentrated hydrochloric acid. Dilute the solution and proceed with the electrolysis as above in the second paragraph.

This method was tested on Bureau of Standards Samples No. 37, 52, and 62. The results were excellent. The current efficiency in these separations was somewhat over 60 per cent if sufficient stannous tin was added to reduce the copper to the cuprous state prior to the electrolysis. The total time involved in a determination depended on the size of the sample taken; using a 0.5 g. sample the determination was completed in 40 minutes.

The Separation of Copper from Antimony. Antimony is deposited completely with copper from a hot, hydrochloric acid solution containing hydroxylammonium chloride as anodic depolarizer. Use was made of this by Schoch and Brown [1] for the separation of copper plus antimony from tin and lead. The electrolysis was carried out at a temperature of 60° and the cathode potential limited to —0.40 volt toward a normal calomel electrode until the current had fallen to 0.1 ampere after which it was allowed to rise to —0.50 volt. The electrode with the deposit of copper and antimony was weighed and the deposit was dissolved in dilute nitric acid in the presence of 10 g. of tartaric acid. Then the copper was deposited at a temperature of 20° with the cathode potential limited to —0.30 volt during the major part of the electrolysis and allowed to rise to —0.65 at the end. The copper deposit was excellent in color. The weight of the antimony was obtained by substracting the weight of the second deposit from the first. The lead (or tin) still in the first electrolyte was determined by deposition on a copper plated electrode. This procedure was tested on mixtures of known amounts of copper, antimony, lead, and tin and the results were very good.

Bismuth is also deposited simultaneously with copper and antimony if present. Schoch and Brown [1] showed that the separation of the three from tin and lead was complete but the subsequent determination of the copper plus the bismuth by deposition from the nitric acid-tartrate bath (as well as from a hydrochloric acid bath in the cold) did not give a clean cut separation from antimony.

The Schoch and Brown procedure for the separation of copper from antimony by deposition from a tartrate solution has recently been studied by Lingane.[8]

Another procedure for the separation of copper from antimony is based on the conversion of the antimony to a pentavalent fluoride from which the antimony is not deposited under the conditions needed for copper. Use was made of this in the analysis of antimony bearing bronze by Lassieur [9] and later by Lindsey and Sand [10] and by Torrance.[11] The copper-antimony deposit was dissolved in a mixture of nitric and hydrofluoric acids, the antimony oxidized to the pentavalent state with bichromate and the copper deposited electrolytically, limiting the cathode potential to —0.4 volt toward a saturated calomel electrode. The procedure for carrying this out is given on p. 39.

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[8] Lingane, *Ind. Eng. Chem., Anal. Ed.*, 17, 640 (1945).
[9] Lassieur, *Electroanalyse*, Paris, 1927, p. 191.
[10] Lindsey and Sand, *Analyst*, 59, 328 (1934).

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[11] Torrance, *Analyst*, 62, 719 (1937).

BISMUTH

$$\mathrm{BiO^+ + 2\,H^+ + 3\,e^- = Bi^\circ + H_2O} \qquad E^\circ = +0.32$$
$$\mathrm{BiCl_4^- + 3\,e^- = Bi^\circ + 4\,Cl^-} \qquad E^\circ = +0.16$$

The first of these potentials is based on measurements on a perchloric acid solution in which there are presumably no complex ions of bismuth present.

The most recent work on the electroanalysis of bismuth has been done by Kny-Jones,[1,2,3] using controlled cathode potential methods. Deposition from chloride solutions is unsatisfactory even in the presence of hydroxylammonium chloride as depolarizer. The deposits are spongy and not weighable. It is difficult to control the cathode potential at the start of the electrolysis, possibly owing to the formation of oxychloride in the cathode layer. Kny-Jones found that the addition of oxalic acid, which is a solvent for bismuth oxychloride, made it possible to control the cathode potential so that good adherent deposits were obtained.

Kny-Jones[2] found also that the deposition of bismuth from sulfate and nitrate solution succeeded well if the cathode potential was controlled. The presence of chlorides lead to poor, nonadherent deposits.

In an early method proposed by Sand[4] bismuth was separated from copper in a cyanide solution in which the copper is present as a double cyanide, in which form a very high potential is required for its deposition. The electrolysis was carried out in an alkaline cyanide solution at 80°, tartrate being added to keep the bismuth in solution. It was necessary to add formaldehyde to prevent the formation of bismuth pentoxide on the anode. Sand reported that the depositions tended to be erratic from these cyanide solutions, possibly owing to anodic polymerization. Later Kny-Jones[3] studied this procedure and found that formaldehyde caused a blackening of the solution owing to the formation of colloidal bismuth. After investigating a number of reducing agents he recommended hydroxylammonium salts as alone being suitable. Equally good deposits were obtained from chloride and nitrate solutions on the addition of tartrate. By always controlling the cathode potential Kny-Jones obtained reproducible results. A solution containing cyanide attacks the platinum of the electrodes but by keeping the amount of added cyanide low Kny-Jones found the attack was not serious; the cathode lost less than 0.5 mg. when 2 g. of potassium cyanide was present in about 100 ml. of electrolyte. The loss appeared to be due to the dissolving and redepositing of platinum, which was afterward lost in cleaning the cathode and had therefore no effect on the results of the analysis. The deposits obtained were of good appearance and adhered well to the electrode. Working details for the Kny-Jones' tartrate-cyanide procedure are reproduced below.

Bismuth may also be deposited from a nitrate solution and in this way separated from lead. Collin[5] recommended hydrazine hydrate as an anodic depolarizer in preference to glucose, tartaric acid, and hydroxylammonium salts, in that it can be easily destroyed following the electrolysis and the lead in the residual solution then deposited as the dioxide.

Procedure for the Deposition of Bismuth from Chloride-Oxalate Solution. (Kny-Jones[1]). Add sufficient concentrated hydrochloric acid to make the solution about 20 per cent in hydrochloric acid. Add 5 g. of oxalic acid, 0.5 g. of hydrazine hydrochloride as depolarizer and dilute to 100 ml. Carry out the electrolysis at 80° to 85°. Regulate the current to give a cathode-saturated calomel electrode potential of —0.15 to —0.17 v. (with higher initial potentials, up to —0.20 v. deposits tend to become non-adherent). When the current has fallen to a small value, raise the potential in steps of about 0.02 v. to a final value of —0.25 to —0.30 v.

Kny-Jones reported six determinations of bismuth by this method on amounts ranging from 0.10 to 0.25 g. of bismuth with an average deviation of 0.8 mg. He reported also that a Brown wire electrode can be used in this case. The identical procedure was used for the separation of bismuth in amounts from 0.1 to 0.28 g. from tin up to 0.25 g. and from lead up to 0.10 g. separately and together; the average and maximum deviations were respectively 0.3 mg. and 0.8 mg. of bismuth.

The same procedure was applied to the determination of bismuth in bismuth-tin-lead alloys used in the manufacture of sprinkler heads. The procedure follows:

Dissolve 0.4 g. to 0.45 g. of the bismuth-tin-lead alloy in 1 to 2 ml. of concentrated nitric acid. After the reaction has subsided in violence, add 10 ml. of concentrated hydrochloric acid and dilute to 100 ml. Add 5 g. of oxalic acid and 0.5 g. of hydrazonium chloride. Heat to 80° to 85° and electrolyze as above.

Eight analyses were reported on alloys containing up to 50 per cent bismuth, 0.4 g. samples; the average and maximum deviations were 0.4 mg. and 0.8 mg. respectively.

Procedure for the Deposition of Bismuth from Sulfate Solution. (Kny-Jones[2]). Dissolve the sample in 10 ml. of sulfuric acid and 1 ml. of nitric acid, heating to effect the dissolution. Cool the solution and dilute with water so that 20 to 25 ml. of sulfuric acid are present per 100 ml. Add 1 g. of hydrazonium sulfate as depolarizer. Heat the solution to 100° and electrolyze, using an initial potential of 0.055 v. toward a saturated calomel electrode. When the current has fallen to

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[1] Kny-Jones, *Analyst*, 64, 172 (1939).
[2] Kny-Jones, *Analyst*, 64, 575 (1939).
[3] Kny-Jones, *Analyst*, 66, 101 (1941).

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[4] Sand, *J. Chem. Soc.*, 91, 373 (1907).
[5] Collin, *Analyst*, 54, 654 (1929).

a small value raise the cathode potential in two or three steps to 0.15 v. Discontinue the electrolysis when the current has fallen to zero under this potential.

Kny-Jones reported seven determinations by this method on amounts of bismuth up to 0.25 g.; the average deviation was 0.27 mg. of bismuth and the maximum deviation 0.7 mg. The deposits were "of good appearance and adhered well to the electrode."

Procedure for the Deposition of Bismuth from Tartrate Solution. (Kny-Jones[3]). To the chloride or nitrate solution add an excess of sodium hydroxide and redissolve the precipitated bismuth hydroxide by adding 2 to 3 g. of sodium hydrogen tartrate. The addition of potassium cyanide appears to be optional. Dilute the solution to about 100 ml. and add 1 g. of hydroxyammonium sulfate. Electrolyze at 75°. Use a saturated calomel reference electrode with a 50 per cent sodium nitrate connection, limiting the potential to 0.76 v. When the current has fallen to zero, raise the cathode-calomel potential in three steps to —0.90 v. Discontinue the electrolysis when the current has fallen to zero at this potential.

Kny-Jones reported eleven determinations by this procedure on amounts of bismuth up to 0.25 g.; the maximum error was 0.4 mg. and the average deviation 0.15 mg. The maximum time required was twenty-five minutes.

Procedure for the Separation of Bismuth from Copper. Make the nitrate solution of the copper and bismuth alkaline by the addition of 3 g. of sodium hydroxide. Redissolve the precipitated bismuth hydroxide by the addition of 2 g. of sodium hydrogen tartrate. Convert the basic copper precipitate into the double cyanide by adding solid potassium cyanide to the cold solution until it becomes colorless, 2 to 3 g. being required. Treat the solution as described above for the deposition of bismuth.

Kny-Jones reported five separations of bismuth in amounts varying from 0.09 g. to 0.23 g. from up to 0.5 g. of copper, the maximum deviation being 0.4 mg. and the average deviation 0.2 mg. of bismuth.

Procedure for the Separation of Bismuth from Lead. (Collin[5]). Dilute the solution of tin and lead, present as nitrates, to 60 ml. Add 3 ml. excess of nitric acid and 4 or 5 drops of 50 per cent hydrazonium hydroxide. Heat to 80° to 85° and electrolyze, limiting the cathode potential to 0.45 v. negative to the 0.01 *N* nitric acid-quinhydrone electrode at the start and raising the potential to —0.6 v. at the end. After the removal of the bismuth add 50 per cent sodium hydroxide to the solution while still hot until the precipitated lead hydroxide has just redissolved. Add sodium peroxide in small quantities and heat the solution until all brown fumes and precipitate have cleared. Continue the addition of sodium peroxide until the last portion produces no further brown fumes. Heat the solution gently for about five minutes and then cool somewhat. Acidify with concentrated nitric acid, add 20 ml. in excess and dilute to 120 ml. Heat to 90° to 95° and electrolyze with a current of 6 to 6.5 amp. Dry the deposit by dipping in alcohol and then ether and holding it at some distance above a Bunsen flame. For calculating the results use as the factor for Pb 0.8660 for amounts of lead up to 0.1 g., 0.8635 for 0.1 to 0.4 g., and 0.8605 for 0.4 to 0.5 g. of lead.

Collin reported six separations by this method on amounts of bismuth from 0.1 to 0.4 g. and of lead from 0.2 to 0.4 g. The average and maximum deviation on the results for bismuth were 0.5 and 1.0 mg. of bismuth respectively; for lead the corresponding figures were 0.5 and 1.0 mg. of lead.

ANTIMONY

$$SbO^+ + 2H^+ + 3e^- = Sb^\circ + H_2O \qquad E^\circ = +0.212$$

Antimony may be deposited from a hydrochloric acid solution containing hydroxylammonium chloride in satisfactory form only if the temperature is maintained from 50° to 70° and the cathode potential is not allowed to exceed —0.40 volt toward a saturated calomel electrode.[1] In this manner antimony may be separated from tin. Schoch and Brown used a solution containing 15 ml. of concentrated hydrochloric acid and 4 g. of hydroxylammonium chloride per 200 ml. of solution. Their results for antimony on mixtures of tin and antimony up to 0.5 g. of each were excellent, the average deviation on eight analyses being 0.3 mg. The results for tin in the remaining electrolyte were not quite so satisfactory but they concluded that the method "is evidently to be preferred to the tedious gravimetric separation of these two metals."

Deposition from a hydrochloric acid solution is not a separation of antimony from copper or bismuth, although the latter elements may be separated from antimony if the latter is converted to a tartrate or to antimonic fluoride. This is discussed under copper, p. 40.

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[1] Schoch and Brown, *J. Amer. Chem. Soc.*, 38, 1673 (1916).

LEAD

$$Pb^{++} + 2e^- = Pb^\circ \qquad E^\circ = -0.126$$

Lead may be deposited on the cathode as the metal from a hydrochloric acid solution at 60° to 70° if a reducing agent be present. Schoch and Brown[1] found that oxalic acid, hydroxylammonium chloride or formaldehyde could be used as the reducing agent. The lead was deposited on a copper plated platinum electrode. The average deviation of ten results reported by Schoch and Brown on amounts of lead as high as 0.66 g. was 0.3 mg. Schoch and Brown felt that the method was more reliable than the deposition of lead dioxide at the anode. Sand, however, thought that the deposition of the oxide was preferable.[2]

The deposition of lead from hydrochloric acid solution is not a separation of lead from tin inasmuch as the potentials at which each is deposited lie too closely together. On this account, and because these metals alloy readily, they are deposited under the same conditions under which either one is deposited. Thus, both may be separated together from the metals from which either one alone can be separated, cadmium for example.

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[1] Schoch and Brown, *J. Amer. Chem. Soc.*, 38, 1673 (1916).

[2] Sand, Electrochemistry and Electrochemical Analysis, Vol. II, Blackie & Son Limited, London, 1940, p. 73.

TIN

$$Sn^{IV} + 2e^- = Sn^{II} \ (1\,M\ HCl) \qquad E^\circ = +0.154$$
$$Sn^{IV} + 4e^- = Sn^\circ \ (1\,M\ HCl) \qquad E^\circ = -0.02$$
$$Sn^{II} + 2e^- = Sn^\circ \ (1\,M\ HCl) \qquad E^\circ = -0.19$$
$$Sn^{++} + 2e^- = Sn^\circ \ (H_2SO_4, HClO_4) \qquad E^\circ = -0.136$$

Tin cannot be deposited from a hydrochloric acid solution unless a reducing agent is present to prevent the evolution of chlorine at the anode. Hydroxylammonium chloride or hydrazonium sulfate are equally satisfactory reducing agents for the purpose,[1,2] The solution should be fairly dilute, not more than 0.5 g. of tin per 300 ml., otherwise large crystals of tin (trees) grow on the upper and lower edges of the electrodes. The electrolysis should be carried out at room temperature, limiting the cathode potential during the initial part of the electrolysis to —0.6 volt against the saturated calomel electrode and raising it to —0.7 volt toward the end. This electrode potential has been determined experimentally to give satisfactory results but can be calculated taking the residual tin concentration as 10^{-6} as a satisfactorily complete deposition.

$$
\begin{aligned}
E &= E^\circ_{Sn^{II}, Sn^\circ} + \frac{0.059}{2}\log Sn^{II} \\
&= -0.19 + \frac{0.059}{2}\log 10^{-6} \\
&= -0.19 + 0.03\,(-6) \\
&= -0.37 \text{ volt (on hydrogen scale)} \\
&= -0.37 - 0.246 = -0.62 \text{ volt} \\
&\qquad\qquad \text{(toward the sat. cal. electrode).}
\end{aligned}
$$

The tin in solution may be in either the stannous or the stannic form. During the prior deposition of copper or copper plus antimony, stannic ions are reduced to stannous but it has been reported[2] that very little reduction occurs on a platinum electrode when tin alone is being deposited. An inspection of the electrode potentials given above indicates that the reduction in hydrochloric acid solutions should proceed stepwise from stannic to stannous and from stannous to metallic tin. Obviously, however, if the cathode potential is sufficiently high both processes may go on simultaneously at the cathode.

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[1] Schoch and Brown, *J. Amer. Chem. Soc.*, 38, 1660 (1916).

[2] Kny-Jones, Lindsey and Penny, *Analyst*, 65, 498 (1940).

It is of interest also in this connection that the equilibrium of the reaction

$$\mathrm{Sn^{IV} + Sn^{\circ} = 2\,Sn^{II}\ (HCl\ solution)}\quad K = 6 \times 10^{11}$$

lies far to the right.

The low results on the deposition of tin from hydrochloric acid solutions, reported by earlier workers, has been reviewed recently by Kny-Jones, Lindsey, and Penney.[2] They concluded that loss of tin by volatilization as stannate was impossible since the latter is decomposed in the presence of tin or of strong mineral acids and that the loss by volatilization as stannic chloride during dissolution of the sample was insignificant if prolonged boiling was avoided. Considerably more serious is the loss by re-solution of the deposit during washing, this loss being promoted by electrolytic action between the tin deposit and the platinum electrode. As was to be expected the loss was less when the cathode was coated with a less noble metal such as copper. Although no tin was detected in the electrolyte after removal of the electrode, considerable amounts were found in the washings. This appears to arise from a thin film of electrolyte covering the deposit just before and during washing. Thus, in a series of twenty-five experiments, when a well-adherent deposit of tin was dipped for ten seconds into the electrolyte from which it had been separated, there was a loss of about 1 mg., rising to 1.8 mg. when the temperature was raised from 20° to 40° and becoming still greater if the electrolyte made contact with the platinum as well as the deposit. The presence of ammonium salts greatly increased the amount of tin redissolved but even in this case the amount of tin redissolved could be reduced to a negligible amount if the solution was neutralized with ammonia just before the end of the electrolysis.

Following the separation of copper and antimony by deposition from a hydrochloric acid solution at a cathode potential of —0.40 volt toward a saturated calomel electrode, tin may be deposited from the same solution. It is best to add a further quantity of hydroxylammonium chloride. The electrolysis is then carried out at room temperature, limiting the cathode potential to —0.60 volt most of the time and raising it finally to —0.7 volt. Since some hydrogen is evolved under these conditions the current does not fall appreciably during the deposition and thus fails to indicate completion of the deposition as in the case of copper. It is best therefore to carry out the electrolysis long enough to ensure complete deposition.

Kny-Jones, Lindsey, and Penney reported twenty-seven results in which tin was plated on platinum electrodes and on copper plated electrodes, and in some of which ammonium salts were present and in some absent. Amounts of tin from 0.15 g. to 0.25 g. were used in these experiments. When ammonium salts were present with either type of electrode results were low by 1 to 4 mg. although, if the solution was neutralized with ammonia just prior to end of the electrolysis, the error was reduced in four determinations with copper plated electrodes to 0.4, 0.4, 0.5, and 0.3 mg. and with platinum electrodes to 0.1, 0.0, and 0.1 mg. With no ammonium salts present and using platinum electrodes the average deviation of six determinations was 0.3 mg. with a maximum deviation of 0.9 mg.; neutralization at the end appeared to make little difference. With no ammonium salts present and copper electrodes the average deviation was 0.4 mg. with a maximum deviation in seven results of 1.1 mg.

The potentials at which tin and lead are deposited from a hydrochloric acid solution are so close together that an electrolytic separation of the two is impossible. On this account and because the metals alloy easily, they are deposited together under the same conditions under which either is deposited. Schoch and Brown[1] recommended the subsequent separation of the tin and lead by the precipitation of metastannic acid. Lindsey and Sand[3] recommended depositing the two together and subsequently dissolving the deposit in nitric acid and hydrofluoric acid and depositing the lead as the dioxide. This procedure is given on p. 55. Torrance[4] later utilized this method for the determination of tin in bearing metals and bronze and reported very satisfactory results (see analysis of bearing metals and brass, p. 55).

The separation of tin from cadmium was studied by Schoch and Brown.[1] The tin was deposited from a hydrochloric acid solution containing hydroxylammonium chloride at 70°, limiting the current initially to 1.5 amperees until the cathode potential attained the value —0.70 volt against a normal calomel electrode. Then the current was reduced in order to keep the cathode potential constant during the remainder of the electrolysis. Schoch and Brown report four separations of 0.47 g. of tin from 0.3 g. of cadmium with errors of 0.0, +0.2, 0.0, and —1.0 mg.

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[3] Linsey and Sand, *Analyst*, 59, 335 (1934).
[4] Torrance, *Analyst*, 62, 719 (1937).

NICKEL

Nickel is usually deposited from an ammoniacal sulfate solution. Under these conditions zinc is also deposited. By limiting the cathode potential to 1.1 volts negative to the saturated calomel electrode it is possible to separate nickel from zinc. The following procedure is that of Torrance[1]:

Procedure for the Determination of Nickel in the Presence of Zinc. If the sample is an alloy containing copper, tin, lead, iron, and aluminum these must first be removed. Copper can be separated electrolytically from tin and lead (p. 38) and thus determined. Tin and lead can be removed electrolytically (p. 49). Iron and aluminum can then be separated by precipitation as the hydroxide, a double precipitation being advisable if the amount of these elements is appreciable.

To the solution containing the nickel and zinc add 20 ml. of concentrated ammonia in excess and 2 g. of sodium sulfite. Heat to 70° and electrolyze for 20 min. using a cathode-saturated calomel potential of 1.0 and 1.1 volt. Zinc can be determined electrolytically in the residual solution.

In the following method, also due to Torrance,[1] which is applicable to aluminum alloys, the iron and aluminum are not removed prior to the deposition of the nickel. Add 5 to 10 g. of tartaric acid, make the solution just alkaline with ammonia and add 20 ml. of concentrated ammonia in excess. Add 2 g. of sodium sulfite. Heat the solution to 70° and electrolyze for 20 min. at a cathode potential 1.0 to 1.1 volts negative to the saturated calomel electrode.

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[1] Torrance, *Analyst*, 63, 488 (1938).

CADMIUM

$$Cd^{++} + 2e^- = Cd^\circ$$

$$Cd(CN)^=_4 + 2e^- = Cd^\circ + 4CN^- \qquad E^\circ = -0.402$$

$$E^\circ = -0.90$$

Satisfactory electrodeposits of cadmium can be obtained from acetic acid and from alkaline cyanide solutions. The principal separation of cadmium is from zinc with which it is commonly associated in naturally occurring materials and in certain alloys. Sand[1] effected this separation by depositing the cadmium from a weak acetic acid solution limiting the cathode potential to 1.20 volts negative to a mercurous sulfate-2 *N* sulfuric acid reference electrode. The electrolysis was carried out at room temperature. The deposits were somewhat loose and in consequence the results not trustworthy for very large quantities of cadmium. The largest amount accurately deposited was 0.15 g. Nitrate had to be absent as its reduction in acid solution prevented the deposition of cadmium. Sand reported four analyses of cadmium zinc mixtures, the cadmium taken being 0.0777 g. and the zinc from 0.25 to 0.49 g.; the cadmium found was 0.0778, 0.0770, 0.0770, 0.0775 g.

At a considerably later date Lassieur[2] carried out this separation in a hydrochloric acid solution neutralized to the cerise color of thymol blue, limiting the cathode potential to —0.650 volt toward a normal calomel electrode but using a millivoltmeter in series with a high resistance rather than a potentiometer. The results on mixtures of cadmium and zinc and on more complicated mixtures, tin, cadmium and zinc, and antimony, copper, lead, tin, cadmium and zinc, the other metals being first removed by deposition from a hydrochloric acid solution containing hydroxylammonium chloride, were good, but are reported only to the nearest milligram.

Two other studies of the cadmium from zinc separation were made about this same time but unfortunately in neither was the cathode potential singled out as the important and controlling factor in the deposition. In the work of Engelenburg[3] the cadmium was deposited from a hydrochloric acid solution containing hydroxylammonium chloride, sufficient hydrochloric acid being present to prevent the deposition of the zinc, 10 ml. of concentrated acid in 200 ml. of solution. The zinc was deposited subsequently by reducing the acidity of the solution of 1.5 ml. of concentrated hydrochloric acid. Four results on the separation of quantities of 0.2 and 0.3 g. each of cad-

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[1] Sand, *J. Chem. Soc.*, 91, 401 (1907).
[2] Lassieur, *Bull. soc. chim.*, 39, 1179 (1926).
[3] Engelenburg, *Z. anal. Chem.*, 62, 277 (1923).

mium and zinc were excellent. In the deposition of cadmium the current was simply limited to 1 amp.

The other work, by Brennecke,[4] was an extensive study of the electrodeposition of cadmium and of zinc and of their separation but since no attention was paid to the cathode potential, the findings relative to the cathode-anode potential which results in a separation are applicable only to the particular electrodes used by Brennecke.

This subject has been recently reviewed by Hammond[5] who reported three fair separations of cadmium from zinc, using an acetic acid solution of pH 3.3 and limiting the cathode potential to 3.5 volt negative to a calomel reference electrode. It is not stated what particular calomel reference electrode was used and certain statements in the paper recommending that the limiting potential be determined by each worker using his own particular circuit and apparatus, together with the fact that Sand[1] effected the deposition of cadmium from essentially this same bath at a cathode potential of —1.20 toward a mercurous sulfate-2 *N* sulfuric acid electrode, makes it uncertain if Hammond was employing a controlled cathode potential method at all. If such results could be duplicated this would be by far the simplest method available.

Work at Iowa State College[6] indicated that the separation of cadmium from zinc can be made using an alkaline-cyanide solution. The results for cadmium, however, were invariably high and unfortunately just enough erratic to prevent the use of an empirical correction. For precise work, therefore, the cadmium must be dissolved and converted to the sulfate or the pyrophosphate for weighing.

The primary standards used in this work were selected crystals of hydrated cadmium sulfate,[7] $CdSO_4 \cdot 8/3H_2O$, anhydrous cadmium sulfate[8] and triple vacuum-distilled metallic cadmium,[9] spectrographically pure. Radioactive cadmium and zinc were used in the study. These isotopes were the 43-day Cd^{115} and the 250-day Zn^{65}. The radioactive metals were first suitably purified and then standard solutions made, from the weighed electrodeposited metal in the case of zinc and from the anhydrous sulfate in the case of cadmium. Studies were first made on solutions containing cadmium but no zinc. The solution of cadmium sulfate was made alkaline to phenolphthalein by the addition of sodium hydroxide. Sufficient five per cent sodium cyanide solution was then added to just dissolve the cadmium hydroxide. The solution was then electrolyzed limiting the cathode potential to —1.50 v. toward a saturated calomel electrode. The electrode and stirring assembly shown in Figure 8, page 24, was used. In twenty-five determinations on amounts of cadmium ranging from 0.1 to 0.6 g. the cadmium recovered was high in every determination by amounts from 0.1 to 5 mg., the average being 1.8 mg. The deposits were smooth, light gray in color and firmly adherent. The deposits usually darkened in color and it was observed that the darkening was associated with the high results; the darkening occurred usually during the entire deposition and in the occasional determinations which gave perfect results the electrode remained brighter in color throughout the deposition. Various factors were shown to be without effect on the deposit. In one series of determinations with about 0.5 g. of cadmium under otherwise uniform conditions the initial current was varied from 0.4 to 4.0 amp.; the results were all high by the same amount. The size of the residual current also did not affect the results. When fresh sodium cyanide solutions were used the current fell to about 0.03 amp. but when cyanide solutions which had stood for several days were used the current remained as high as 1.5 amp. This effect had no influence on the deposition of cadmium and no investigation was made as to its cause. Again, washing with a spray of distilled water removed all the alkali and proved to be a satisfactory wash; in one case a deposit already dried and weighed was soaked for five minutes in very dilute hydrochloric acid, neutral to methyl orange and containing a little aerosol for better wetting, then washed, dried, and weighed, and found to have lost only 0.2 mg. The high results are of course directly due to the presence of foreign material in the deposit. Careful qualitative tests showed the absence in amount greater than 0.1 mg. of sulfide, sulfate, nitrogen, carbon, and cyanide. The increased weight of the cadmium is due to some reaction with the electrolyte. An electrode covered with freshly deposited cadmium was made the cathode in a cadmium-free solution containing the same quantities of alkali and cyanide present in the electrolyte used in these studies. A current of 2 amp. was passed through the solution for sixty minutes. The cadmium deposit darkened somewhat over part of the surface and the cathode gained 0.5 mg. in weight. A repetition of this experiment gave the same result. A blank determination using a clean platinum electrode proved that no base metal impurities were present.

To determine the amount of cadmium which remained undeposited radioactive cadmium was used. The electrolysis was carried out as usual and the electrode was removed with the current flowing by

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[4] Brennecke, *Z. anal. Chem.*, 75, 321 (1928).

[5] Hammond, *Trans. Electrochem. Soc.*, 88, 393 (1945).

[6] Crouthamel, Brouns and Diehl, unpublished work.

[7] Hulett and Quinn, *J. Amer. Chem. Soc.* 37, 1997 (1915).

[8] Perdue and Hulett, *J. Phys. Chem.*, 15, 157 (1911); Baxter and Wilson, *J. Amer. Chem. Soc.*, 43, 1236 (1921).

[9] Obtained from the New Jersey Zinc Company, Palmerton, Penna.

gradually lowering the beaker containing the electrolyte and at the same time spraying the electrodes with distilled water. The washings were thus collected in the electrolyte. A solution of cadmium sulfate containing 25 mg. of ordinary cadmium was then added to the bath and the solution electrolyzed with a clean platinum cathode. The cadmium so deposited was dissolved in a minimum of concentrated hydrochloric acid and the resulting solution evaporated on a watch glass and its radioactivity measured. Above a cathode potential of —1.3 v. the amount of cadmium found in the electrolyte was less than 0.3 mg. and there was no correlation between the limiting cathode potential used and the amount of undeposited cadmium.

After experiments with cadmium alone had shown that complete depositions were obtained at cathode potentials of —1.3 v. and higher, the separation of cadmium from zinc was studied. In some of the experiments radioactive zinc was used to determine the amount of zinc deposited with the cadmium. Anhydrous cadmium sulfate (or the standard cadmium sulfate solution dispensed from a weight buret) and anhydrous, active zinc sulfate were weighed in these experiments. To the solution of the two sulfates was added 10 ml. of 40 per cent sodium hydroxide solution. The cadmium hydroxide was then dissolved by the addition of a fresh solution of sodium cyanide. Thus, nitrate and chloride were absent from this solution. The cadmium was then deposited using an initial current of 2.0 amp. and limiting the cathode potential to —1.4 v. In the determinations involving radioactive zinc, the cadmium deposit was dissolved in a minimum of hydrochloric acid and the solution evaporated to dryness on a watch glass and the activity measured. Less than 0.3 mg. of zinc was deposited with the cadmium and the separation may be regarded as satisfactory for practically all analytical work. The results for cadmium were high in conformity with the results found for cadmium alone.

THE ANALYSIS OF BEARING METAL, BRASS, AND BRONZE

The electrochemistry of the various metals in these alloys has been discussed in the preceding sections. The direct determination of copper in bronze is given in the section dealing with copper. Alloys of copper, tin, antimony, and lead segregate seriously on solidification and this fact should be kept in mind when comparing the results of analyses on such alloys.

Procedure for the Determination of Antimony, Copper, Lead and Tin in Bearing Metal. (Torrance[1]). Weigh 0.2 to 0.4 g. of the alloy (drillings or fine sawings) into a beaker. Dissolve the alloy by warming with a mixture of 10 ml. of concentrated hydrochloric acid, 10 ml. of water, and 1 g. of ammonium chloride (to minimize loss of tin as the tetrachloride). Complete solution may be hastened by the addition, drop by drop, of a saturated solution of potassium chlorate. When all the alloy has dissolved, boil off the excess chlorine and add 5 ml. of concentrated hydrochloric acid. Dilute to 150 ml. Add 1 g. of hydrazonium chloride and electrolyze at 70 to 75° limiting the cathode potential to 0.4 volts negative to a saturated calomel electrode. Copper and antimony are deposited together. After the current has fallen to a low value flush out the tip of the calomel electrode if it is the type in which this is necessary. Finally discontinue the electrolysis and dry and weigh the copper plus antimony.

Dissolve the copper plus antimony deposit in a mixture of 5 ml. of concentrated nitric acid, 5 ml. of 40 per cent hydrofluoric acid and 10 ml. of water. Boil off oxides of nitrogen, dilute to 150 ml., and add slowly a solution of potassium dichromate, drop by drop, until the liquid is distinctly yellow. Deposit the copper by electrolyzing for 20 min. at room temperature, limiting the cathode potential to —0.4 volts. The weight of antimony is obtained by difference.

To the solution from which the antimony and copper have been removed by the electrolysis just described, add 1 g. of hydrazonium chloride. Deposit the tin and lead together by electrolyzing for 20 minutes at room temperature limiting the cathode potential to 0.7 volts. Dissolve the deposit in a mixture of 15 ml. of nitric acid, 5 ml. of hydrofluoric acid and 15 ml. of water. Boil off the oxides of nitrogen and dilute the solution to 150 ml. Deposit the lead as the peroxide by electrolyzing the solution for 20 minutes at 90° to 95° with a current of 6 to 6.5 amps. Low lead alloys will give a solution containing insufficient lead for deposition from a nitric acid — hydrofluoric acid solution as lead dioxide. For such alloys add 20 ml. of a standard 0.5 per cent solution of lead (as nitrate), dilute to 150 ml. and electrolyze. Weigh the lead dioxide deposit and deduct the weight of lead added. Calculate the weight of lead, using the factor given on p. 46, usually 0.866. Obtain the weight of tin by difference.

Torrance reported the following results by this method:

(a) Carriage and wagon white metal (high lead)

Composition: Sb, 11.9; Cu, 2.7; Pb, 34.0; Sn, 51.4 per cent.

Weight of Alloy Taken g.	Antimony Found Per Cent	Copper Found Per Cent	Lead Found Per Cent	Tin Found Per Cent
0.2500	12.0	2.7	34.2	51.1
0.2500	11.9	2.7	34.2	51.2
0.2500	11.9	2.7	34.2	51.1
0.3000	11.9	2.7	34.3	51.0

(b) Locomotive white metal (low lead)

Composition: Sb, 9.6; Cu, 6.0; Pb, 5.1; Sn, 79.3 per cent.

Weight of Alloy Taken g.	Antimony Found Per Cent	Copper Found Per Cent	Lead Found Per Cent	Tin Found Per Cent
0.2500	9.6	6.0	5.0	79.2
0.2500	9.6	6.0	5.2	79.0
0.2500	9.5	6.0	5.0	79.2
0.2500	9.6	6.0	5.1	79.1

Procedure for the Determination of Copper, Lead, Tin and Zinc in Brass and Bronze. (Torrance[1]). Dissolve 0.2 to 0.4 g. of the alloy in a mixture of 10 ml. of concentrated hydrochloric acid, 2 ml. of concentrated nitric acid, 10 ml. of water and 1 g. of ammonium chloride. Add 5 ml. of concentrated hydrochloric acid and electrolyze for 20 minutes at 50°, limiting the cathode potential to 0.4 volt toward a saturated calomel reference electrode. Use an initial current of 3 to 4 amps. This should fall rapidly to about 0.1 amp. All the copper is thus deposited, together with any arsenic which may be present. In order to free the copper of arsenic dissolve the deposit in a mixture of 5 ml. of concentrated sulfuric acid, 5 ml. of nitric acid, and 10 ml. of water. Boil off the oxides of nitrogen, dilute the solution to 150 ml. and electrolyze for 20 minutes at room temperature, at a cathode potential 0.4 volts negative to the saturated calomel electrode.

Deposit the tin and lead from the original solution and subsequently separate them as described above under the analysis of bearing metals.

Oxidize the solution remaining after the removal of tin and lead by boiling it with a little bromine water until colorless. Add filtered ammonia carefully until the solution is just alkaline to phenolphthalein, heat to boiling, and filter off the small precipitate of ferric and aluminum oxides. These may be ignited and weighed together and the iron then determined colorimetrically. Cool the filtrate and add 10 ml. of concentrated ammonia. Electrolyze for 20 minutes at room temperature with a current of 3 amps. Weigh the deposit of zinc.

Torrance[1] reported the following results obtained by this method:

(1) Composition: Cu, 84.6; Pb, 3.8; Sn, 6.9; Zn, 4.4 per cent.

Weight of Alloy Taken g.	Copper Found Per Cent	Lead Found Per Cent	Tin Found Per Cent	Zinc Found Per Cent
0.2500	84.4	3.8	7.0	4.5
0.2500	84.5	3.8	7.0	4.4
0.2500	84.6	3.7	6.9	4.5
(2) Composition: Cu, 82.8; Pb, 4.1; Sn, 6.9; Zn, 5.9 per cent.				
0.2500	82.9	3.9	6.9	6.9
0.2500	82.8	4.0	6.9	5.9
0.2500	82.9	4.0	6.9	6.0
(3) Composition: Cu, 83.6; Pb, 2.8; Sn, 11.9; Zn, 1.3 per cent.				
0.2500	83.6	2.8	12.0	1.4
0.2500	83.7	2.8	12.0	1.3
0.2500	83.6	2.8	11.8	1.3

As discussed on p. 35, Diehl and Brouns[2] found that in this method for copper, which is essentially that of Schoch and Brown,[3] the deposition of copper may not begin or may begin and proceed for a while and then redissolve. With a sufficiently high concentration of hydrochloric acid and a high initial cathode potential the deposition proceeds satisfactorily.

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[1] Torrance, *Analyst*, 62, 719 (1937).

[2] Diehl and Brouns, *Iowa State College J. Sci.*, 20, 155 (1945).

[3] Schoch and Brown, *J. Amer. Chem. Soc.*, 38, 1660 (1916).