

Some applications of controlled potential electrolysis to analytical chemistry

Author:

Aylward, Gordon Hillis

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SOME APPLICATIONS OF
CONTROLLED POTENTIAL ELECTROLYSIS
TO ANALYTICAL CHEMISTRY.

A THESIS FOR THE DEGREE OF MASTER OF SCIENCE OF
THE NEW SOUTH WALES UNIVERSITY OF TECHNOLOGY.

BY: G. H. AYLWARD, B.Sc., A.S.T.C., A.A.C.I.

SUBMITTED DECEMBER 1953.

This thesis is offered in part fulfilment of the requirements of the New South Wales University of Technology Broadway, by G. H. Aylward, for the Degree of Master of Science.

It embodies work carried out by the candidate in the School of Applied Chemistry, New South Wales University of Technology.

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DECLARATION.

The candidate, Gordon Hillis Aylward, hereby declares that none of the work incorporated in this thesis has been submitted by him to any other University or institute for a higher degree.

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ADVANCED SUMMARY.

Electro-deposition at controlled potential has been known in principle for more than fifty years but has received little attention in the past because of the tedium involved in carrying out separations with manual apparatus. There is no doubt that the recent developments in this field are due to the application of instrumentation to this technique.

The research described in this thesis has been concerned principally with the development of new methods of electro-separations of metals at controlled potential and with the designing and building of an automatic electronic instrument to control these separations.

A method is described for the quantitative separation of copper and lead from tin by cathodic deposition from phosphoric acid electrolyte. The tin forms an anionic complex which is not reduced at the cathode and the copper is separated from the lead by deposition at a controlled potential. The lead is deposited as the metal and then the tin is estimated volumetrically. The difficulties associated with the quantitative cathodic deposition of lead have been investigated and the optimum working conditions established.

The automatic instrument was designed and built in collaboration with Mr. S. Graves of the Electrical

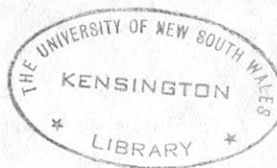
Engineering School. The instrument was constructed entirely from equipment already on hand. It is less costly to build than most of the previously published designs, yet it has a fast response time and it gives accurate and reliable control.

Using this instrument a number of new methods for separating metals by controlled potential electrolysis has been developed. These include the separation and estimation of copper in the presence of bismuth, arsenic and antimony; the separation of bismuth from lead; and the separation and estimation of lead in the presence of cadmium.

The theoretical introduction to this thesis has been condensed because the theory of the subject is well established and an extensive survey of its development is available in text books of electrochemistry.

This thesis comprises the four following sections

- (I) The theory of electrode reactions
 - (II) The measurement and control of electrode potentials
 - (III) The quantitative separation of copper and lead from tin by cathodic deposition
 - (IV) The applications of the automatic instrument.
-



SECTION I

THE THEORY OF ELECTRODE REACTIONS



Historical Development.

The first use of an electric current for quantitative deposition of a metal from its solution was reported by Wollcott Gibbs (1864) (1) in his method for the estimation of copper by deposition on a platinum cathode from sulphate solution. In the next twenty-five years many papers appeared describing methods for the separation and determination of various metals using this new technique. Separations were achieved by simultaneous deposition of one metal on the cathode and the oxide of another on the anode (2); by the use of complexing agents (3); and by the introduction of mercury as a cathode (4). The mechanism of selective deposition of metals at an electrode, however, was not understood and early workers assumed that the current was the controlling physical factor on which the process of electrolysis depended.

The accepted explanation of preferential electrode reactions originated from the hypothesis put forward to account for the specific voltage a metal takes up when immersed in a standard solution of its ions. Helmholtz (1882) (5) attempted to explain this phenomenon by ascribing to a metal a specific attraction of electricity, while Wiedemann (1885) (6) assumed that attractive forces between the metals and the ions of the electrolyte gave rise to this voltage.

W. Nernst (1889) (7) introduced the concept of metal solution pressures, as a basis for developing the theory of electrode potential. Using this hypothesis he presented the first feasible quantitative treatment of the phenomenon. He assumed that metals exert a positive pressure to force ions into solution. This electrolytic solution pressure he considered analogous to vapour pressure, but the metal passing into solution as positive ions gives up electrons to the metal surface and equilibrium is quickly established due to the electrostatic attraction of the opposite charges. The value of the electrode potential was found by considering the opposing effect of the osmotic pressure of the solution. When the osmotic pressure is less than the solution pressure, ions enter the solution leaving the metal negative and the solution positive and thus a potential difference is established between the solution and the metal. Conversely, if the osmotic pressure is greater, the potential difference is established between the metal (+) and the solution (-).

On the basis of the solution pressure theory it was possible to deduce an equation for the potential of an electrode which has been found by experiment to represent the actual dependence of electrode potential on the concentration of the reducible ions.

Two years later, Le Blanc (8) published the first definite measurements of decomposition voltages for a number of normal solutions of acids and alkalis in water. He

concluded from these voltages, since they were in the vicinity⁵ of 1.7 volts, that the same fundamental electrolytic process occurs in each case. In 1893 the same worker (9) modified his apparatus by the introduction of a cell to make possible the measurement of the potential difference between each electrode and the electrolyte. Le Blanc threw further light on the discharge of ions at an electrode by demonstrating that the algebraic difference between the two separate electrode potentials is approximately equal to the total voltage across the cell, provided that there is no appreciable voltage drop in the solution due to its resistance.

Correlating the advances made by Nernst and Le Blanc, Freudenberg (1893) (10) gave a detailed explanation of known metal separations in terms of solution pressure and osmotic pressure. He indicated that the separation of two metals could be achieved by setting the applied voltage so that, at very low current density, one metal would be deposited completely before the decomposition pressure of the second metal was reached. He explained the effect of complexing agents by the use of the Nernst equation. The reduction of the concentration of the ions of one metal by complexing alters its decomposition pressure and the separation can then be carried out at any suitable current density.

The work of Nernst, Le Blanc and Freudenberg showed conclusively that it was incorrect to regard the current

or the current density as the only factor determining the course of a particular electrolytic process. It is, as these workers pointed out, the electrode potentials which determine whether or not a particular electrode reaction will occur, or which of several possible reactions will take place at the electrode. The current is the result, not the cause of the reaction, and the current density merely reflects the rate at which the reaction proceeds per unit area of electrode surface.

The Nernst Equation.

As shown by Glasstone (11), the Nernst equation is derived simply by considering the difference in the electrical energy expended in dissolving one gram ion of a metal electrode in two solutions of its ions of differing osmotic pressure and relating this to the free energy change. When the activity (a) of the reversible ions is included in the equation it becomes

$$E = \frac{RT}{nF} \ln a + \text{constant} \quad (1)$$

where E is the potential of the electrode, R is the universal gas constant, T the absolute temperature, n the valency of the ions and F the Faraday number.

This derivation does not require an hypothesis for the origin of electrode potential for it is the "consequence of the thermodynamic treatment"(12). Thus the agreement of the Nernst equation with observed potentials does not make valid the concept of solution pressure. Owing to the difficulty

of attributing any physical significance to electrolytic solution pressure, this concept has met with a great deal of criticism. (The electrolytic solution pressure of magnesium is calculated as 1.1×10^{43} atmospheres and platinum as 1×10^{-36}). Notwithstanding the many objections and the recent theories, which are outside the scope of this thesis, electrolytic solution pressure, together with the theory of electrolytic dissociation, has given a deeper insight into the mechanism of electrode reactions.

Standard Electrode Potentials.

This thesis deals entirely with aqueous solutions, and the Nernst equation is used to give the potential of an electrode immersed in a solution of its ions. If all gases involved in the electrode reaction are at a (thermodynamic) pressure of 1 atmosphere and all dissolved substances at a thermodynamic concentration of unity, the term $\frac{RT}{nF} \ln a$ in equation (1) is zero and E equals the constant. This constant E_0 is known as the standard electrode potential. The equation (1) then becomes

$$E = E_0 + \frac{RT}{nF} \ln a \quad (2)$$

Since any reaction involves only the difference in potential between two couples, the potential of the hydrogen gas - hydrogen ion couple has been accepted as an arbitrary zero. The potentials of all other couples then are expressed in terms of this hydrogen reference couple. A list of the

of the standard potentials (E_0) (13) at 25°C of some metals is given in Table 1.

Table 1

Some Standard Potentials E_0 , 25°C

Reaction	E_0 Volts
$\text{Hg}^{++} + 2e \rightleftharpoons \text{Hg}^0$	0.7986
$\text{Ag}^+ + e \rightleftharpoons \text{Ag}^0$	0.7995
$\text{Cu}^{++} + 2e \rightleftharpoons \text{Cu}^0$	0.3448
$\text{BiO}^+ + 2\text{H}^+ + 3e \rightleftharpoons \text{Bi}^0 + \text{H}_2\text{O}$	0.32
$\text{H}^+ + e \rightleftharpoons \frac{1}{2}\text{H}_2$	0.000
$\text{Pb}^{++} + 2e \rightleftharpoons \text{Pb}^0$	- 0.126
$\text{Sn}^{++} + 2e \rightleftharpoons \text{Sn}^0$	- 0.136
$\text{Ni}^{++} + 2e \rightleftharpoons \text{Ni}^0$	- 0.250
$\text{Cd}^{++} + 2e \rightleftharpoons \text{Cd}^0$	- 0.4020
$\text{Zn}^{++} + 2e \rightleftharpoons \text{Zn}^0$	- 0.7620

Sign Convention.

Two sign conventions, commonly known as the "British" and the "American", are in use in electrochemical literature. The former adopts a positive sign, and the latter a negative sign, to indicate the potentials of element to ion couples where the ions are more easily reducible than the hydrogen ion. The British System is used in this thesis, i.e. the potential of the silver - silver ion couple is taken as positive since less energy is required to discharge silver ions than hydrogen ions, and zinc - zinc ion couple is considered as negative potential since hydrogen ions are more easily reduced than zinc ions.

Theoretical Aspect of Separations at the Cathode.

It is apparent, from inspection of their standard

potentials (Table 1) that metals may be divided into two easily separated groups. The metals of the first group will be deposited completely from acid solution and then hydrogen will be liberated and, while the solution remains acid, metals of the second group are not deposited. The separation of copper from zinc in sulphuric acid solution is an example of this.

It is not correct, however, to assume that all metals with a standard potential positive to hydrogen can be separated by deposition in acid solution from those which are negative to hydrogen. Before a correct prediction of electrode reactions can be made the activities of the particular ions present and the phenomenon of hydrogen overpotential on the electrode must be considered. Let us examine the electrolysis of a particular electrolyte to show the effect of activity and overpotential.

Let the electrolyte contain copper and lead ions of 0.01 activity respectively in a solution of pH 1. From the values of the standard potentials it would be assumed that on electrolysis the copper would be deposited first and then hydrogen would be liberated. Thus a separation of the copper from the lead would be achieved. The potential of a metal electrode immersed in a solution of known metal ion activity can be found from equation (2). Since R is 1.985 x 4.184 joules and F is 96,500 coulombs, using logarithms

to the base of ten, at 25°C the equation reduces to

$$E = E_0 + \frac{0.059}{n} \log a$$

For a copper electrode in a solution in which the cupric ion activity is 0.01

$$\begin{aligned} E_{\text{Cu}^0/\text{Cu}^{++}} &= 0.346 + 0.0295 \log 10^{-2} \\ &= 0.286 \text{ volt} \end{aligned}$$

If a copper cathode has a potential of 0.286 in this solution, no reaction will take place - a static condition, or a "electrical equilibrium" is obtained. For the reaction $\text{Cu}^0 \rightleftharpoons \text{Cu}^{++} + 2e$ to proceed in one direction, energy must be supplied to the system by means of the applied voltage. If the voltage applied to the electrode E_1 is higher than E , i.e. $(E_1 - E)$ is positive, the copper dissolves at the electrode. If $(E_1 - E)$ is negative, copper ions will be deposited at the electrode. $(E_1 - E)$ can be considered as the overpotential, ΔE i.e. the extra potential above the reversible potential, as shown by the Nernst equation, required to bring about the reaction. This means that copper would deposit from this solution at a cathode potential slightly more negative than 0.286 V. As the cupric ions are deposited from the solution at the cathode the activity of the cupric ions decreases and the cathode potential becomes more negative. When the cupric ion activity is reduced to 10^{-4} of its original value (by which time the deposition of copper may be considered quantitatively

complete) the cathode potential would be slightly more negative than $0.286 + 0.0295 \log 10^{-4} = 0.166$ volts.

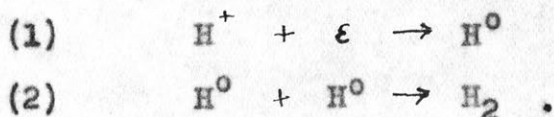
The potential of hydrogen gas in contact with hydrogen ions can also be found from the Nernst equation in the form

$$E = E_0 + \frac{RT}{nF} \ln \frac{[H^+]}{P^{1/2} H_2} \quad (4)$$

If P , the pressure of the hydrogen gas is considered to be one atmosphere, and since $-\log [H^+]$ is the pH, equation (4) becomes

$$E = E_0 - 0.059 \text{ pH}. \quad (5)$$

The reversible potential of the hydrogen gas - hydrogen ion couple in this system will be -0.059 V. since the electrolyte has a pH1. However, the reaction potential necessary to form hydrogen bubbles on the cathode varies considerably depending on the surface and on the metal of the electrode. The explanation for the slowness of the hydrogen reaction is to be found in the reaction mechanism. The liberation of hydrogen at a cathode is assumed to take place in two steps



The first step is considered to be the rate limiting step presenting a potential barrier to the electron transfer. The discharge of hydrogen ions from solution normally requires appreciable activation energy and the variation of this overpotential with the surface and the metal of the

cathode is attributed to the heat of adsorption of hydrogen atoms on the surface and the catalytic effect of the metal in the adsorption.

A list of minimum hydrogen overpotentials on some metals obtained by Caspari (14) is given in Table 2.

Table 2

Minimum Hydrogen Overpotential for Hydrogen in 2N . H_2SO_4 .

	Volts		Volts
Platinised Platinum	0.005	Copper	0.23
Gold	0.02	Tin	0.53
Iron (in alkaline soln.)	0.08	Lead	0.64
Smooth Platinum	0.09	Zinc	0.70
Silver	0.15	Mercury	0.78

This minimum overpotential is the excess potential above the reversible potential required to produce visual evolution of gas. The metals, such as platinum, that have very high catalytic adsorption properties have very low overpotentials and may be used as reversible hydrogen electrodes, the function of the metal in the discharge process being solely to eliminate the barrier separating the hydrogen ion and hydrogen atom. Metals with low catalytic properties exhibit high overpotentials.

The minimum overpotential of hydrogen at a cathode appears to be practically independent of the hydrogen ion concentration of the solution, so the overpotential of hydrogen on copper, in the electrolyte under consideration, can be taken as approximately 0.23 V. Then the potential

E_{H_2/H^+} at which hydrogen will be evolved from the copper electrode is

$$= -0.059 - 0.23 = -0.29 \text{ V.}$$

The reversible potential of the lead - lead ion couple

$$\begin{aligned} E_{Pb/Pb^{++}} &= -0.126 + 0.0295 \log 10^{-2} \\ &= -0.185 \text{ V.} \end{aligned}$$

and for a one ten thousandth reduction of the original lead ion activity $E_{Pb/Pb^{++}}$ becomes -0.305 V. At a potential slightly more negative than -0.185 V. lead will begin to deposit. Once the electrode is covered with lead the liberation of hydrogen from the solution will be controlled by the minimum overpotential of hydrogen on lead. This means that hydrogen discharge will not take place until the cathode potential reaches approximately $-(0.059 + 0.64) = -0.7 \text{ V.}$

From the above considerations it is seen that both copper and lead will deposit at the cathode from this electrolyte within quantitative limits before hydrogen is liberated.

In the above example, if the anodic reaction is considered to be the discharge of oxygen $4OH' \rightarrow O_2 + 2H_2O + 4e$, the increase in the hydrogen ion concentration, due to the discharge of the hydroxyl ions, will not affect appreciably the pH of the electrolyte.

Not only must one consider the effect of the activity of the ion and hydrogen overpotential in the prediction of

preferential electrode reactions, but also the ΔE value for the discharging ions. This value includes both the metal - metal ion overpotential and the concentration polarisation.

Metal - Metal Ion Overpotential.

The metal - metal ion overpotential, although in most cases very small can be high enough to effect the electrode reactions. The standard potentials of cadmium and iron are separated by only 0.04 V. but, because cadmium deposits with very low overpotential and iron with a high overpotential, cadmium deposition actually takes place in preference from a solution of equal concentration of the simple ions of the two metals. The metal ion overpotential also appears to depend on the material of the cathode. The author found that, while the deposition potentials of lead and antimony from phosphoric acid complexes on a copper electrode differ by 0.3 V., the two metals cannot be separated. Once the electrode is covered with lead the overpotential of the antimony is reduced and the two metals deposit simultaneously.

Concentration Polarisation.

Concentration polarisation is ascribed to the slowness of diffusion of ions. As an electrolysis proceeds there will be a decrease in the concentration of the discharging ions in the immediate vicinity of the cathode. The replacement of these ions is dependent on the rate of their diffusion to the electrode surface. This sets up a concentration

gradient in the vicinity of the cathode. The potential of the electrode at which the discharge is taking place is more negative than a stationary electrode in the same solution. The increase in the negative potential of the electrode due to the concentration gradient is called the concentration polarisation. This polarisation is negligible if the current density is small, but, as the current is increased, or the concentration decreased, this potential increases. It can be reduced if the rate of diffusion of the reducible ions is increased by heating or stirring the electrolyte.

Because of the difficulty of measuring the metal - metal ion overpotential independently of the concentration polarisation, it is customary to include them in the one term overpotential ΔE . Variations in this value in the course of an electrolysis, due to its dependence on current density, temperature, concentration, stirring, and the material and condition of the working electrode, increase the difficulty of predicting electrode reactions. Therefore it is often necessary to determine experimentally deposition potentials and reduction or oxidation products and to use these data in conjunction with theoretical considerations to follow the course of electrode reactions.

Methods of Separation at the Cathode.

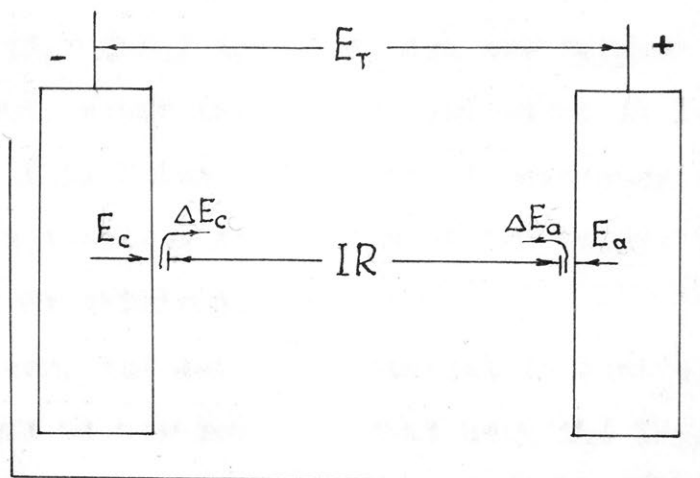
Use of Depolarisers. The separation of two metals, such as lead and copper, can be achieved by adding to the electrolyte a compound whose ions are reduced at a potential between that of the two metals. The metal with the more positive deposition potential will deposit and then the added ions will be reduced in preference to those of the second metal. The addition compound is referred to as a cathodic depolariser. To achieve a quantitative separation the concentration of the depolariser must be many times greater than the second metal ions and it, or its reduction products, must not react with the previously deposited element.

Nitric acid acts as a depolariser in the separation of copper from lead. The lead deposits as the dioxide on the anode while the presence of a high nitrate concentration prevents its cathodic deposition, the nitrate ions being preferentially reduced at the copper cathode. In this particular reduction the copper acts as a catalyst bringing about the reaction at a more positive potential than that necessary to reduce the lead ions. However, in the high nitric acid concentration required, the copper deposit is attacked and the simultaneous deposition of copper and lead dioxide is not satisfactory.

The ferric - ferrous system has been used by Furman (15) to act as a depolariser in the separation of silver from copper. In the presence of a ferric - ferrous mixture silver ions can be reduced to silver but cupric ions cannot be reduced to copper for preferential reduction of the ferric ions takes place at the cathode. The ferrous ions are re-oxidised at the anode and this cyclic reaction controls the cathode potential without the need for external potential control.

While satisfactory separations of two metals can be achieved by the use of depolarisers, the estimation of the metal that is left in the solution is often difficult unless the depolariser can be destroyed or removed with ease. Separation by controlling the potential of the cathode obviates the necessity of adding compounds, and thus does not interfere with the determination of elements left in the solution.

Controlled Potential Electrolysis. If a constant potential source is connected to two platinum electrodes immersed in the copper and lead electrolyte considered earlier (page 9) the potential (E_T) applied to the cell distributes itself as shown in the diagram below. The total potential drop is equal to the potential drop at the anode surface, plus the drop in potential across the



solution due to its resistance R to the flow of the current I , plus the potential drop at the cathode surface. The potential drop at the anode surface consists of the reversible potential (E_a) of the platinum electrode to the oxidisable hydroxyl ions and the overpotential at the anode ΔE_a . The potential drop at the cathode surface is due to the opposing reversible potential E_c of the electrode to the reducible ions plus the overpotential at the cathode ΔE_c . The total potential drop is made up as indicated in the following equation:-

$$E_T = (E_a + \Delta E_a) - (E_c + \Delta E_c) + I R.$$

As the electrolysis proceeds first copper ions deposit at the cathode. This causes an increase in the negative potential of the electrode (see page 11). The potential drop at the anode, if we again consider oxygen to be the anode product, remains virtually constant. If $(E_c + \Delta E_c)$ becomes more negative but E_T remains constant,

$(E_a + \Delta E_a) - (E_c + \Delta E_c)$ increases and the current should decrease. But, since the cathode potential is free to drift it will fall below the potential necessary to deposit the lead and a complete separation of the copper from the lead will not be obtained.

If, however, the cathode potential is controlled, i.e. it is held at a value such that only the deposition of copper ions can occur, then this reaction proceeds with virtually 100% current efficiency and the decrease in the current is a reliable indication of the progress of the electrolysis. From the previous calculations (page 10) it is seen that copper will begin to deposit at a cathode potential a little less than 0.286 V., and if the cathode potential is held at a value a little more negative than 0.166 V., a quantitative separation of the copper from the lead will be obtained. The lead ions cannot deposit until the cathode potential falls below -0.185 V., so the potential can be held at a value much nearer to, but more positive than, -0.185 V. This will allow a larger initial current to be used.

The separation of two metals by controlling the cathode potential is applicable only if the difference in deposition potentials is sufficient to allow for a quantitative deposition of one metal before the deposition

potential of the second is reached. It is difficult to give a minimum value for this difference, for hydrogen and the metal overpotentials and concentration polarisation are often the determining factors and not the difference in potential as calculated from the Nernst equation.

However the use of complexing agents extends the range of electrical separations.

Use of Complexing Agents. Since the deposition potential of a metal is dependent on the activity of the discharging ions in the electrolyte, a reduction of the activity will cause a negative shift in this potential. This is the principle underlying the use of complexing agents to separate two metals whose deposition potentials are too close to allow for a controlled potential separation. If the ions of one metal can be complexed the activity of its simple ions will be reduced, depending on the instability constant of the complex ion formed.

The electrode potential of a metal immersed in a solution of its complex ions can be derived from the Nernst equation and the instability constant of the complex ions. Suppose $M_m X_x^+$ is the formula of a complex ion where M^+ and X^- are the positive and negative ions from which the complex is formed, and with which it is in equilibrium, thus $M_m X_x^+ \rightleftharpoons mM^+ + xX^-$. From the law of mass action the

overall instability constant K can be represented by

$$K = \frac{a_{M^+}^m \cdot a_{X^-}^x}{a_{MX}^{\pm}}$$

The activity of the simple metal ions is given by

$$a_{M^+} = \left[\frac{K \cdot a_{MX}^{\pm}}{a_{X^-}^x} \right]^{1/m}$$

Substituting this value in the Nernst equation

$$\begin{aligned} E_{\text{complex}} &= E_0 + \frac{RT}{nF} \ln \left[\frac{K \cdot a_{MX}^{\pm}}{a_{X^-}^x} \right]^{1/m} \\ &= E_0 + \frac{RT}{mnF} \cdot \ln K + \frac{RT}{mnF} \ln \frac{a_{MX}^{\pm}}{a_{X^-}^x} \end{aligned}$$

If the activities of the complex ion and the complexing anion are unity the equation reduces to

$$E_{\text{complex}} = E_0 + \frac{RT}{mnF} \ln K.$$

If the instability constant of the complex ions is small enough, the shift in the deposition potential of the metal ions complexed can be great enough to allow hydrogen liberation to take place before E_{complex} is reached.

The author has developed a method (see page 75) for the estimation of copper, lead and tin in which the copper is deposited in the presence of the lead and tin by

controlling the cathode potential. The separation of the lead from the tin depends on the formation of an anionic tin phosphate complex. The standard potentials of lead and tin are separated by only 0.01 V., thus the quantitative separation of the two metals from a solution of their simple ions is not possible. However, in the presence of phosphoric acid the tin is complexed and its deposition potential is shifted to such an extent that hydrogen is liberated before the tin deposition occurs. Therefore the lead can be separated from the tin by constant potential electrolysis.

SECTION II

MEASUREMENT AND CONTROL OF ELECTRODE POTENTIALSMethod of Measuring the Electrode Potential.

The electrode potential is measured against a reference half cell. The tip of the half cell is placed very close to the surface of the electrode to minimise the ohmic potential drop, i.e. the IR drop, due to the resistance of the solution between the half cell and the electrode. The potential difference between these two electrodes is measured on a vacuum tube voltmeter of high impedance to limit the current drawn through the reference half cell. An electronic titrimeter was used as a voltmeter in the work to be described but later this was replaced by a rapid time response speedomax which gave a continuous graph of the cathode - half cell potential against time.

The saturated calomel half cell was used in preference to other half cells. It is set up easily since no standard solution is necessary and it can be used with a saturated potassium chloride salt bridge without the necessity of having a special intermediate solution, for the cell itself contains saturated potassium chloride solution. Although as a half cell it is not as accurate as most others, unless it is very carefully prepared (16), it is sufficiently reliable for following cathode potentials

during the course of an electrolysis.

A copper electrode immersed in a solution of cupric ions of unit activity has a potential of $+ 0.346$ V. referred to the hydrogen scale. Now if a saturated calomel electrode (potential $+ 0.246$ V.) is used as the half cell to measure this potential, the difference in potential, $0.346 - 0.246 = +0.100$ V., will be recorded by the voltmeter.

Control of the Potential Of an Electrode.

During an electrolysis the potential of the cathode becomes more negative to the half cell and control is brought about by limiting the potential difference between the cathode and the half cell to a fixed value. This is achieved by reducing the potential applied to the electrolysis cell. Reduction of this potential can be done manually or automatically.

Manual Control.

Fig. 2 shows a simple manual potential control circuit in which the potential difference across the electrodes of the electrolysis cell is reduced by increasing the resistance, R , connected in series with the cell. In Fig. 3 a potential divider circuit, for control of potential, is illustrated. The applied potential to the cell is increased or decreased by moving the contact to the right or to the left along the rheostat R .

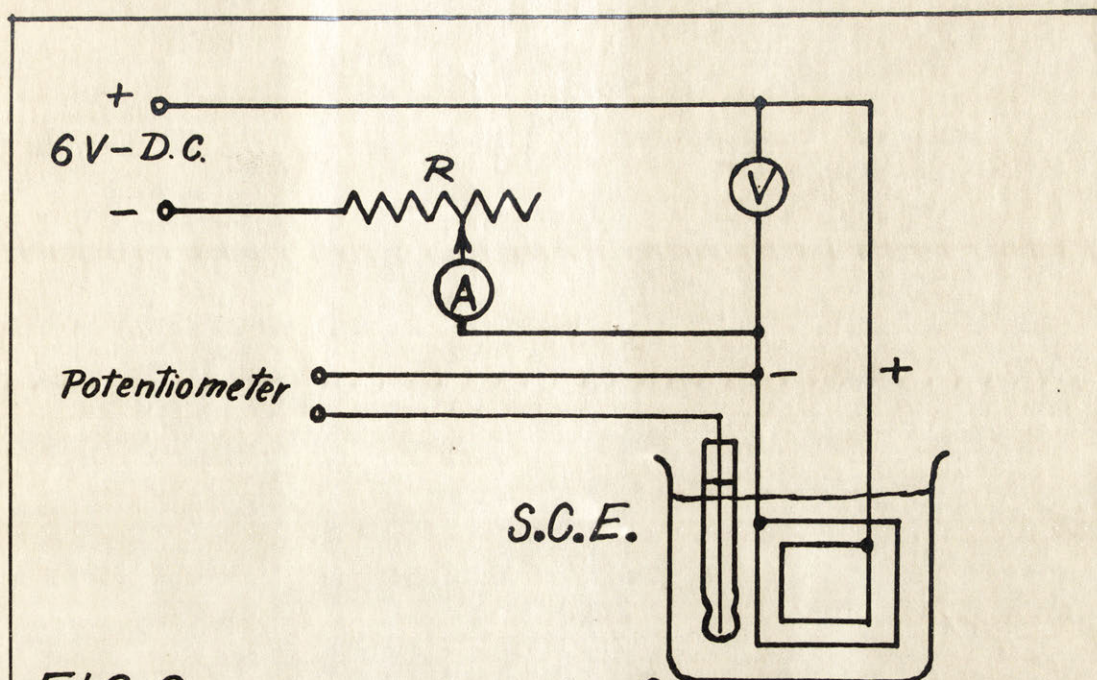


FIG. 2 - Series Resistor Circuit.

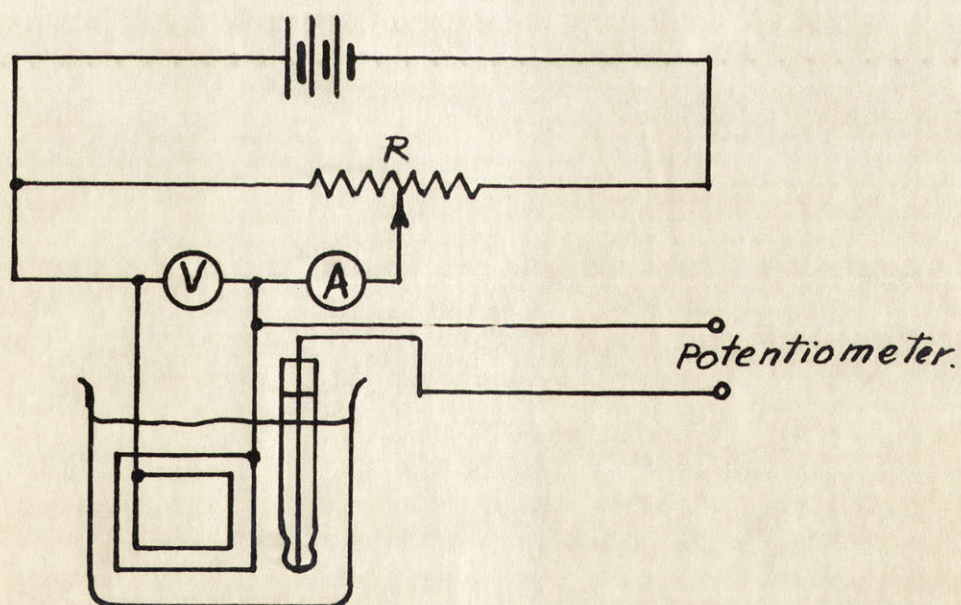
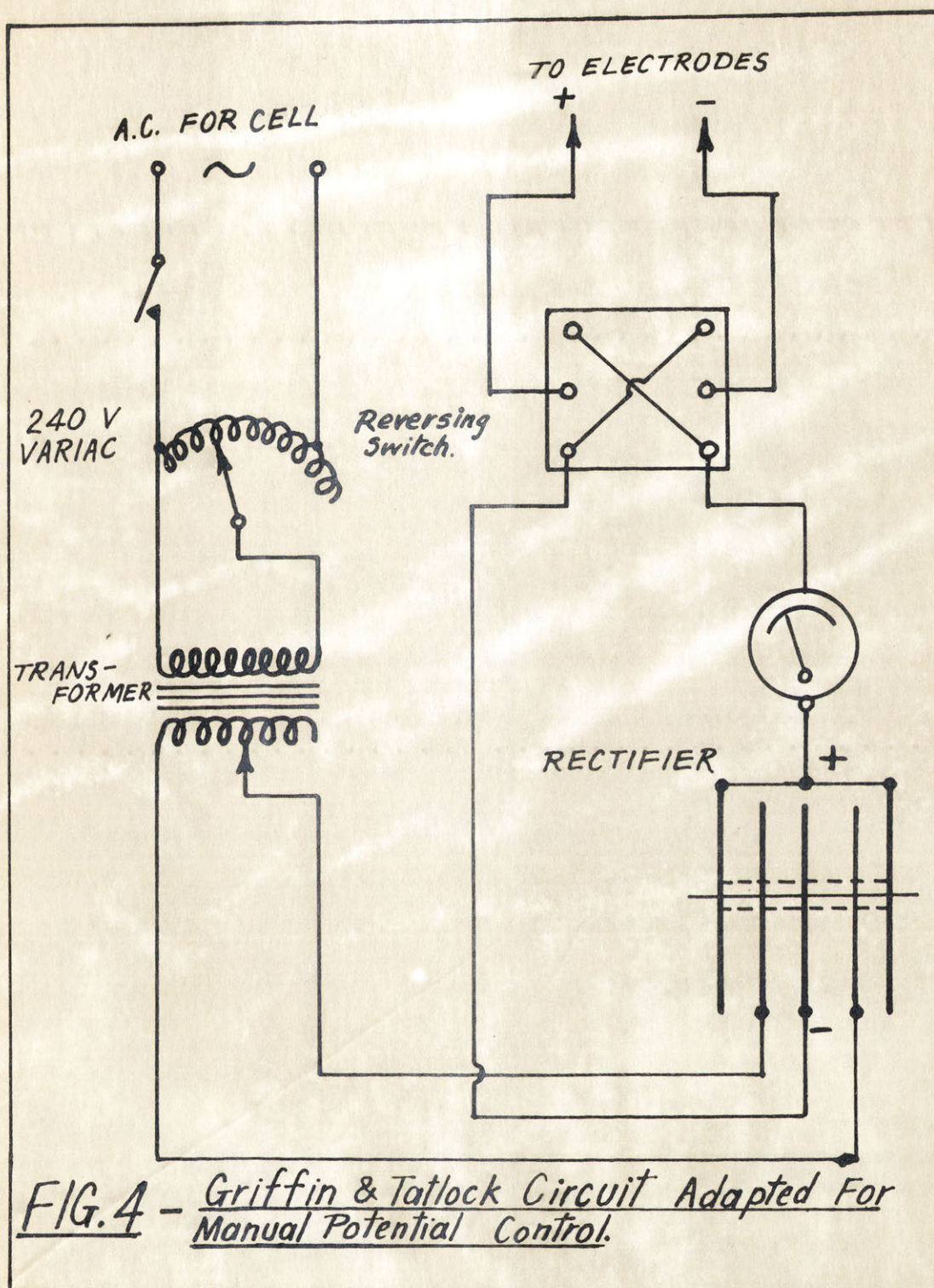


FIG. 3 - Potential Divider Circuit

The manual control apparatus used by the author (Fig. 4) comprised a Griffin and Tatlock electrolysis unit adapted for manual potential control by wiring a 240 volt variac into the electrode input circuit of the instrument. The applied potential to the cell is decreased by reducing the alternating voltage applied to the primary of the step down transformer in the electrolysis unit. A better control of the applied potential is achieved with this circuit than with those shown in Figs. 1 and 2. In the deposition of copper from the phosphate electrolyte, (see page ⁴⁹), a change of 60 V. on the variac produces a difference of only 0.5 V. in the D.C. potential applied across the electrolysis cell. By continually adjusting the variac during the deposition the cathode potential can be held to within 20 mV of the required value.

Automatic Control of the Electrode Potential.

Electro-deposition at controlled potential has been known in principle for sixty years and, despite the manually controlled apparatus developed, this valuable technique has only recently received the attention it deserves. There is no doubt that the revival in interest in the technique, over the past ten years, is due to the development of suitable automatic apparatus which has relieved the tedium formerly involved in carrying out determinations by the manual method.



Eleven years ago Hickling (17) constructed the first instrument to automatically control the potential of an electrode to a set value. He called this instrument a potentiostat. Since then many designs have appeared in the literature.

The general principles on which automatic control is based are outlined below. The potential difference between the working electrode and the calomel electrode is compared with the desired control potential set on a variable reference voltage circuit. These two potentials are connected in opposition and will cancel when the working electrode - calomel electrode reaches the desired potential i.e. when $(E_c + \Delta E_c)$ vs $E_{S.C.E.} = E_{set}$. Now, if the cathode potential changes during the course of the electrolysis, the difference in potential produced in the balance circuit is used to control a device which alters the potential applied to the cell in such a way as to correct for the change.

The automatic instruments constructed for controlling electrode potentials differ in the method by which this small error potential, the signal, is employed to alter the potential applied to the cell and so correct for the change. This method of control may be mechanical or electronic.

Mechanical Control.

With only a few exceptions all the published potentiostat circuits depend on the mechanical movement of a variac in the supply circuit to the electrolysis cell to adjust the applied potential and thus correct for change in the electrode potential. The error voltage produced by the change is amplified and then used to control the movement of a synchronous motor which is coupled to the variac. The circuit is wired so that the sign of the feed back produced by the signal is opposed to the change causing it. The designs differ in the method of amplification of the signal and in the method of controlling the rotation of the motor. It will suffice to give a brief outline of one of these instruments. (A more detailed description of potentiostats is given in the author's B.Sc. thesis) (18).

A simplified block diagram of a motor control regulator (19) is shown in Fig. 5. In operation the cathode reference cell potential is opposed by a set potential on a precision potentiometer. If the cathode potential alters in any way during the electrolysis the signal produced is amplified by the three stage D.C. amplifier, the output of which operates one of the two relays depending on the sign of the signal. These relays in turn control the reversible motor driving the variable arm of the variac supplying the current for the electrolysis. Hence the potential

applied to the cell is automatically adjusted to eliminate the error signal.

Electronic Control.

Electronic control of the applied potential is preferable to mechanical control for it can be made continuous and instantaneous. The time factor involved in the operation of a relay is eliminated and the hunting due to the inertia of a rotor is avoided. The first all-electronic instrument, developed by Hickling (17), depended on the firing of a thyatron valve which discharged a condenser in the cell circuit and thus reduced the potential to the cell. Heyd, Ohmart and Hites (20) later developed an all electronic apparatus which had a much faster response and a more reliable control than the thyatron circuit. In both these circuits all the current to the cell is passed through vacuum tubes and, as a result, the regulators are considerably limited in current capacity, the former having a maximum output of 300 mA and the latter only 60 mA.

Milton J. Allen (1950) (21) designed an electronically controlled potentiostat for large scale electrolytic reduction of organic compounds. Allen overcame the disadvantages of the previously described instruments. His circuit supplies currents as high as 20 amp and a potential up to 75 volts. He utilises an electronic amplidyne as

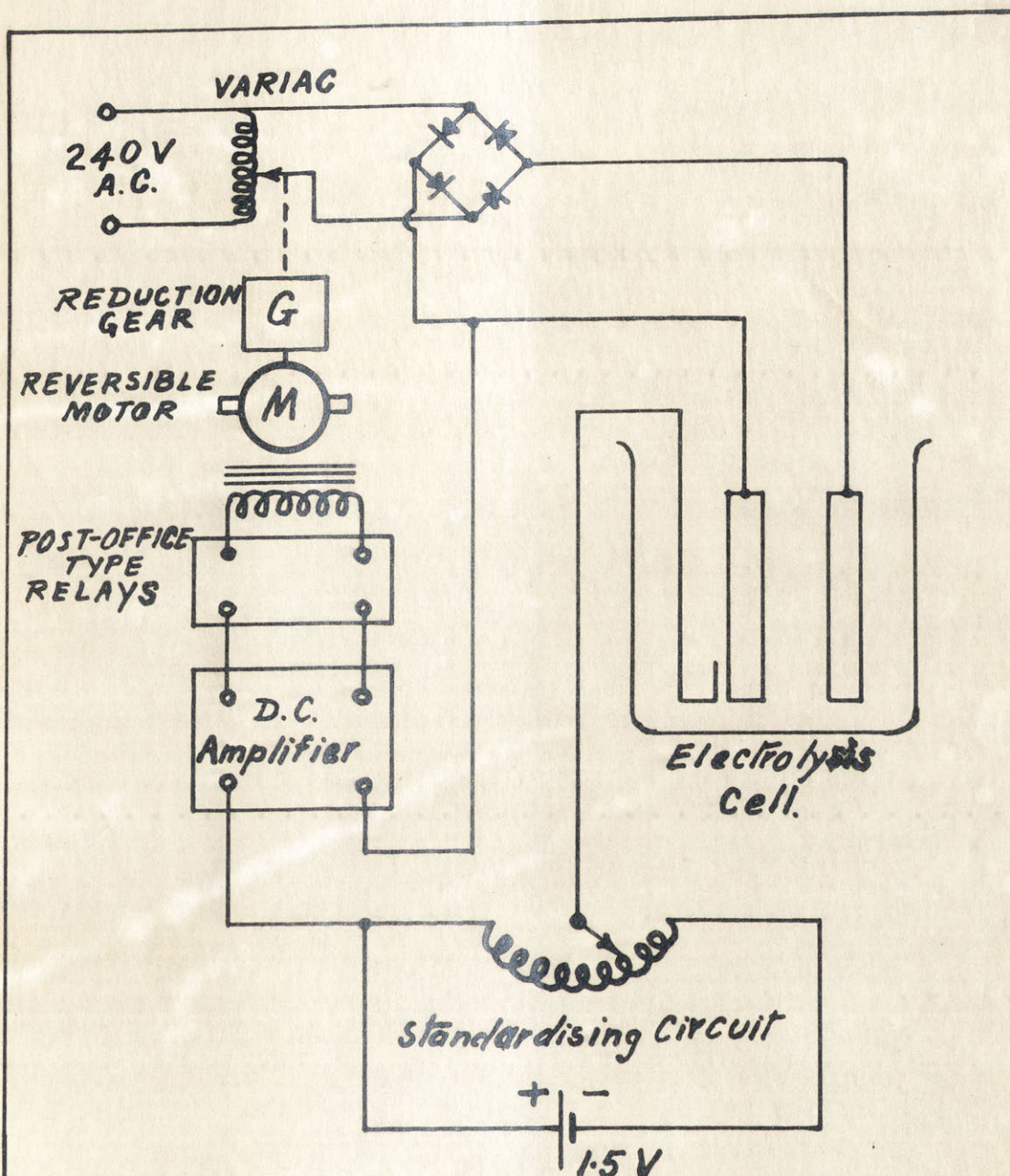


FIG.5 - MOTOR CONTROL REGULATOR.

a control and a current source. It gives the relatively high currents or applied potentials required for the reduction of many organic compounds at cathode potentials as high as 6 volts. It will control in both directions and its response is instantaneous with negligible hysteresis characteristics. The off balance sends a signal to the amplifier which is the controlling unit for the amplidyne. This signal causes the amplifier to adjust the field winding potential of the amplidyne so that its output is decreased or increased to correct the unbalanced condition.

This design overcame the difficulty of the small current output from the earlier electronic types while it maintained all the advantages of an electronic device compared to a mechanical control.

The Author's Potentiostat.

An automatic device to control electrode potentials was considered necessary to facilitate investigations of metal separations by controlled potential electrolysis. However, most of the suitable instrument designs have come from America and they contain components which are not easily procurable in this country. So the author, in collaboration with Mr. S. Graves of the Electrical Engineering School, set out to construct a simple and cheap potentiostat which could be used in this research

project.

In the building of this instrument particular attention had to be paid to economy and so, to simplicity of construction and maintenance. Consequently, as much use as possible was made of equipment already on hand.

The possibility of controlling the output of a D.C. generator by applying to its field winding the negative feed back produced by amplifying the error signal was investigated. This principle of control was suggested to the author from a study of M. J. Allen's circuit.

A block diagram of the instrument constructed is shown in Fig. 6. It incorporates the principle of controlling the output of a D.C. generator by the amplified error signal caused by a change in the potential of the working electrode. In operation the cathode - reference cell potential is opposed by the balancing potential through the pair of electrometer tubes which comprises the first stage of the D.C. amplifier. The D.C. level of the amplifier is adjusted to give the desired initial running conditions. In practice the balancing potential is not exactly equal to the input potential but the difference in level is kept small so as not to unbalance the input stage to any great extent. If the D.C. level between the two tubes alters in any way during an electrolysis, from

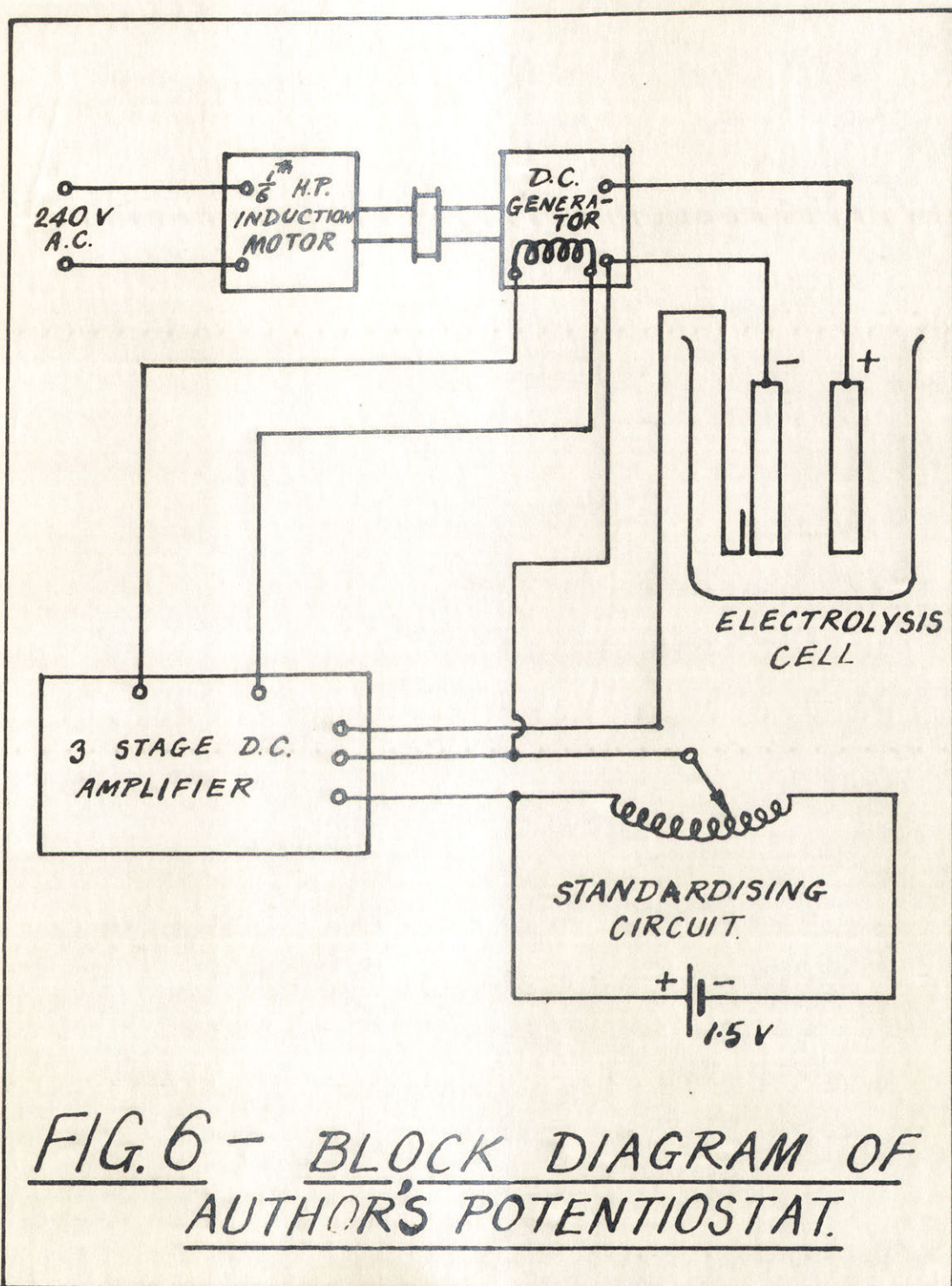


FIG. 6 - BLOCK DIAGRAM OF
AUTHOR'S POTENTIOSTAT.

the level set, this difference is amplified by the three stage D.C. amplifier, the output of which is fed onto the field winding of the D.C. generator. The amplifier is wired so that an increase in the difference of potential between the working electrode and the half cell produces a decrease in the output potential of the amplifier.

This reduction in the potential applied to the field winding of the generator, in turn, reduces its D.C. output to the electrolysis cell. Hence, the cell potential is adjusted to correct for the change. In this manner positive or negative changes in the cathode potential during the course of an electrolysis are automatically and instantaneously corrected.

Certain parts of the instrument are considered in greater detail below.

The Balancing Circuit. The balancing circuit consists simply of a battery of suitable potential connected across a potential divider. A precision potentiometer is not necessary since the instrument will operate at any potential level, within certain limits, above or below the value set on the balancing circuit.

The D.C. Amplifier. The first stage of the three stage D.C. amplifier consists of a pair of MML400 electrometer tubes. This long-tailed pair input circuit has many

advantages over the more conventional designs. It is self-balancing since changes in the tubes tend to average out. Inphase potentials imposed on the input circuit, in particular 50 cycle hum, balance out and so do not appear in the output. This is a great advantage when the grid is attached to a large electrode; By having an equal reference potential applied to each tube large input D.C. levels may be handled, providing the variation in the input circuit is small. The use of these electrometer type tubes stabilises the amplifier's D.C. level and also provides a high input impedance. This high input impedance is necessary to limit the current drawn through the reference half cell so as to prevent polarisation of this electrode and to minimise any resistive effects in the electrolysis cell. The output of this stage is equal to the difference of the input potentials multiplied by a constant A which is approximately equal to half the gain of one tube.

The second stage of the amplification is provided by means of a high gain triode 12AX7, working with a constant current load. Two high mutual conductance triodes, 6J6's, wired in parallel were used for the output stage. These valves are small and they will work into a low impedance load such as that provided by a typical field coil.

ME 1400

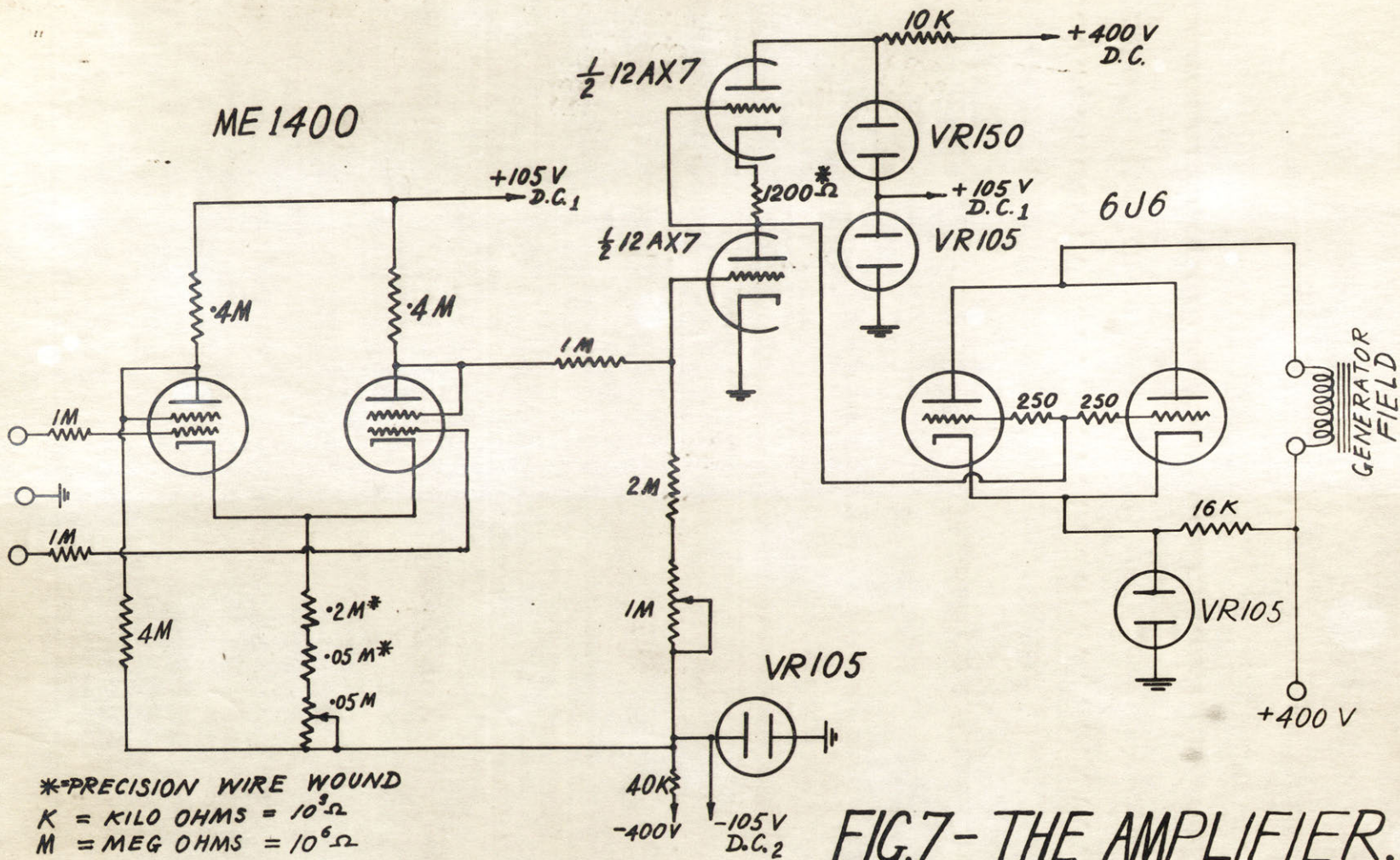


FIG. 7 - THE AMPLIFIER.

The VR105 and the VR150 valves stabilise the plate voltage supply to the valves of the amplifier.

The measured gain of the amplifier input to the field terminals was 7,000. The amplifier circuit, excluding the conventional power supply circuit, is shown in Fig. 7.

The Generator.

An ex-disposals 1FF type generator motor was used for the generator. The gears were removed and the fields were rewound and connected in parallel to give a load of 5,000 ohms. This is the working load required for the output stage of the amplifier (6J6's). The generator was coupled to a 1/6th H.P. 1,450 R.P.M. induction motor. The use of this machine enables a low potential - high current D.C. source to be obtained more readily than is possible using most other methods. It also has the additional advantage that a power gain may be achieved. The machine has the only long time constant in the system - approximately 1/10th second response. With this particular generator the maximum potential output is 6 volts and this is produced when 120 volts are applied to the field windings.

The Stability of the Instrument.

To test the stability of the instrument, the generator output wires were connected across a potential divider and a fraction of the output potential was fed onto the input

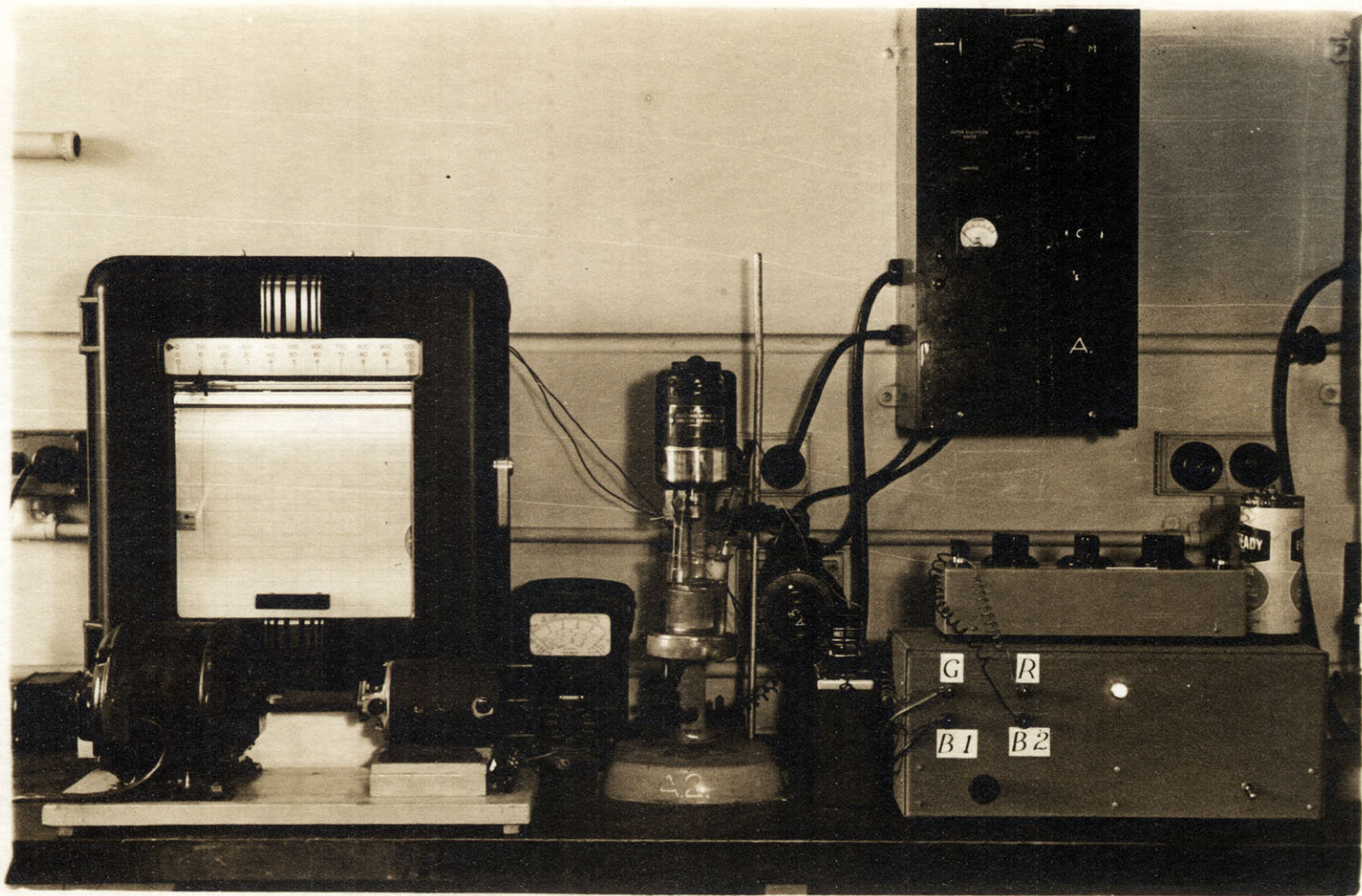
terminals of the amplifier. This input potential was opposed by an equal potential from the balancing circuit. The speedomax was connected across the input terminals of the amplifier to record any drift in the control potential. The potential divider setting and the balancing potential were adjusted to test input potentials to the amplifier ranging from 0.1 to 0.7 volts.

The recorded input potential, on the first setting, drifted slowly during the first 90 minutes of running. The drift amounted to a change of 75 mV over the 90 minutes. During this period the rate of the drift decreased steadily until it finally disappeared. After this period the control was excellent. On all settings the graph of the input potential showed no deviation from the set potential except for some minor fluctuations due to line voltage variations. These fluctuations were eliminated by placing a stabiliser between the 240 A.C. power input to both the amplifier and the speedomax.

The D.C. amplifier requires an appreciable "warm-up" period of approximately one and a half hours before using. This is a disadvantage inherent in D.C. amplifiers.

The Operation of the Instrument.

For the initial warm-up period the arrangement described above of feeding part of the output of the generator onto the input terminals of the amplifier was



found most suitable. After the one and a half hours, the output of the generator is switched to the electrolysis cell and the cathode - S.C.E. potential is switched into the amplifier input circuit.

The photograph, Fig. 8, shows the instrument in operation during a separation of copper from bismuth. The D.C. supplied from the generator is connected to the Griffin and Tatlock electrode stand and the stirrer motor of this apparatus is used to agitate the solution. The S.C.E. is connected to the green terminal (G) which is wired through the one meg-ohm resistor to the grid of one electrometer tube. The cathode is connected to the black earth terminal B1. The positive lead from the balancing circuit is connected to the red terminal (R) which is joined through the one meg-ohm resistor to the grid of the other electrometer tube. The other lead is earthed at B2. The speedomax is connected across the S.C.E. - cathode input circuit to the amplifier. This records the stability of the automatic control during the course of the electrolysis.

The application of the instrument to the determination of deposition potentials and to metal separations is dealt with under these headings (see page 93). The performance under varied working conditions is discussed at the end of the above section (page 101).

Section iii

THE QUANTITATIVE SEPARATION OF COPPER AND LEAD FROM TIN BY CATHODIC DEPOSITION.

In recent years increasing attention has been given to the problem of separating copper, lead and tin by controlled potential deposition. Several of these methods (19,22,23,24) depend on the deposition of copper/^{by} controlled cathode potential followed by simultaneous cathodic deposition of tin and lead. The tin and lead deposit is then dissolved and the metals determined separately. It is, however, possible to increase the difference between the deposition potentials of these two metals by forming stable anionic tin complexes. Lassieur (25) used this method to separate copper and lead dioxide simultaneously from tin in a solution containing hydrofluoric and nitric acid. Boric acid, sodium oxalate, hydroxylamine and sodium hydroxide were added and then the tin was deposited cathodically from the hot solution. His results, reported to the nearest milligram, showed errors in each estimation up to 1mg. Lingane and Jones (26) complexed tin as the tartrate and carried out the separation of copper from lead in slightly acid solution in the presence of hydrazine dihydrochloride. After the deposition of lead, hydrochloric acid was added and the tin deposited. No more than 50mg of lead could be held in solution and the lead figures showed

losses of from 0.3 to 2.1 mg, while five tin figures had an average deviation of 0.7 mg. Norwitz (27) used phosphoric acid to keep tin in solution in a nitric acid electrolyte and thus avoided the tedious separation of metastannic acid prior to electrolytic deposition of copper. The stability of tin phosphate complexes is further demonstrated by the fact that antimony chloride can be distilled at 160°C without interference from stannic chloride if phosphoric acid is present (28). These facts prompted the author to examine the electrolytic reductions of copper, lead and tin in phosphoric acid.

Preliminary Investigation of Reduction Potentials.

A preliminary polarographic investigation of the behaviour of copper lead and tin in phosphoric acid was undertaken using a recording Tinsley polarograph. A dropping mercury capillary was used as the cathode and a saturated calomel electrode of 6.6 sqcm mercury area as a reference anode. The results obtained are listed in table (3). Both copper and lead give reduction waves which are far enough apart to suggest the possibility of a separation on the macro scale, whereas no reduction step is obtained from the tin in acid or ammoniacal solutions.

In the reduction of metal ions at a mercury cathode, the heat of formation of the amalgam results in the discharge taking place with the expenditure of less energy

than that required to reduce the ions to the solid metals. Also the deposition of a solid metal requires a measurable overpotential which makes the discharge process less reversible than at a mercury cathode. It was necessary, therefore, to verify these polarographic predictions by determining the deposition potentials under the actual conditions existing in electrolysis with platinum ^{electrodes} /on the macro-scale.

Solution of the metals.

Norwitz, in his method for the deposition of copper in the presence of tin dissolves the sample, without heating, in 20ml of 1.1 nitric acid, 10 ml of water and 10 ml of phosphoric acid are added before boiling to remove the oxides of nitrogen. This method of solution was not satisfactory for it was found that, if the weight of tin present is greater than 60 mg, the metastannic acid precipitated during solution will not dissolve completely on the addition of phosphoric acid. However, if a mixture of hydrochloric and nitric acid is used the tin is not precipitated and this difficulty is overcome.

The presence of nitric acid in the electrolyte acts as a cathodic depolariser which prevents deposition of lead on the cathode. Lead dioxide will deposit on the anode but this is by no means quantitative, the phosphoric acid inhibiting the precipitation. Hydrochloric acid, in the concentration used to dissolve the metals, causes simultaneous

deposition of lead and tin metal. These tests indicated that the nitric and hydrochloric acids must be removed before determining the cathode deposition potentials of each metal. Evaporation of the solution to expel these acids proved to be the simplest, yet most effective method for their removal.

Procedure.

97 mg of copper were dissolved in 10 ml of the acid mixture (5 ml of 10N.HCl + 5 ml of 15N.HNO₃). When solution was complete, 10 ml of phosphoric acid (Sp.gr., 1.75) were added and the solution acids evaporated. The solution was cooled and diluted to 150 ml with distilled water.

The solution was electrolysed using Griffin and Tatlock platinum gauze cylindrical electrodes. The larger electrode (surface area 125 sq.cm) was used as the cathode and the smaller inner electrode (75 sq.cm) as the anode. The solution was agitated by a motor driven glass stirrer spinning inside the inner electrode. A Cambridge dip type "saturated calomel electrode" (S.C.E.) was placed as close as possible to the cathode. The potential difference between the cathode and the S.C.E. was measured on a vacuum valve voltmeter.

The potential applied to the platinum electrodes was gradually increased from zero using the author's manual variac circuit (see page 26). The deposition potential was

taken as the cathode - S.C.E. potential at which visual deposition of the metal occurred on the electrode. A multi-ammeter was included in the circuit and the surge of the current also indicated deposition.

A copper plated platinum electrode was used to determine the deposition potentials of lead and tin respectively from $10^{-2}M$ solutions prepared by the same method. The copper electrode was used because the deposition potentials of lead and tin on copper are the figures of interest.

TABLE 3.

Deposition Potentials of Copper, Lead and Tin from Phosphoric Acid.

Polarographic determinations with dropping Hg electrode.			Macro electrolytic determinations with Pt electrodes.	
Conc.	Deposition potentials in volts	Half wave potential Vs. S.C.E.	Conc.	Observed deposition potential in volts Vs. S.C.E.
Copper				
$10^{-3}M$	+0.07	-0.06	$10^{-2}M$	-0.01
Lead				
$10^{-3}M$	-0.42	-0.46	$10^{-2}M$	-0.52
Tin				
$10^{-3}M$	No reduction		$10^{-2}M$	No deposition
Tin soln.				
Made ammoniacal	No reduction			No deposition

Both the polarographic deposition and half wave potentials are compared to the observed deposition potentials in the table above. The deposition potential on the polarogram

is taken as the potential at which the surge in diffusion current begins.

The difference in the deposition potentials obtained at the mercury and at the platinum electrode are illustrated in the above table. From the results of these preliminary experiments it was established that separations of the three metals are possible, and should be quantitative. Separate determinations of each metal were undertaken to ascertain whether deposits from phosphoric acid electrolyte are suitable for quantitative analysis, and if ^{so} the range to which the method could be applied.

The Determination of the Copper.

Since the proposed method includes a new technique for the preparation of the electrolyte, the first step was to test the solubility of copper salts in phosphoric acid under the treatment followed in the method. Different weights of A.R. Copper metal were dissolved in 10 ml of the acid mixture. When solution was complete 10 ml of phosphoric acid were added and the solution acids fumed off. It was found that if more than 450 mg of copper are present, a white insoluble copper compound is formed during the evaporation of the acids. This compound will not dissolve on diluting with water and boiling. The formation of this compound appears to result from the increase in temperature of the solution on prolonging the heating after the removal of

the volatile acids. It can be avoided either by increasing the quantity of phosphoric acid or by taking less than 450 mg of copper. The latter alternative is recommended for it was found that an increase in the phosphoric acid concentration increases the difficulties associated with handling the lead plate.

From the phosphoric acid electrolyte the copper deposited as a bright salmon coloured adherent plate but if the current density exceeded 1.5amp/sq.dm the deposit tended to powder and could be removed by rubbing. When the deposition was complete, the stirrer was switched off and, as the beaker was lowered, the electrodes were washed with a stream of water from a wash bottle. The current was switched off and the cathode removed, rinsed in alcohol, dried at 105°C cooled and weighed. The result (shown in table 4) obtained for a range of 15 mg to 380mg of the metal compare favourably with those obtained by recommended procedures and thus verify the suitability of this method for the quantitative analysis of copper.

Table 4

Quantitative Test of Copper Deposition from Phosphoric Acid

Exp. No.	A.R. Copper taken in mg.	Copper found in mg	Difference
1	15.3	15.2	-0.1
2	65.3	65.1	-0.2
3	155.4	155.4	0.0
4	382.1	382.2	+0.1

Separation of copper from lead.

Having established that the deposition of copper from this electrolyte is quantitative the next step was to investigate the deposition of copper in the presence of lead. To the weighed A.R. copper samples were added different volumes of a standard lead solution and the sample was prepared for electrolysis as previously described. The electrolysis apparatus was assembled as described in the initial deposition experiments (page 45) again using the larger electrode as the cathode. The speed of the stirrer motor was adjusted to give efficient stirring and the applied potential fixed to give a current flow of 1 amp. The course of the electrolysis was followed by taking readings of the cathode - S.C.E. potential and the current at one minute intervals. The cathode potential was allowed to drift until it reached -0.35 V to S.C.E. At this point the applied potential to the cell was reduced to hold the cathode at this potential. -0.35 V to S.C.E. is recommended in most of the published methods (19,22,23,24), previously mentioned, for the separation of copper from lead and tin and from the inspection of the observed potentials (see page 46) this control point should apply in this method. When the current became constant, (after about 35 minutes) the stirrer was stopped and the electrodes washed and handled as before. The various quantities of copper separated from the lead and the results

obtained are shown in the table below.

Table 5.

Separation of Copper from Lead.

Exp. No.	A.R. Copper taken in mg	Copper found (mg)	Difference (mg)	Wt of lead present (mg)
1	372.3	372.3	0.0	50.0
2	105.4	105.2	-0.2	100.0
3	25.7	25.8	-0.1	200.0

In this series of experiments copper has been quantitatively separated from a range of copper and lead in ratios from 7 Cu : 1 Pb to 1 Cu : 8 Pb.

The course of the electrolysis during a separation is shown by graphing the cathode - S.C.E. potential against time and the current against time. The graph in Fig. (9) was drawn from readings taken during the separation of 372.3 mg of copper from 50 mg of lead. Before the current was switched on the platinum electrode was 0.65 V. more positive than the S.C.E., the measuring system being (Pt/Cu⁺⁺ satd. KCl Hg₂ Cl₂/Hg). When the applied potential was adjusted to give the initial current flow of 1 amp, deposition of copper immediately occurred and the cathode potential fell to -0.12 V. negative to the S.C.E. The measuring system had changed to (Hg/Hg₂ Cl₂ satd KCl : Cu⁺⁺/Cu⁰) and the leads to the voltmeter had to be reversed to make the reading. This change is indicated by the sudden drop from A to B on the

*Cathode potential versus time & current
versus time for a controlled potential
separation of Cu from Pb.*

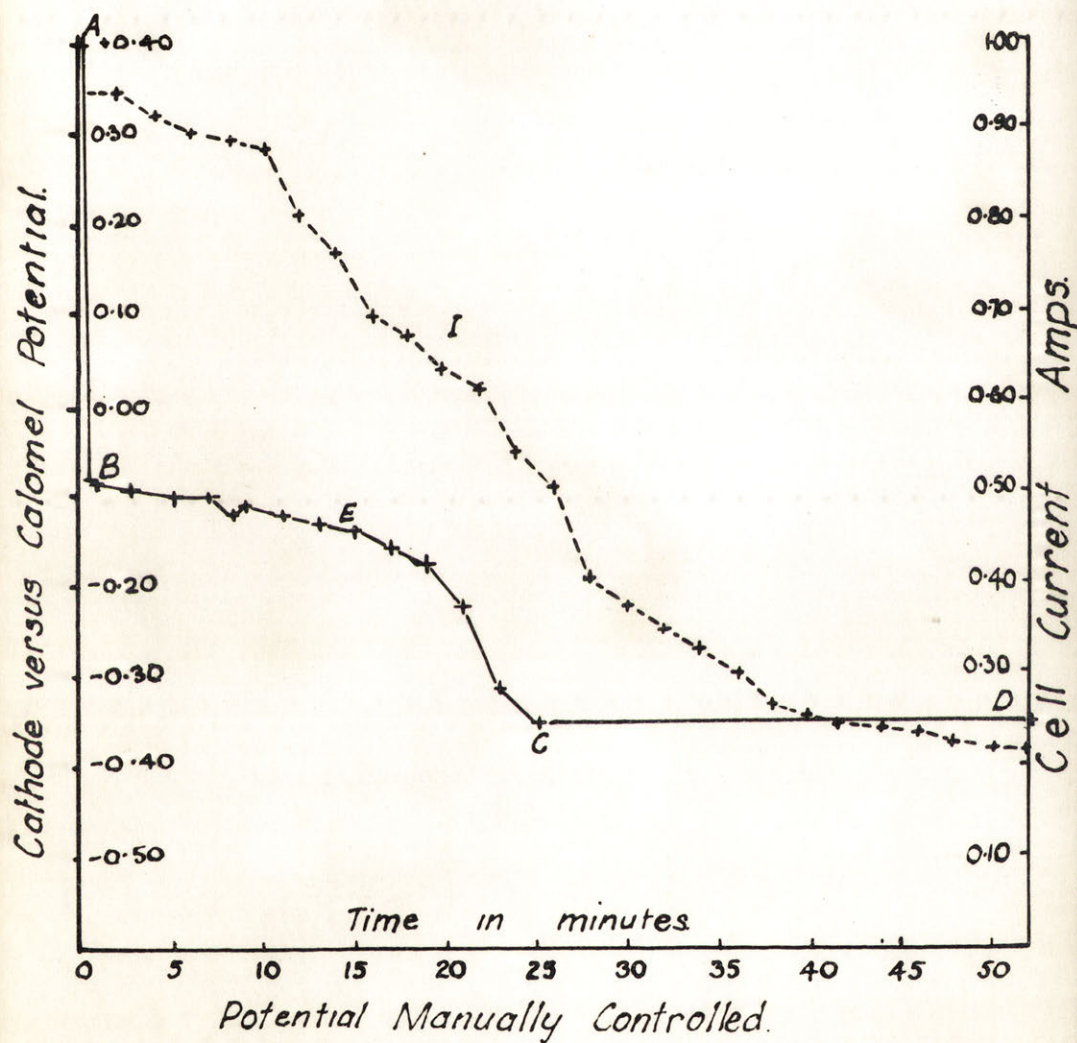


FIG. 9.

potential curve. The electrolysis then proceeded at constant applied potential (from B to C) and the change in cathode potential is brought about by the diminution of the copper ion concentration in accordance with the Nernst equation. After 20 minutes the cathode potential reached -0.35 V. below the S.C.E. and the applied potential was decreased by means of the variac to keep this value constant (C to D). On controlling the cathode potential the fall off in current (Graph I) became exponential as its value depended on the controlled rate of discharge of the copper ions and after 35 minutes electrolysis the current virtually reached a constant value indicating that the rate of removal from the solution of the copper ions has reached equilibrium with the rate of resolution of the copper by the acid and oxygen stirred into the solution at the anode. This was taken as the end point and the electrolysis was discontinued.

The determination of the lead.

First the solubility of lead salts in phosphoric acid was examined in the same manner as described for the copper. On addition of the 10ml of phosphoric acid after dissolving the lead, a heavy white lead salt was precipitated. However this precipitate redissolved on evaporation of the volatile acids and as much as 1 g of lead will remain in solution, even on dilution and boiling.

A solution containing 50mg of A.R. lead was electrolysed

using the smaller inner electrode as the cathode. This electrode was coated with copper to protect the platinum. The applied potential was adjusted to a value which produced lead deposition but did not cause liberation of hydrogen at the electrode. The lead was deposited completely within one hour. This was confirmed by spot testing with sodium sulphide solution. The lead plate, however was dark and spongy. It did not adhere sufficiently to the electrode to allow washing.

This trouble was encountered in the early days of lead electroplating and was overcome by Betts⁽²⁹⁾ who used gelatin as an addition agent to the bath to improve the plate. Experiments using different weights of gelatin in the electrolyte showed that the addition of the surface active agent entirely altered the nature of the plate producing a bright grey deposit which was both metallic and adherent. If more than 2 ml of a 0.5% gelatin solution were added to 150 ml of electrolyte the stirring produced considerable frothing at the surface of the liquid. This was undesirable for it interfered with the washing of the plate. 1 ml of the gelatin solution gave a good plate and did not cause frothing. If the current density exceeded 0.6 amp/sq.dm hydrogen gas was discharged at the electrode and this resulted in a powdery deposit. It was found that the design of the stirrer had some effect on the nature of the deposit. The most satisfactory stirrer was one

which forced the flow of the electrolyte evenly through the mesh of the electrode. Under these conditions of deposition the plate is more uniform and finer in texture.

Having improved the nature of the deposit the method was subjected to quantitative tests. Samples of A.R. lead metal were dissolved and electrolysed using the same apparatus as for the copper deposition. The applied potential was adjusted to give a current flow of 0.3amp. On completion of the deposition the deposit was washed by a stream of water from a washbottle, rinsed in alcohol followed by ether, dried at 100°C, cooled and weighed. The results obtained were usually high, but this could not be attributed to oxidation during the drying process, for very little change in the colour of the plate occurred. On testing the electrolyte with hydrogen sulphide, lead was detected while quantitative tests on the dissolved lead deposit revealed the presence of phosphorous. The presence of lead in the electrolyte was proved to be due to resolution on washing. On removing the electrolyte beaker and substituting a beaker of distilled water in its place, lead was detected in the distilled water but not in the electrolyte. Attempts were made to eliminate resolution during washing and phosphate contamination.

Resolution of Lead during washing.

Schoch and Brown (22), in their method for the deposition of lead from hydrochloric acid, washed the lead by

substituting for the electrolyte successive beakers of distilled water, alcohol and ether. The greatest error in ten results was 0.7 mg with an average deviation of 0.5 mg. They recommended this method in preference to the anodic deposition of lead dioxide. Sand (30), however, preferred the deposition of the dioxide owing to the oxidisability of the lead deposit. Lingane and Jones (26) who deposited lead from tartrate solutions recognised the loss of lead during washing and made the following comment: "This loss averages 1.5 ± 0.6 mg and is sufficiently reproducible so that it can be added as a correction to obtain lead results which generally will be correct to well within 1 mg".

On using the technique of washing described by Schoch and Brown (22) the wash solutions invariably were found to contain lead, although none remained in the electrolyte. This finding was reported by Kny - Jones, Lindsey and Penney (31) in connection with the re-solution of tin deposits from hydrochloric acid. These workers recognised that the loss was due to resolution of the deposit by the film of electrolyte left in contact with the plate on the removal of the electrolysis beaker. The procedure, suggested by these authors, of neutralising the electrolyte with ammonia prior to washing was examined in the following experiment.

The solubility of lead in phosphate solutions of increasing pH.

This experiment was designed to duplicate as near as

possible the conditions under which the lead plate is washed. In the washing process the electrolyte beaker is removed and replaced by the wash beaker. During this procedure the plate, covered by a film of electrolyte is exposed to the air for a few seconds. Resolution of lead is assumed to take place during this step, so the experiment should include a similar exposure test. On adding ammonia to the electrolyte heat is generated and again this should be duplicated if the results are to be significant. Finally fresh lead deposits should be used for each test to avoid the formation of protective coatings on the lead surface and to produce the heating effect that will occur on the addition of different volumes of ammonia.

100 mg of lead were deposited from the phosphoric acid electrolyte. The ammonia was added and the beaker was dropped below the electrodes and the plate was exposed to the air for three seconds. The electrodes were immersed in the solution again for one second and the beaker set aside for testing. The procedure was repeated on 100 mg deposits plated under the same conditions for each volume of ammonia shown in the results.

The pH of each solution was found using a Cambridge pH meter. The test solution was evaporated to less than 100 ml and its PH was adjusted to 5 using either ammonia or phosphoric acid. The volume was made up to 100 ml in a measuring

Table 6.

Polarographic tests for resolution of lead in phosphate solutions of increasing pH.

Vol. of conc. ammonia added (ml)	pH	Step height in divisions	Range uA per 100 divisions	Wt. of pb (mg)
-	0.8	14	1.0	2.5
4.0	1.3	12	1.0	2.2
8.0	2.1	9	1.0	1.8
10.8	3.0	9	0.5	0.9
12.0	3.6	4	0.5	0.4
14.0	5.4	2	0.4	< 0.2
18.0	6.2	2	0.4	< 0.2
22.0	7.2	2	0.4	< 0.2
26.0	8.2	2	0.4	< 0.2
30.0	8.9	3	0.4	0.2- 0.25
36.0	9.3	3	0.5	0.3
Standards		7.5	1.0	1.5
		5.0	0.5	0.5

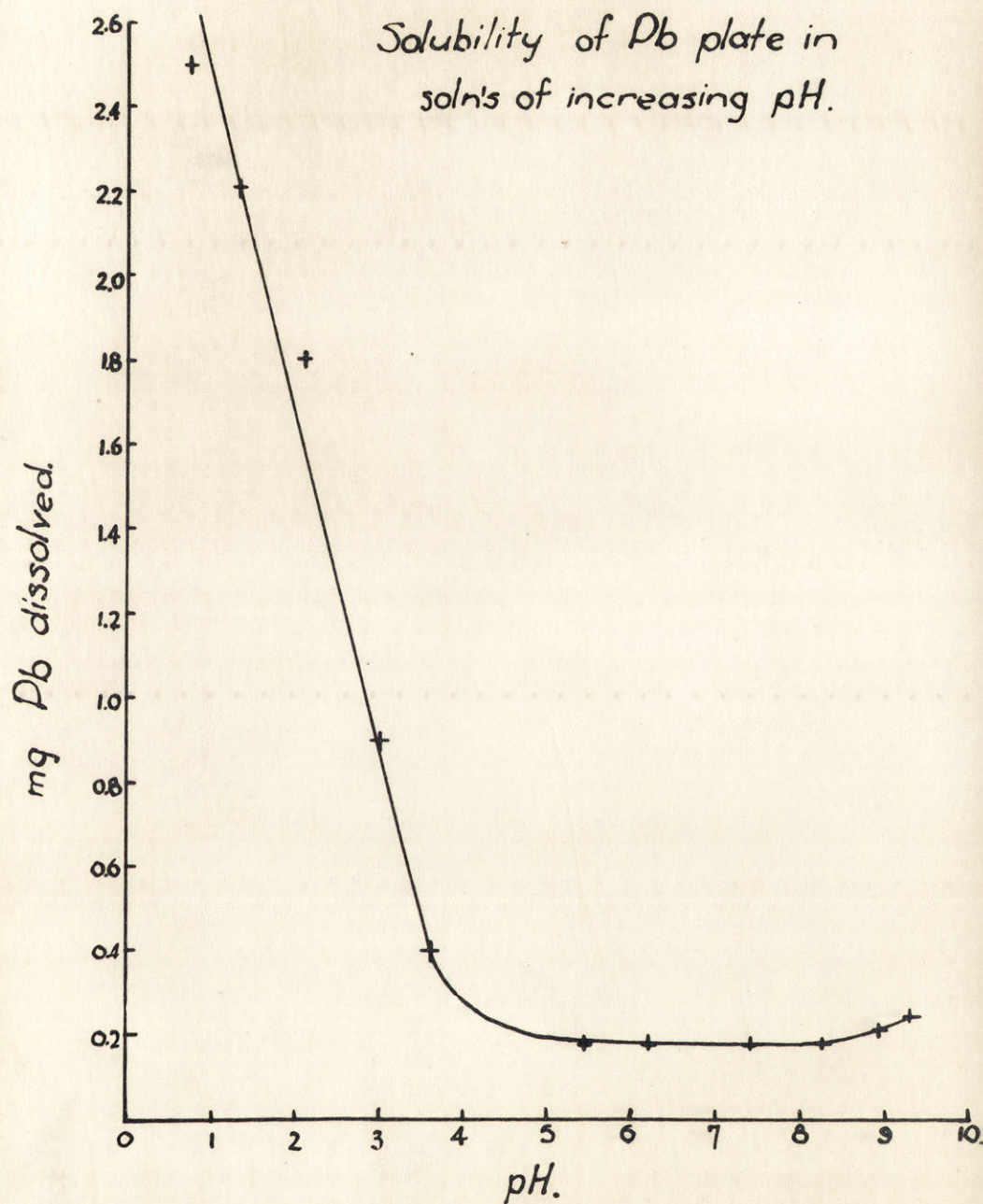


FIG. 10

cylinder and the polarograms were run using the Tinsley instrument. Two standards containing 1.5 mg of lead/100 ml and 0.5/100 ml were treated in the same manner as above.

The results are shown in table (6).

While the polarographic determination in the phosphate supporting electrolyte did not prove extremely sensitive the results were still comparative. The graph (Fig 10) of the pH of the test solution against its lead content due to the resolution showed that, for the surface area taken, the solubility of lead in solutions of pH less than 5 was quite appreciable. Minimum solubility occurred between pH of 5 to 8. For solutions of pH greater than 8 there was a very slight increase in the solubility. Since a solution of 5.4 pH is obtained by the addition of 14ml of 15 N NH_4OH to 150 ml of electrolyte and a pH of 8.2 by adding 26 ml. this experiment indicates that, providing the volume of ammonia exceeds 14 ml, the exact volume added is not critical as far as the lead resolution is concerned.

Resolution Tests of Lead Deposited on Copper.

Lindsey (32), in 1950, published the second paper on tin estimation from hydrochloric acid which followed up the earlier work. In this paper he pointed out that the errors involved in the washing were reduced to a minimum if the electrolyte was neutralised at the end of the electrolysis, and if the platinum electrode was previously coated with copper. The reason for coating the platinum electrode with

copper was based on a series of experiments mentioned in his earlier paper. Well adherent deposits of tin were dipped for 10 seconds into the electrolyte from which they were deposited. They showed losses of about 1 to 1.8 mg which became still greater if the electrolyte made contact with the platinum as well as the deposit. The loss was less when the cathode was coated with a less noble metal such as copper. Thus it was concluded that re-solution was promoted by electrolytic action between the tin deposit and the platinum electrode, and the coating of the electrode with copper reduced this galvanic couple. However, these experiments were carried out in the acid electrolyte and the deductions were applied to the washing technique which is done in slightly ammoniacal solution. The author considered that it was incorrect to assume the two conditions identical. The following experiment was performed to test the validity of the deductions applied to the behaviour of the metals in ammoniacal solution.

In the first test half the copper electrode was covered with lead deposited from the phosphoric acid electrolyte. When deposition was complete, the electrolysis beaker was raised to immerse the whole of the electrode. 22ml of 15 N ammonia were added to neutralise the acid. The electrolysis beaker was quickly replaced by a beaker of distilled water. This procedure was repeated leaving one quarter of the

copper electrode and finally one tenth of an inch above the solution.

Lindsey relied on the difference between the theoretical and the actual weight of the deposit as a test of re-resolution but the author considered that more reliable information could be obtained by analysing the electrolyte and the wash solution for the presence of both copper and lead.

Polarographic methods were used to examine these solutions for it was quick and sufficiently accurate for diagnosis. Its value lay in the fact that the two elements could be analysed simultaneously in the one solution. Although the method is not as accurate as other micro methods, its advantages, applied to these tests, more than justify its use. The polarographic determination of lead and copper in phosphate solution of pH5 as the supporting electrolyte had been used previously (page 59) and so the electrolytes were tested in the same manner. The wash water was analysed using sodium potassium tartrate as the supporting electrolyte. The preliminary calibration tests for lead and copper in an $\frac{M}{2}$ solution of this electrolyte showed the method to be more sensitive than the phosphate electrolyte giving well defined reduction steps for both copper and lead.

Particulars of the determinations made are given in Table (7). They showed conclusively that copper if exposed was attacked by the ammonia.

Table 7.

Resolution tests of lead deposited on copper during washing procedure.

Copper surface exposed.	Electrolyte.		Wash solution.	
	Weight of copper (mg)	Weight of lead	Weight of copper(mg)	Weight of lead
1/2 electrode	4.5	-	2.2	tr
1/4 electrode	2.9	-	2.0	tr
1/10 th electrode	0.6	-	-	0.2

Even the attack on the very small area of copper exposed in the last experiment caused a loss of 0.6 mg. This re-solution occurs in the few seconds taken to disperse and neutralise the ammonia. Thus it was found that, if copper was exposed to the solution, it increased rather than decreased the loss due to re-solution. To avoid this loss the copper must be covered completely by the lead deposit. Deductions of the galvanic effect of the electrode metal on re-solution of the deposit in acid solution do not apply to ammoniacal solutions since copper, the less noble metal chosen for the electrode, is itself attacked by ammonia.

Lindsey's results were examined more closely in the light of the above experiment. When ammonium salts were present with either type of electrodes results were low by 1 to 4 mg although, if the solution was neutralised with NH_3 at the end of the electrolysis, the error was reduced in four determinations with copper electrodes to - 0.4, -0.4,

-0.5 and 0.3 mg, and with platinum to -0.1, 0.0, and 0.1 mg. These and the other determinations reported, were erratic as regards gains and losses in the weights of the deposits.

It is apparent that compensating errors, such as increases due to oxidation on drying, reduce the reliability of deductions on the re-solution of deposits from their weights. His results on losses using copper electrodes compared to platinum electrodes could be interpreted to support the claim that plating the platinum electrode prior to lead deposition does not reduce re-solution if the electrolyte is neutralised with ammonia before washing.

Phosphate contamination of lead deposit.

The washing technique in all the above experiments was standardised, as near as possible, to a one second contact of the deposit with 120 ml of distilled water contained in a 150 ml squat beaker with the stirrer and the current running. In the next experiment the time of contact of the plate with the wash water was varied from one second to one minute in six steps. The phosphate tests on the plates showed no significant decrease with increased washing time. However, on testing the wash solutions they were found to contain from 165 to 195 mg of phosphates calculated as PO_4'' .

Finally, the results of a series of experiments in which separate plates were treated with an increasing number of distilled water washes indicated that if four separate wash

beakers were used the phosphate content of the plate was reduced to a negligible quantity. This appeared to be the most promising approach to the problem of removing the phosphates from the lead deposit, but its success depended on the quantity of lead lost on increasing the number of wash solutions.

It has been reported several times in the literature (19 24,26) that lead deposits must be washed as quickly as possible with the minimum quantity of water to avoid re-solution. The author first attempted to improve the wash technique by substituting other wash solutions for the distilled water. 0.1% solutions of ammonium nitrate, ammonium sulphate, ammonium chloride and hydroxylamine were tried in turn. A fresh lead plate was immersed three times in 120 ml of each solution by moving the beaker up and down with the stirrer running. Each solution was tested polarographically for lead. The ammoniumsulphate was the only solution to offer any advantages over distilled water. Slightly less lead was present in this solution and the plate did not discolour during drying.

Now, the re-solution of lead was examined when the deposit was immersed consecutively in four separate wash solutions. 50 mg of lead were deposited on platinum electrodes previously plated with copper. Care was taken to ensure that the lead completely covered the copper. When the lead was completely deposited the electrolyte was neutralised with

ammonia and the beaker quickly replaced, in succession, by four separate wash solutions of 120 ml volume contained in 150 ml beakers. The current was left on throughout the wash period which took approximately 35 seconds. The stirrer was switched off as each beaker was lowered, and switched on again as the next wash solution covered the stirrer blades. To achieve quicker washing each wash beaker was moved up and down three times while in contact with the electrodes without exposing the plate to the air. The first tests were carried out using three washes of 0.1% ammonium sulphate solution and then one wash with distilled water. In the second series four separate distilled water washes were used.

The wash solutions were evaporated to half bulk and then made up to 100 ml in a measuring flask to give an $\frac{M}{2}$ solution of sodium potassium tartrate. Lead standards were made up under the same conditions with and without the ammonium sulphate. Polarograms on the standard solutions in the dilutions used showed no difference in step heights or half wave potentials in the presence of the ammonium sulphate. In these analyses, the temperature was controlled at 25°C, nitrogen was bubbled through the solution for 15 minutes and the drop time of the mercury cathode was maintained at 10 drops per 30 seconds. In all the polarograms a mercury pool was used as the anode. The step height in each case was taken as the vertical height through the mid-point of the step

between the intersection with the top and bottom extrapolated curves. The impurities in the supporting electrolyte gave a step at approximately - 0.15 V. but, since this was far in advance of the lead step and since it was duplicated in the analyses of the standards and in the blanks, it did not interfere with the determination.

Particulars of the determination are shown in table (8). From the comparison of these two sets of results it was seen that little difference existed between the two wash solutions as regards the re-solution of the lead but, since the ammonium sulphate gave a dried plate of a better appearance, this solution is recommended by the author. A small quantity of lead was found in the first wash beaker and negligible quantities in the other three. The presence of the lead in the first wash resulted from re-solution of the deposit by warm film of neutralised electrolyte left in contact with the plate and the air on the change of beakers. Once this was removed from the electrode no further loss of lead occurred.

Since these findings are somewhat contradictory to the methods advocating a rapid wash of lead plates with the minimum of wash solution, the actual polarograms obtained in the above experiment are included here (Fig. 11)

The washing technique described previously, of washing the plate with an increasing number of wash solutions was repeated using ammonium sulphate in place of distilled water.

Table 8.

Polarographic results of lead content of wash solutions.

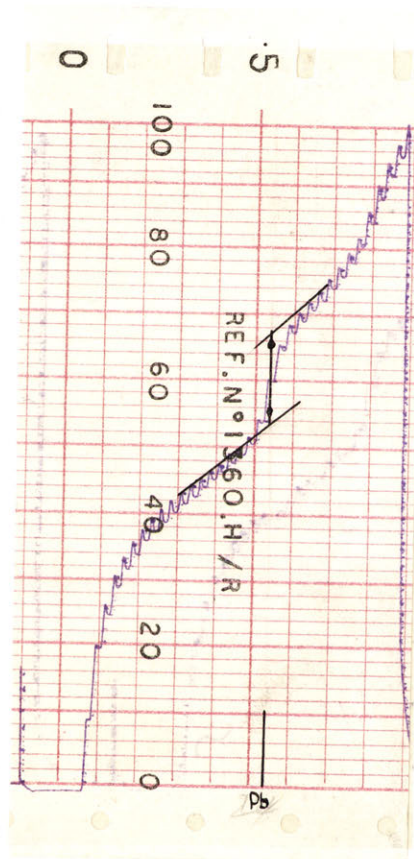
Wash Solution.	Step Height.	Wt. of lead present.
(a) Distilled water.		
1st beaker	0.05uA	0.13 mg.
2nd beaker	about 0.02 uA	about 0.04 mg
3rd beaker	-	negligible
4th beaker	-	negligible
(b) 0.1% Ammonium sulphate.		
1st beaker	0.04(5) uA	0.12 mg.
2nd beaker	About 0.01uA	0.02 to 0.03 mg
3rd beaker	-	negligible
4th beaker (distilled water)	-	negligible
Standards	0.14 uA	0.4 mg
	0.07(5) uA	0.2 mg

A 50 mg deposit was washed with one beaker of 0.1% ammonium sulphate. The weighed deposit was dissolved in nitric acid and its phosphate content determined. This procedure was repeated using (b) two ammonium sulphate wash solutions; (c) two ammonium sulphate solutions and one distilled water wash; (d) three ammonium sulphate solutions and one distilled water wash.

All wash solutions in the last experiment were tested for phosphates.

The results are included in the following tables. They

Standard containing 0.4mg/100ml.

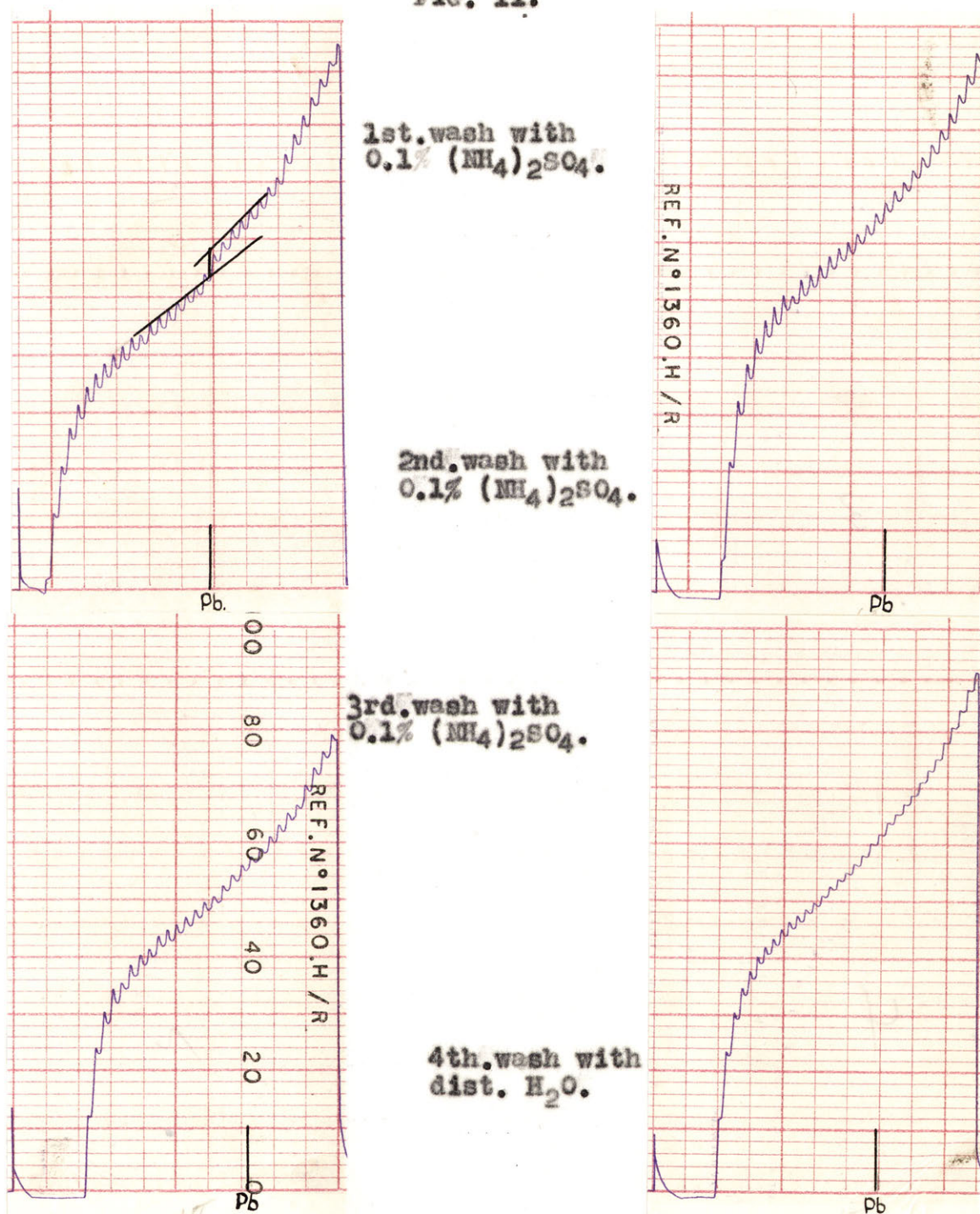


Sensitivity - 1uA Full scale deflection.

Pb step -0.48V, from first step.

Step height - 0.14uA.

FIG. 11.



POLAROGRAMS OF LEAD CONTENT OF WASH SOLUTIONS.

show the necessity of washing the lead deposit with at least three separate volumes of wash solution to reduce the weight of adsorbed phosphates to less than 0.05 mg.

Table (9)

Phosphate content of lead plate using an increasing number of wash solutions.

Wash method	Wt. of Pb. taken.	Pb. found.	Diff.	Wt. of phosphate as $\text{PO}_4^{''}$ on Pb plates
	(mg)	(mg)	(mg)	(mg)
(a) 1 beaker of 0.1% $(\text{NH}_4)_2\text{SO}_4$	50.0	51.0	1.0	0.8
(b) 2 beakers of 0.1% $(\text{NH}_4)_2\text{SO}_4$	50.0	50.3	0.3	0.18
(c) 2 beakers of 0.1% $(\text{NH}_4)_2\text{SO}_4$ & 1 beaker of dist. H_2O	50.0	49.9	-0.1	0.03
(d) 3 beakers of 0.1% $(\text{NH}_4)_2\text{SO}_4$ & 1 beaker of dist. H_2O	50.0	49.9	-0.1	negligi- ble

Table (10)

Phosphate analyses of wash solutions of (d) in Table (9).

Wash beaker	Phosphate content as $\text{PO}_4^{''}$
First	171.6 mg
Second	6.4 mg
Third	0.46 mg
Fourth	0.12 mg

The high phosphate content of the first wash solution, due to the carry over of the electrolyte, explained the reason for the earlier failure to remove the adsorbed phosphates by increasing the washing time using only one wash solution. These results also gave a rough indication of the carry over of the ions left in the electrolyte to the other wash solutions. The original electrolyte contained approximately 17 g

of phosphates while in the second wash solution only 6 mg were detected. This represented approximately one part in three thousand of the ions remaining in the electrolyte. Thus, for subsequent estimations after the removal of lead, the analyst would be justified in including only the first wash solution.

The Recommended Procedure for depositing and handling lead metal.

From the results of all the preceding experiments on the handling of the lead plate it is recommended that the following procedure be closely followed to reduce the loss of lead to a minimum and to decrease the quantity of phosphates adsorbed on the plate to a negligible amount.

First deposit a protective coating of copper on the platinum electrode. Add a surface active agent, such as gelatin, to the electrolyte and deposit the lead over the copper at a low current density. When deposition is complete neutralise the solution with ammonia. Switch off the stirrer and quickly replace the electrolyte beaker by the first beaker of ammonium sulphate wash solution. Switch on the stirrer and move the beaker up and down threetimes. Repeat this procedure with two other wash solutions and then with distilled water. Follow this by an alcohol and an ether rinse. Switch off the current and disconnect the cathode. Dry the plate quickly at 100°C. cool and weigh.

Range of lead determination.

Using the above technique, quantities of A.R. lead ranging from 10 to 400 mg were dissolved and deposited to test the range of the method. Since both adsorption and re-solution are related to the surface area of the deposit the large electrode (125sq.cm) was used for deposits above 100mg while the smaller electrode (75 sq.cm) was used for 100 to 50mg deposits. For less than 50mg the lead was deposited on to an electrode of 30 sq.cm surface area.

The particulars of the determinations are given in table (11). The method was found applicable over a range of 10mg to 400 mg and gave results which were comparable to those obtained using recognised methods for lead determinations.

During the deposition of the higher amounts of lead, 150 mg and above, the anode became slightly discoloured due to the deposition of lead dioxide. However, when the concentration of the lead ions decreased sufficiently, as a result of their discharge, the anode coating re-dissolved and the lead was completely deposited on the cathode. This re-solution of the anode coating indicated the end point of the electrolysis.

If the initial volume of the solution was less than 120 ml, an ammonium phosphate salt was precipitated on adding the ammonia at the end of the electrolysis. This salt slowly dissolved on prolonging the stirring of the electrolyte.

Its formation was avoided however, by diluting the solution to 200 ml before electrolysing.

Table (11)

Range of lead deposition

A.R. lead taken (mg)	Lead found (mg)	Difference. (mg)
10.0	9.9	-0.1
10.0	9.8	-0.2
25.0	24.8	-0.2
50.0	50.1	0.1
150.0	149.8	-0.2
200.6	200.3	-0.3
300.0	300.0	0.0
400.3	400.5	0.2

SEPARATION OF LEAD FROM TIN.

Solutions containing known mixtures of lead and tin were electrolysed using the procedure described for the lead estimation. Again insoluble salts were formed on the addition of the phosphoric acid. These suddenly re-dissolved in the phosphoric acid as the last traces of the volatile acids were removed.

The lead results, given in table (12) below, showed that satisfactory separations were obtained.

This experiment also established that the lead washing technique could be applied in the presence of tin in the electrolyte, for, on neutralising the solution with ammonia, tin

was not precipitated from the phosphate complex.

Table (12)

Separations of lead from tin.

Lead taken (mg)	Lead found (mg)	Difference (mg)	Tin present (mg)
50.0	49.8	-0.2	50.0
50.0	49.9	-0.1	150.5
55.2	55.5	0.3	300.0
100.0	100.2	0.2	300.1

The Behaviour of Tin in Phosphate Solution.

In the initial tests on the method of solution (page 44) it was found that up to 500 mg of tin would remain in solution in 10 ml of phosphoric acid on the evaporation of the volatile acids. Since the tin remained in the solution on neutralising with ammonia, the first experiment was designed to test the stability of the tin phosphate complex on electrolysis in ammoniacal solution.

A copper plated platinum electrode was used as the cathode and in each experiment the solution was electrolysed for ten minutes at a current of one amp. A neutral solution and electrolytes containing 10 ml, 20 ml and 30ml excess ammonia respectively, were tested. 300 mg of tin were present in each solution. The electrodes were immersed in the electrolyte with the current running to prevent re-solution of the copper.

In each case vigorous evolution of gas took place at each electrode but no deposition of tin occurred. This meant

that the tin complex was not reduced before the hydrogen deposition potential from ammoniacal solution was reached.

On neutralising the electrolyte with ammonia to reduce the lead loss tin remains in solution but it does not deposit, and therefore its presence will not interfere with the lead washing technique.

ESTIMATION OF THE TIN.

If 30 ml of hydrochloric acid and 2 g of hydroxylamine were added to the electrolyte after the removal of the lead the tin could be deposited on the cathode. However, from the author's previous experience with tin depositions from chloride solution, he considered that if a straight volumetric analysis of the tin were possible, it would be more preferable. With this view in mind, the applicability of the iodine estimation of tin was tested.

Phosphate solutions were prepared containing different quantities of A.R. tin. These were diluted to 320 ml and transferred to a conical flask. 320 ml would be the approximate volume after adding the first lead wash solution to the electrolyte. 75 ml of 10N HCl and 20 ml of nickel shot were added and the solutions were boiled for 30 minutes. They were cooled in a CO_2 atmosphere and titrated with iodine using acid starch indicator. The iodine was standardised against A.R. tin dissolved in sulphuric acid and reduced in the same volume as the test solution in the presence of the

same quantity of hydrochloric acid. The quantities of tin taken and found are listed in Table (13)

Table (13)

Iodimetric Estimation of the Tin.

Wt. of tin taken. (mg)	Wt. of tin found. (mg)	Difference. (mg)
95.5	95.8	0.3
119.9	119.6	-0.3
173.8	174.0	0.2
276.6	276.4	-0.2

These results showed that the tin could be estimated successfully by volumetric analysis. This method of determining the tin was much quicker and more convenient than electrolytic deposition from the large volume of solution remaining after the lead separation. The tin standard was dissolved in sulphuric acid to check if tin was lost during the evaporation of the solution acids but no loss was apparent.

The Recommended Method for Separation and Estimation of Copper Lead and Tin.

Different combinations of the three A.R. metals were taken to reproduce the compositions of some copper based alloys. These were analysed using the final procedure described below. The A.R. metals were used in preference to the actual alloys for the known figures on each element are then absolute. They are not dependent on the accuracy of other quantitative

methods, nor are they influenced by errors due to segregation in the alloy or faulty sampling of the alloy.

Recommended Procedure.

To the weighed sample, containing not more than 400 mg of copper, add 5 ml of 10N hydrochloric acid and then 5ml of 15N nitric acid and heat if necessary. When solution is complete, add 10 ml of phosphoric acid (sp.gr.1.75) and evaporate the volatile solution acids. Cool, add 120 ml of distilled water and electrolyse using platinum electrodes, the smaller gauze electrode being the cathode. Control the cathode potential at -0.35 V to the S.C.E. For the best copper deposit the initial current density should not exceed 1.5 amp/sq.dm. When the current becomes constant at the control potential, after approximately 35 minutes, switch off the stirrer and lower the electrolysis beaker while washing the electrodes, calomel electrode and stirrer with distilled water. Switch off the current and remove the cathode. Rinse in alcohol, dry at 105°C , cool and weigh.

Replace the weighed copper plated electrode in the circuit. Add 1 ml of 0.5% gelatin to the electrolyte and adjust the level so that all the copper is covered by the solution (approx. 200 ml bulk). Electrolyse at a current density of such a value that no hydrogen gas is liberated during the deposition of the lead. This is approximately 0.4 amp/sq.dm or at a cathode potential more positive than -0.8V to the S.C.E.

When electrolysis is complete, after $1\frac{1}{4}$ to $1\frac{1}{2}$ hours, neutralise the electrolyte with 15N ammonium hydroxide. Switch off the stirrer and quickly replace the electrolysis beaker by a 150 ml beaker containing 120 ml of 0.1% ammonium sulphate solution. With the stirrer running immerse the electrodes three times by quickly moving the wash beaker up and down. Repeat this procedure with two fresh sulphate solutions and follow this by a distilled water, an alcohol and an ether rinse. Switch off the current and remove the cathode. Quickly dry the deposit at 100°C , cool and weigh.

After the removal of the copper and lead, transfer the solution to a 500 ml conical flask and add to this the first lead wash solution. Add 75 ml of 10 N hydrochloric acid, reduce with nickel shot and estimate the tin by iodine titration using acid starch to detect the end point.

The results of the determinations are given below in Table 14.

The results indicated that the separations and estimations could be applied, with equal success, to the estimations of the three metals in copper based alloys and to the determinations of copper and tin in white metals.

Table 14.

The Separation and Estimation of Copper, Lead and Tin from Phosphoric Acid.

Copper		Lead		Tin	
Wt. taken (mg)	Wt. found (mg)	Wt. taken (mg)	Wt. found (mg)	Wt. taken (mg)	Wt. found. (mg)
385.0	385.2	97.5	97.5	15.6	15.4
386.2	386.0	76.0	76.2	38.9	38.8
400.9	401.1	49.8	49.6	51.0	50.9
358.2	358.2	25.0	24.9	103.8	103.6
275.0	275.0	10.0	9.8	-	-
245.2	245.1	10.0	9.9	-	-
75.0	75.0	-	-	198.2	198.0
45.2	45.0	-	-	195.5	195.4

TESTS FOR INTERFERING ELEMENTS

Elements that interfere due to low solubility in phosphoric acid.

A number of elements was tested for solubility in the phosphoric acid. No more than 500 mg of the soluble metals were taken because it was considered that this weight would be well above the limit met in analyses of alloys for which this method was developed. Each metal was dissolved in 10 ml of the mixed acids and then 10 ml of phosphoric acid were added and the solution acids removed by evaporation. The solution was diluted to 150 ml and then made alkaline with ammonia. The results for the metals tested are listed in Table 15. Copper, lead and tin are included in this

table.

Bismuth, if more than 60 mg are present, vanadium and titanium are the only metals of those tested which will interfere because of the formation of insoluble phosphates.

Table 15.

Solubility of some metals in Phosphoric Acid.

Metal.	Weight soluble in 10ml H_3PO_4	Effect of dilution to 150 ml.	Solubility in NH_3 solution.
Arsenic			
Antimony			
Zinc			
Cadmium	greater	colourless	colourless
Tin	than	solution	solution
Molybdenum	500 mg		
Nickel		green solution	blue solution
Cobalt		Red pink "	violet "
Iron		mauve "	amber "
Chromium		green "	dark green "
Manganese		purple "	dark brown "
Copper	max. 450 mg	blue "	deep blue "
Lead	500 mg	colourless "	white precipitate
Bismuth	max. 60 mg	slight hydrolysis	" "
Titanium	slightly soluble	" "	soluble in excess colourless solu- tion.
Vanadium	" yellow residue	blue precipitate	soluble in excess blue green solu- tion

Iron, aluminium and manganese do not precipitate on making the solution ammoniacal. This means that the hydroxides of these elements will not contaminate the lead plate on applying the recommended wash technique. This does not apply to Lindsey's wash procedure for tin (32) or to Milner and Whitten's method for washing the combined lead and tin deposit (19) for these estimations are carried out in hydrochloric acid electrolyte. The above authors have not mentioned these interferences in recommending their methods.

METALS CO-DEPOSITED WITH THE COPPER AND LEAD.

The metals which are deposited together with the copper and the lead are discussed briefly below. These conclusions are based on experiments undertaken to determine the electrochemical behaviour of other metals in the phosphoric acid electrolyte. The details of these experiments are reported in the section dealing with the applications of the automatic instrument (page 83).

If bismuth is present in solution it will deposit with copper if the cathode potential is controlled at $-0.35V$ to S.C.E. Arsenic, if more than 100 mg are present will also co-deposit at this potential. Antimony will not interfere with the copper deposition but will deposit with the lead.

If nickel, iron or zinc are present in appreciable quantities they will deposit from slightly ammoniacal solution. However, if the initial condition of applied

voltage is adhered to for the lead deposition, on neutralising the electrolyte the cathode potential will remain more positive than the deposition potentials of these metals and they will not deposit. This is a second point that has not received attention by the previous authors recommending the ammoniacal wash technique.

Application of the method to the Analyses of Copper based alloys.

Samples of bronzes were analysed using both the phosphoric acid method and the conventional method. In the conventional method the tin was precipitated as metastannic acid, filtered off and then dissolved in sulphuric acid. The carbon was destroyed and the tin was estimated iodimetrically. The lead was precipitated by fuming with sulphuric acid and then determined gravimetrically. Then the copper was electrolysed from a sulphuric-nitric acid electrolyte.

The results are shown in table 16.

In the two methods the elements are estimated in the reverse order. The agreement between the tin figures is most significant since the tin is estimated first in the conventional method and last in the phosphate method. The copper in the conventional method is estimated after two filtrations and an evaporation to low bulk. This probably accounts for the consistently lower figures in the A results compared to those by the phosphate method where the copper

Table 16.

Analyses of Copper based Alloys.

Method	% Copper	% Lead	% Tin	Balance.
(1) A	76.69	20.63	2.35	trace Fe
B	76.81	20.57	2.35	
(2) A	73.94	16.22	7.99	0.5Ni, 1.0%Zn
B	74.06	16.30	7.95	
(3) A	76.46	13.89	7.75	trace Fe
B	76.54	13.82	7.78	0.5Ni, 1.0%Zn
(4) A	53.83	3.27	8.30	1%Fe & ^{tr} Ni
B	53.95	3.23	8.27	balance Zn.

Method A - conventional method Method B - H_3PO_4 method.

The phosphoric acid method enables the determination of copper, lead and tin in an alloy to be completed within $3\frac{1}{2}$ hours. It avoids the tedious separation of the tin as metastannic acid and the separation of large quantities of lead by fuming with sulphuric acid. The method has two further advantages; it avoids filtering, and, if the solution of the alloy and the electrolytic processes are carried out in the one beaker, then, only one vessel transfer of the analysis solution is necessary in the course of the estimation.

This method has been introduced into the second year analytical chemistry course of this University as an example of a controlled cathode potential separation. It has given satisfactory results in the hands of the students.

Section iv

APPLICATION OF THE AUTOMATIC INSTRUMENT.

The behaviour of other metals in Phosphoric Acid Electrolyte.

Deposition Potentials. The following experiments were carried out to determine the deposition potentials of the metals which remain in solution in the acid or ammoniacal electrolyte. Where possible, 200 mg of the A.R. metal or the equivalent weight of the oxide were dissolved in the same manner as described in the copper, lead and tin procedure and diluted to 200 ml. A copper plated electrode was used as the cathode for the acid solutions and a platinum electrode for the ammoniacal solutions. The D.C. output of the generator was connected to the electrodes and a multi-ammeter was wired in series with the cell. The expected deposition potential was set on the reference potential divider circuit and the potential applied to the cell was adjusted to give a cathode - S.C.E. potential of approximately 0.2 V. more positive than the set reference potential.

The applied potential was increased by increasing the gain of the amplifier to decrease the cathode potential in steps of 10 mV. The cathode potential was held constant for five minutes after each increase. The current flowing in the cell was recorded and any change in the appearance of the cathode was noted. The deposition potential was

indicated by a sudden increase in the current flowing and by the change in the nature of the plate. During a run the cathode - S.C.E. potential was graphed against time on a recording three range speedomax.

Because of the limiting solubility of the bismuth salts in phosphoric acid, only 40 mg of this metal were taken. The current reading corresponding to the cathode potential are included to show the change in current which occurs when the deposition potential is reached.

Cathode vs. S.C.E.	-0.08	-0.10	-0.12	-0.13	-0.14	-0.15	-0.16
potential in volts							
Current flowing in	8	10	13	15	17	21	102
m amp.							
Cathode vs. S.C.E.	-0.17	-0.18					
Current flowing	125	155					

Visual deposition occurred immediately the potential was changed from -0.15 to - 0.16.

The deposition potentials are listed in order in table 17. Copper and lead are included for comparison.

The deposition potentials from ammoniacal solution were not as easily detected as those from acid for the deposition does not proceed with 100% current efficiency. This is due to preferential or simultaneous hydrogen ion discharge which masks the surge in current at the deposition potential. The deposits also are difficult to see on platinum. Deposition of antimony in acid solution and manganese in ammoniacal solution occurred slowly, without appreciable change

in current. Manganese deposited on both the cathode and the anode. As was expected, aluminium, chromium, molybdenum, titanium and vanadium do not deposit from ammoniacal solution.

Table 17.

Deposition Potentials from Phosphate Electrolyte.

Metals in acid soln.	Deposition Potn. vs.S.C.E. in volts.	Metals in ammoniacal soln.	Deposition Potn. vs/ S.C.E. in Volts.
Copper	-0.01	Nickel	approx -1.10
Bismuth	-0.16	Cobalt	" -1.12
Lead	-0.52	Iron	" -1.18
Antimony	approx -0.76	Zinc	" -1.40
Cadmium	-0.76	Manganese	indefinite
Arsenic	No deposition.		

These experiments were attempted using the manual control before the construction of the automatic instrument was complete but it was found that, as the deposition potential was approached, fluctuations were so great and manual control so difficult that deposition potentials could be determined only roughly. The automatic instrument, however, held the cathode potential stable enough to determine the value to within 5 m V.

This experiment also demonstrated another particular advantage of this instrument. The cathode can be controlled at potential levels above or below the set reference

potential. This enables the operator to increase or decrease the electrode potential, within certain limits, by simply varying the gain of the D.C. amplifier and thus avoid the necessity of switching off the instrument to reset the reference potential before any change can be made.

Separation of copper from bismuth.

It is seen from table (18) that if the cathode potential is controlled at -0.35 V. vs. S.C.E. as recommended for the separation of copper from lead, bismuth, if present, will co-deposit with the copper. The following experiments were carried out in an endeavour to separate these two metals using the automatic instrument.

The first set of experiments was designed to find the cathode potential at which copper deposition is complete. It was also used to test the control of the instrument under conditions where a definite tendency exists for the electrode potential to become more negative i.e., in controlling the potential at values where copper deposition is by no means complete.

The same weight of copper (317.8 mg) was taken in each case and the cathode potential controlled automatically at the values shown below in the table. The electrolysis was continued in each experiment until the current flowing in the cell became constant. The cathode was then removed and the deposit weighed. Fresh solutions were electrolysed in

each experiment to avoid dilution errors which would result from washing each deposit between the potential steps.

In these experiments the instrument's control was followed by recording the cathod - S.C.E. potential on the speedomax.

Table 18.

Test for complete Deposition of Copper.

Cathode Potn. vs S.C.E.	Wt. of copper deposited (mg)	% Deposition	Time for deposition. (Hours)	Av. dev- iation of cont- rol.
-0.025	81.4	25.162	1 $\frac{1}{4}$	\pm 2mV
-0.050	245.9	77.43	1 $\frac{1}{2}$	\pm 2mV
-0.080	315.6	99.30	1 $\frac{1}{2}$	\pm 2mV
-0.100	317.4	99.87	1 $\frac{1}{2}$	\pm 2mV
-0.125	317.7	99.97	1 $\frac{1}{2}$	\pm 3mV

Deposition was quantitatively complete between -0.100 and -0.125V. to S.C.E. The automatic instrument controlled the cathode potential to within \pm 2 mV of the starting potential throughout the full time of the deposition. In the last experiment a rapid fluctuation in the recorder produced a line of thickness equivalent to 5 mV. The centre of this line however, did not vary by more than 3 mV from the starting potential.

The solutions containing copper and bismuth were now electrolysed. The applied potential was adjusted to give an initial cathode potential of - 0.10 V. This potential was held constant until the current decreased to 500 mA and

When the cathode potential was gradually decreased to -0.14 V. The electrolysis was continued until the constant current indicated the end point. The cathode - S.C.E. potential was recorded to check the performance of the instrument.

The results of the two separations are shown below.

Table 19.

Separation of Copper from Bismuth.

Wt. of copper taken. (mg)	Wt. of copper found. (mg)	Wt. of bismuth present. (mg)
188.3	187.9	35.0
307.5	307.7	50.7

The separation of copper from bismuth was achieved although only 40 mV separated the cathode potential necessary to give complete deposition of copper from the deposition potential of the bismuth. This separation is not possible by manual control for if the deposition potential of the bismuth is approached to within 20mV the control is very difficult to maintain and any fluctuation in the applied potential is likely to bring about bismuth deposition.

Unfortunately this method is limited in application because of the low solubility of bismuth salts in phosphoric acid.

Separation of copper from arsenic. (See over)

Separation of copper from arsenic.

Arsenic does not deposit on a copper electrode from phosphoric acid electrolyte even at a cathode potential of -1.0 V. to S.C.E. where a current of 3 amp flows in the cell and considerable hydrogen evolution takes place. Since arsenic can be deposited with copper as a copper arsenide from hydrochloric acid electrolyte, the behaviour of arsenic in the presence of copper ions was examined.

An electrolyte containing 300 mg of copper and 100 mg of arsenic was electrolysed at a constant current of 1.0 amp (without cathode control). The potential of the cathode - S.C.E. was recorded during the electrolysis. The copper deposited as a bright metallic plate but at cathode potential of -0.5 V to S.C.E. the deposit began to darken and soon became black. After 40 minutes the electrolysis was discontinued and the deposit weighed. The deposit was 6 mg heavier than the weight of copper taken.

In a second analysis of a solution containing the same weights of arsenic and copper, the cathode potential was controlled automatically at - 0.35V to S.C.E. Towards the end of the deposition the plate again darkened. The deposit weighed 2 mg heavier than the weight of the copper taken.

The two deposits from the above experiments were dissolved in a minimum of nitric acid and this was then

removed by fuming with sulphuric acid. The Gutzeit's test for arsenic using cuprous chloride to remove the phosphine gave strong positive tests for arsenic on each solution.

In a third, experiment, the cathode potential was controlled at -0.25 V to S.C.E. and a complete separation of copper from arsenic was achieved giving quantitative deposit of the copper. The copper plate was replaced in the solution and the cathode potential was increased gradually and finally held for 15 minutes at -0.8 V to S.C.E. where a current of 1.5 amps flowed in the cell. The copper remained bright and there was no increase in weight.

From these experiments it appeared that a small quantity of arsenic is deposited with copper from the phosphoric acid if the cathode potential becomes more positive than approximately -0.25 V to S.C.E. Torrance (33), in his work on the deposition of copper arsenide showed that the compound deposited only in the presence of hydrochloric acid from the trivalent arsenic solution. No deposition was obtained from sulphuric and nitric acids. On testing each of the above electrolytes they were found to contain traces of chloride. It was feared that the deposition of arsenic might result from the presence of these chlorides so the following experiment was carried out to check this point.

The arsenic and copper electrolyte was prepared using only nitric acid. This acid was fumed off with phosphoric

and the solution was diluted to 200 ml with distilled water. The electrolysis was carried out at a constant current of 1 amp. The calomel electrode was connected by a potassium nitrate bridge to the cathode.

After 15 minutes the bright copper deposit darkened (cathode potential - 0.52 V to S.C.E.). The electrolysis was discontinued after 40 minutes and the deposit weighed. The deposit was 4 mg high.

The deposit was dissolved in nitric acid and then taken down to fumes with sulphuric acid. The solution was diluted and sodium sulphite added to reduce the arsenic. A paper chromatogram was run on the solution using butanol saturated with 2N hydrochloric acid as solvent. On exposing the dried paper to hydrogen sulphide the positions of added copper and arsenic spots were established. The paper was then charred and arsenic and copper spots were revealed in the test strip.

From the above experiments it is seen that arsenic is co-deposited with copper to a small extent during constant electrolysis. If the cathode potential is carefully controlled the copper can be quantitatively separated from the arsenic and once the copper has been removed from solution arsenic deposition will not occur ^{even} at high current densities.

Separation of copper from antimony.

Antimony deposits on a copper electrode from the

phosphoric acid electrolyte at - 0.76 V. to S.C.E. but the deposition is not complete. In constant current electrolysis of a solution containing 100 mg of antimony and copper respectively, the copper deposit darkened at - 0.82 V to S.C.E. After 40 minutes electrolysis the deposit was found to contain 20 mg of antimony.

The copper was separated from antimony by controlling the cathode potential at - 0.35 V to S.C.E. Successful quantitative separations of approximately 100 mg of copper were achieved from solutions containing antimony in the ratio of one to five times the weight of copper. These results are shown below.

Table 20

Separation of copper from antimony.

Wt. Copper taken. (mg)	Wt. copper found. (mg)	Antimony present (mg)
1. 129.0	128.8	100
2. 93.5	93.6	250
3. 96.6	96.8	500

The deposit obtained in experiment (2) above was placed back in the electrolyte and the cathode potential was increased to - 0.7 V to S.C.E. and held at this value for half an hour. No increase in the weight of the deposit resulted. The potential was then increased gradually. Visual deposition of antimony occurred at -0.75 V. without any appreciable increase in the current flowing in

the cell. After controlling the cathode potential at -0.9 V. for 15 minutes, 17 mg of antimony were deposited.

Separation of Bismuth from Lead.

Bismuth deposits on copper at a cathode potential of -0.16 V. and lead at a potential of -0.52 V. These potentials are far enough apart to achieve a quantitative separation of bismuth from lead.

To test this separation a solution containing 40 mg of bismuth and 100 mg of lead was electrolysed at a controlled cathode potential of -0.4 V. As usual the electrolysis was continued until a constant current flowed in the cell. The deposit was washed by quickly replacing the electrolysis beaker by one containing distilled water. This was followed by an alcohol and then an ether wash. The electrode was dried at 105°C , cooled and weighed. The deposit weighed 0.9 mg less than the weight taken. It was black and slightly powdery and easily detachable by rubbing.

Polarograms on the electrolyte showed that the bismuth had been quantitatively removed from the solution and a polarogram on the dissolved deposit showed no trace of lead. The missing bismuth was found along with lead in the wash solution. The lead was carried over from the electrolyte and the bismuth was dissolved by the film of electrolyte which was left in contact with the plate during the beaker transfer. The pH of this solution could not be reduced by

the addition of ammonia because the lead would precipitate.

The bismuth separation was repeated using gelatin in the solution and depositing the metal on silver plated electrodes. However this did not improve the physical nature of the deposit sufficiently to make it suitable for quantitative analysis.

Although bismuth can be deposited quantitatively from phosphoric acid in the presence of lead, the deposit is not suitable for handling and the method cannot be recommended as a quantitative procedure.

Lead deposition in the presence of Arsenic.

In three experiments where 50, 100 and 150 mg of lead were deposited by constant current electrolysis in the presence of 100 mg of arsenic, the deposits were high by 1 to 2 mg. Chromatograms on the dissolved deposits, carried out in the same manner as described on page , showed positive tests for arsenic.

The lead deposits contained less arsenic than the copper deposits obtained by constant current electrolysis but the current density during the lead deposition did not exceed 0.5 amp/sq.dm and very little hydrogen was liberated at the electrode.

Lead depositions in the presence of Antimony.

The deposition of antimony on a copper electrode from a solution containing 200 mg of the metal in 200 ml begins

at a cathode potential of -0.76 V. It was found that lead can be deposited completely from the electrolyte at a cathode potential of -0.68 V. so it should be possible to obtain a separation of lead from antimony by controlling the electrode potential between these two values.

A solution containing approximately 100 mg of lead and antimony respectively was electrolysed at a controlled cathode potential of -0.7 V. After two hours the electrolysis was discontinued and the deposit washed by the recommended washing technique. The deposit was weighed and then dissolved in nitric acid. This solution was chromatographed using butanol $-2N$ HCl as solvent and the spots were developed with hydrogen sulphide.

The experiment was repeated with one fifth the weight of antimony present. The cathode potential was controlled at -0.65 V.

The particulars of these experiments are included in the table below.

Table 21.

Co-deposition of lead and antimony.				
Cathode Potn.	Weight of metals taken.		Wt of deposit	Test
	Lead	Antimony.		for
(V)	(mg)	(mg)	(mg)	Antimony
-0.70	110.8	97.8	143.5	Strong positive tests
-0.65	106.8	17.2	115.6	

It is apparent from these results that lead and antimony cannot be separated from each other although their

deposition potentials on copper are separated by 0.26 V. The overpotential of antimony on lead must be much less than antimony on copper for antimony appears to deposit as soon as the copper electrode is covered with lead.

Separation of lead from cadmium.

In the following experiments attempts were made to separate lead from cadmium, in the phosphoric acid electrolyte, using the automatic instrument to control the cathode potential.

The solutions containing the two metals were electrolysed at a cathode potential of - 0.70 V. using a copper plated platinum electrode as the cathode. The particulars of the mixtures analysed and the results obtained are shown in table (22), below.

Table 22.

Separation of Lead from Cadmium.

Lead taken. (mg)	Lead found. (mg)	Cadmium present. (mg)
100	99.8	110.7
100	99.7	193.3
150	149.6	100
150	149.8	200

Each lead plate was dissolved in 6 ml of 5N sulphuric acid plus 2 ml 5N nitric acid. The solution was evaporated to fumes, diluted, boiled and cooled. The lead sulphate was filtered off, 2 ml of 5N nitric acid were added

and the copper removed by electrolysis. The solution was polarographed using the 0.5 uA sensitivity range with the zero setting adjusted to depress the lead wave. No trace of cadmium was detected in any of the deposits. Polarograms run on the electrolyte after the deposition of the lead showed no lead wave using the 0.5 uA sensitivity.

These experiments show that lead can be separated quantitatively from at least 200 mg of cadmium.

When the cathode potential was controlled at -0.6 V. for the first hour and then decreased to -0.7V., no lead dioxide formed on the anode but if the deposition was carried out at -0.7 V. from the beginning, the anode covered with the dioxide coating. It appears that the lead dioxide can be prevented from depositing if its anodic deposition potential is not reached. However, there is no advantage in preventing the formation of the oxide for it always redissolved towards the end of the electrolysis and this indicates the approach of complete deposition.

This separation would be most tedious without the automatic instrument, for the time of deposition is approximately two and a half hours and, since only 80 mV separates the cathode potential at which lead is deposited quantitatively from the potential at which cadmium begins to deposit the manual apparatus would require constant attention during the deposition.

The deposition of Nickel from Phosphate Solution.

In a series of experiments designed to examine the deposition of nickel from ammoniacal phosphate solution, different weights of nickel were dissolved using the recommended solution method and then diluted to 150 ml. 30 ml 15N ammonia were added in excess of the volume required to neutralise the phosphoric acid and the electrolysis was performed at a constant current of 1 amp using a platinum cathode.

Table 23

Deposition of Nickel from Phosphate Solution.

Nickel taken (mg)	Nickel found (mg)	Difference. (mg)
49.3	49.1	- 0.2
98.0	98.4	+ 0.4
196.0	195.7	- 0.3

The nickel deposited quantitatively (see results above) from this solution as a bright metallic deposit which was not easily distinguished from the platinum electrode.

It was considered that, if nickel could be separated from tin in ammoniacal solution, it would give a much improved method of separating and estimating copper, nickel and tin in alloys. This prompted the following experiments.

Nickel in the presence of tin.

The above experiment was repeated in the presence of

tin. The various mixtures of nickel and tin taken are shown in the results.

Table 24.

Deposition of nickel in the presence of tin.

	Nickel taken. (mg)	Nickel found. (mg)	Difference. (mg)	Tin Present. (mg)
(1)	89.9	90.8	+ 0.9	100
(2)	89.9	91.0	+ 1.1	150
(3)	45.5	46.1	+ 0.6	200

To the electrolyte from experiment (2) dimethylglyoxime was added and the solution boiled. No trace of nickel was found in the electrolyte. The deposit was dissolved in 5N nitric acid and the solution evaporated to dryness. On dilution and boiling a trace of insoluble remained. This solution was then tested for phosphates with ammonium molybdate but a negative test resulted.

The increase in weight of the deposit appeared to be due to the presence of tin. To confirm this the electrolyte from experiment (1) was analysed for tin. Excess hydrochloric acid was added and the tin reduced by boiling the solution with nickel shot. The iodine titration revealed that 1.2 mg of tin had been lost in the nickel separation.

Constant current electrolysis of an ammoniacal phosphate solution containing nickel and tin does not give complete separation of the nickel from the tin. The deposits of

nickel contained up to 1.1 mg of tin when deposited from solution containing 100 to 200 mg of tin.

THE PERFORMANCE OF THE AUTOMATIC INSTRUMENT.

The recorded performance of the stability of the instrument under varied working conditions is shown in Fig (12). This is a reproduction of the speedomax chart on which the cathode vs S.C.E. potential has been graphed against time.

The first graph was recorded during the separation of copper from bismuth. The instrument was first set to control at -0.1 V and, after the current had decreased, the applied potential was increased in three steps to give a final cathode potential of -0.14 V. The stability of control during a separation of copper from arsenic at -0.25 V is shown in the second graph. The third graph was obtained during the separation of copper from lead. The fourth graph was recorded during the separation of bismuth from lead and the fifth during the separation of lead from cadmium. In the first three separations recorded, the large electrode was made the cathode, while in the last two the small electrode was used as the cathode.

The graphs show how constant the instrument maintains the cathode potential to the initial control setting. No changes from the set potentials of -0.1 and -0.7 V are recorded. In these two electrolyses the attenuator in the cell is changed by a factor of 7 and the electrode reactions and the area of the electrodes are altered. This stable control at both ends of the range illustrates the suitability

SPEEDOMAX RECORDINGS SHOWING THE
STABILITY OF
AUTOMATIC CONTROL.

Chart rate - 15 inches per hour.

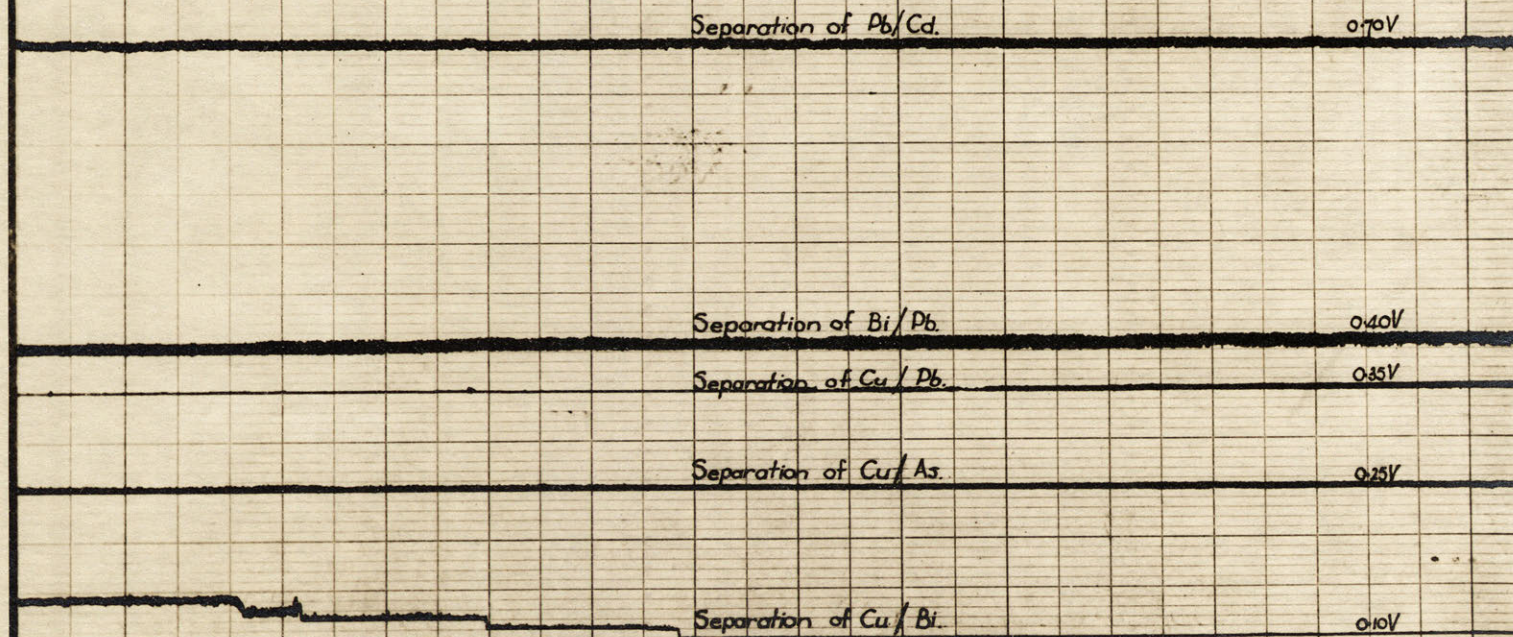


FIG. 12.

of the instrument and the efficiency of its performance in metal separations.

It has been established that the oscillations of the recorder, shown by the thickness of the lines at different control points, ~~are~~ due to electrode reactions and not, as first thought, to a fault in the electronic circuit. The graphs show that these oscillations are dependent on the surface area of the electrodes, being greater when the larger electrode is used as the anode. The actual nature and cause of these oscillations ~~are~~ under investigation at present. However, as shown by the graphs, they do not interfere with the efficiency of separations at the cathode.

This chart serves as a summary of the metal separations that the author has achieved using the phosphoric acid electrolyte. Phosphoric acid, as an electrolyte, has all the advantages of hydrochloric acid but none of the disadvantages. It is non-oxidising acid and when electrolysed oxygen is the anodic product, so no depolarisers are required to protect the platinum anode. Furthermore, separations that are not possible from hydrochloric acid solution can be achieved from phosphoric acid. These include the separations of copper from bismuth, arsenic and antimony as well as the separation of lead from tin. It has greater applicability to electro-analysis than nitric acid which is an oxidising acid whose anions act as a cathodic depolariser.

Finally, it is superior to sulphuric acid for the many soluble complexes that it forms increases its range of application.

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