CONTROLLED-POTENTIAL ELECTROLYSIS IN THE ANALYSIS OF BISMUTH-BASED ALLOYS

by

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ABSTRACT

Part I is a critical examination of the determination of bismuth and lead from a tartrate electrolyte and of cadmium from an ammoniacal electrolyte by controlled-potential electro-gravimetry with platinum electrodes. The separation of these metals from indium and tin was studied, and a brief examination made of the deposition of indium from tartrate solutions on platinum and copper electrodes.

In the determination of bismuth, study was made of the effect of pH, stirring, electrode surface and temperature on the completeness of deposition, and of the loss of bismuth during washing. In the determination of lead, particular attention was paid to the loss on washing, and various means of decreasing this were evaluated. A method is proposed for protecting lead deposits with a deposit of copper. A similar study was made on cadmium, but no means for protecting the deposit were considered.

Part II is a study of a new application of the electrolytic dissolution of cadmium amalgams at controlled anode potential for the separation of macro-amounts of cadmium from lead, tin and bismuth. The separation of cadmium from indium was found to be uncertain.

The Appendix contains results for the successive determination of bismuth, lead and cadmium in mixtures similar to those found in the commercial alloys 'cerrobend' and 'cerrobase'.

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INTRODUCTION

This thesis falls conveniently into two parts. In Part I, work is described on the controlled-potential electro-gravimetric determination of bismuth, lead and cadmium in solutions containing one or more of these elements and also in the presence of tin and indium. Such mixtures of metals frequently occur in low melting-point bismuth-based alloys. The factors affecting completeness and speed of recovery and overall accuracy have been carefully evaluated.

The electrolytic dissolution of cadmium from cadmium amalgams at controlled anode potential has been studied in Part II and is put forward as a separation for cadmium from bismuth, lead and tin.

No work has been done on the electro-gravimetric determination of tin, as it may be more accurately determined by established titrimetric methods.

'Controlled potential' rather than 'constant current' electro-gravimetry was chosen on account of the greater specificity provided by controlling the cathode potential at a value such that only one electrode reaction occurs, the elimination by this means of undesirable reactions such as the deposition of hydrogen, and the higher speed at which electrolysis can be conducted.

PART I

CONTROLLED POTENTIAL ELECTRO-GRAVIMETRIC DETERMINATION OF BISMUTH, LEAD AND CADMIUM.

Chapter I

Fundamental Principles of Controlled-Potential Electrolysis

1) Current - Potential Relationships

The total e.m.f. (E) applied to the electrolysis cell distributes itself as follows:

$$E = E_c + E_a + iR \qquad \text{(i)}$$

where E_c and E_a are the potentials of the cathode and anode respectively ($E_c + E_a$ is the 'back' e.m.f.), i is the current in amperes and R is the resistance of the cell. The reduction reaction at the cathode is represented by the expression

$$Ox + ne \rightleftarrows Red \qquad \text{(ii)}$$

and so the cathode potential is

$$E_c = E_o - \frac{RT}{nF} m \frac{a_{red}}{a_{ox}} - \eta \qquad \text{(iii)}$$

where E_o is the thermodynamic standard potential of reaction (ii) and η is the overvoltage. The anode reaction is also represented by a similar expression. At the cathode the ratio of the concentration of reduced to the concentration of oxidized species increases with continued electrolysis, therefore a_{red}/a_{ox} increases and so at constant current the cathode potential tends to become more negative. Similar considerations show that the anode potential tends to become more positive and the net effect is an increase in the 'back' e.m.f. ($E_c + E_a$) during the electrolysis. However, except in metal peroxide deposition, the

anodic reaction is usually the oxidation of an anion such as hydroxide or halide whose concentration is relatively large so that it does not alter sufficiently to make an appreciable change in the anode potential before the completion of the cathodic reaction. Unwanted anodic reactions are prevented by maintaining the anode potential at a less positive value with an anodic depolarizer such as hydrazine. Hence the increase in the 'back' e.m.f. is due almost entirely to the increase in the cathode potential. If this increase in the cathode potential is not checked it proceeds until the reduction potential of some other substance is reached, such as ions of another metal or hydrogen ions. Referring back to equation (i) the increase in E_c can be most conveniently counteracted by decreasing the value of the total applied e.m.f.E.

When the cathode is controlled at a potential such that only a single electrode reaction can occur with virtually 100 per cent current efficiency, the current is almost always governed by the rate of diffusion of the reducible ions from the solution to the electrode surface. From Faraday's Laws the current at any instant is given by the expression

$$i_t = nF \frac{dN}{dt} \qquad \text{(iv)}$$

where n is the number of electron equivalents per molar unit of the electrode reaction, F is the faraday, and $^{dN}/_{dt}$ represents the number of moles that react at the electrode in unit time (seconds). When $^{dN}/_{dt}$ is controlled by the rate of diffusion

from the body of the solution, then from Fick's First Law

$$\frac{dN}{dt} = DA \frac{dC}{dx} \qquad (v)$$

where D (cm^2/sec) is the diffusion coefficient of the reducible substance, A is the electrode area (cm^2) and $^{dC}/_{dx}$ is the concentration gradient at the electrode surface. From this the instantaneous current is given by

$$i_t = nFDA \frac{dC}{dx} \qquad (vi)$$

From Nernst's work, the concentration in the thin diffusion layer is virtually a linear function of distance from the electrode when the solution is thoroughly stirred and so

$$\frac{dC}{dx} \cong \frac{C - C_e}{\delta} \qquad (vii)$$

where C is the concentration in the body of the solution, C_e is the concentration at the electrode surface and δ is the thickness of the diffusion layer. Under experimental conditions C_e is so much smaller than C that $^{dC}/_{dx}$ is very nearly equal to $^{C}/_{\delta}$ and equation (vi) becomes

$$i_t \cong nFDA \, {}^{C}/_{\delta} \qquad (viii)$$

This equation demonstrates that the current will be greater on improving the efficiency of the stirring since the value of δ is decreased by increasing the stirring. Also, since the current is directly proportional to the diffusion coefficient D, raising the temperature of the solution causes the current to increase. The current at any instant is also proportional to the concentration and hence to the number of moles of the

remaining substance. From equations (iv) and (viii)

$$i_t = nFDA\,C/\delta = nF\frac{dN}{dt}$$

$$\frac{DA}{\delta}C = \frac{dN}{dt} = V\frac{dC}{dt}$$ since N = CV where V = volume of solution

$$\frac{DA}{\delta V}\,dt = \frac{dC}{C}$$

$$C_t = C_o\, e^{-\frac{DAt}{V\delta}} \qquad \text{(ix)}$$

and so

$$i_t = i_o\, e^{-\frac{DAt}{V\delta}} = i_o\, 10^{-\frac{0.43DAt}{V\delta}} \qquad \text{(x)}$$

where the subscript o denotes the initial values of the current and the concentration at zero time.

On making $k = 0.43DA/V\delta$ (xi)

equation (x) simplifies to $i_t = i_o\, 10^{-kt}$.

It will also be seen that the current will be greater, the greater the ratio (A/V) of electrode surface to volume of solution. A/V.

2) Decomposition Potential

The control potential for the reaction given in equation (ii) can be calculated from equation (iii), but in general no a priori knowledge of the overpotential will be available nor usually will the pertinent activity coefficients be known in the relatively concentrated electrolyte solutions involved in practical analysis.

The most reliable method of determining the working potential is to determine the current-electrode potential curve of the particular reaction under exactly the same conditions that will prevail in the actual analysis. The potential of the working electrode is increased in steps by increasing the total e.m.f. applied to the cell and it is measured against an appropriate reference electrode. The current is noted at each value of the potential. This can be done very conveniently by using micro-electrodes and a microammeter. The experimental set-up is described in Chapter IV. This technique is especially advantageous in systematic studies of the influence of factors such as pH, complexation and surface-active agents on the working-electrode potential.

The curve obtained in the deposition of a metal onto a cathode which is not initially in equilibrium with the solution as is the general case in electro-gravimetry, is shown in fig1.1. As the applied potential is increased from zero, a very small, but gradually increasing, positive current is observed (xy). In the neighbourhood where deposition starts, the current rises comparatively suddenly (yz). Further increases in potential produce large increases in current. Note that there is no definite value of the cathode potential at which the electrode reaction begins to occur.

Clearly the concept of 'decomposition potential' has no exact significance in the general case where the working

electrode is not in equilibrium with the solution before the applied potential is impressed. However it is common practice to define it by extrapolating the electrode-potential vs current curve to zero current. Although this value has no exact significance it does serve to indicate the approximate minimum value of the electrode potential which must be exceeded in order to carry out the electrolysis fast enough to satisfy practical demands.

It is clear from equation (4i) that at electrode potentials much below the region of the 'decomposition potential', the value of a_{red}/a_{ox} is very small. If the reduced form stayed at the electrode surface it is evident that only a small momentary current which quickly decreased to zero would be observed. The small, but continuous, residual current actually observed results from the fact that the reduced form continually diffuses away from the electrode.

In the deposition of a metal onto an electrode not in equilibrium with the solution it might be expected that the activity of the deposited metal would be constant. This is doubtless true after sufficient metal has been deposited to cover the electrode completely. However, the gradual rather than abrupt increase in current in the vicinity of the 'decomposition potential' indicates that the first small amounts of metal deposited which do not completely coat the electrode must have an activity which is variable and smaller than that of the

massive metal. This has been demonstrated in the deposition of silver onto platinum cathodes by Rogers et.al (58).

3) Working Potential

For nearly reversible reactions, assuming the activity of the deposited metal is unity, equation (iii) becomes

$$E \cong E_o + \frac{RT}{nF} \ln C_{ox} \qquad \text{(xii)}$$

The cathode potential at the finish of the electrolysis will be different from that at the beginning, and from equation (xii) the difference is given by

$$E_i - E_f = \frac{RT}{nF} \ln \frac{C_{ox\ i}}{C_{ox\ f}} \qquad \text{(xiii)}$$

where subscripts i and f are initial and final states respectively. For 99.99 per cent completion of deposition $C_{ox\ f}$ = 0.01 per cent of the initial concentration and $C_{ox\ i}/C_{ox\ f} = 10^{-4}$. Hence $E_c - E_f$ is equal to 0.24V for n = 1 and 0.12V for n = 2 at 25°C. Hence for virtual completion of deposition, in most cases even for irreversible depositions, the cathode potential need not be more than 0.2V greater than the decomposition potential.

When the solution contains more than one reducible ion such as in figl.1 where curves of two divalent reducible ions are shown, it is clear that no deposition of either A or B will occur if the potential is kept below a, between a and b only A will be deposited and above c both A and B will be

deposited. A can be determined in the presence of B provided that ab is greater than 0.1V. However, it should be noted that the potential at which a metal co-deposits with some other metal may be considerably different from the potential at which it deposits in the absence of other metals. When two metals form an alloy the activity of each of them usually will be smaller than that for the separate pure metals. Consequently the 'back' e.m.f. for each metal is decreased and the potential required to deposit the alloy is smaller than either of the individual deposition potentials (42).

4) Factors Affecting the Physical Characteristics of Deposits

Since in electro-gravimetric analysis assay is made by weighing the deposit, it is essential that this fulfils certain minimum conditions. The most important chemical characteristic required of a metal deposit is that it be pure, and the most important physical characteristic is that it be adherent, so that it can be washed without mechanical loss. Most adherent deposits are smooth, though some rough deposits are quite adherent. However some metals, notably lead and cadmium, tend to undergo loss during washing as a result of aerial oxidation and in such cases it is highly desirable that the deposit be smooth so that its surface area is as small as possible.

The two cardinal principles governing the adherence

and smoothness of metal deposits are : (i) rough deposits invariably result when much hydrogen evolution accompanies the metal deposition and (ii) deposits from simple (uncomplexed) metal salt solutions as a rule are much less smooth and less adherent than those obtained from solutions in which the metal is present as a complex ion (42).

a) Prevention of hydrogen evolution

Hydrogen evolution can be prevented by limiting the cathode potential below the value at which hydrogen ion is reduced and if necessary by keeping the concentration of hydrogen ion at a minimum. In some instances a cathodic depolarizer which undergoes reduction without gas evolution at a lower potential than that required for hydrogen ion reduction may be added to prevent hydrogen evolution.

According to Lingane (42) , the deleterious effect of the co-deposition of hydrogen is probably a purely mechanical effect rather than, as has been suggested, the formation of metal-hydrogen compounds which supposedly decompose to leave the metal in a finely divided, loose condition.

b) Addition of surface-active agents

Small amounts of surface-active agents or 'brighteners' may improve the physical properties of metal deposits. However no single simple interpretation is able to explain how they work (74). It is possible that some 'brighteners' form Werner-type co-ordination compounds with metal ions. Others are

possibly adsorbed to a greater extent on the incipient 'high spots' of the surface than in the 'valleys' and consequently they prevent the build-up of crystals at 'high spots' and hinder the further growth of the 'high spots' themselves.

c) Complexation

In general, deposits from complexing solutions are smoother and more adherent than those from simple salts.

It has been suggested that the nature of the co-ordinating group as well as the thermodynamic stability of the complex ion is important in determining whether deposits having good physical properties will be formed (74). In general, large co-ordinating substances, or those containing aromatic ring systems, give deposits having poor physical properties. It has also been observed that complexes that are reduced either with great difficulty, or very easily, do not give good deposits. Complexes in an intermediate range of stability give metal deposits of good physical properties.

The deposition of a complex ion may involve dissociation to form the free metal ion followed by combination of the latter with electrons according to

$$MX_p^{(n-pb)} = M^{n+} + pX^{-b} \qquad \text{(xiv)}$$

$$M^{n+} + ne = M \qquad \text{(xv)}$$

or it can occur by direct electron transfer to the complex

$$MX_p^{(n-pb)} + ne = M + pX^{-b} \qquad \text{(xvi)}$$

It has been established chronopotentiometrically that the reduction of some complex metal-ions does entail prior dissociation. This appears to be so with the cyanide, tartrate, ammonia and dipyridyl complexes of cadmium. On the other hand, the zinc ammonia complex, the silver ammonia complex and the copper-ethylenediamine complex seem, from their chronopotentiometric characteristics, to be reduced directly (41).

Even 'simple' metal ions exist as aquo complexes and the reduction of aquo complexes liberates water at the electrode surface :

$$M\,(H_2O)_p^{n+} + ne = M + p\,H_2O$$

which results in a dilution of the solution right at the electrode surface. Conversely, in the reduction of the other types of complex ion, the number of complexing ions or molecules (such as NH_3) liberated at the electrode will tend to make the solution more 'concentrated' very close to the electrode. Lingane (42) believes that these 'dilution' and 'concentration' effects are intimately related to the different character of the deposits from 'simple' and complex metal salts.

d) Limitation of current density

At very large current densities deposits tend to be rougher and less adherent than at smaller current densities. However the maximum permissible current density is a characteristic of the particular metal, the type of solution from

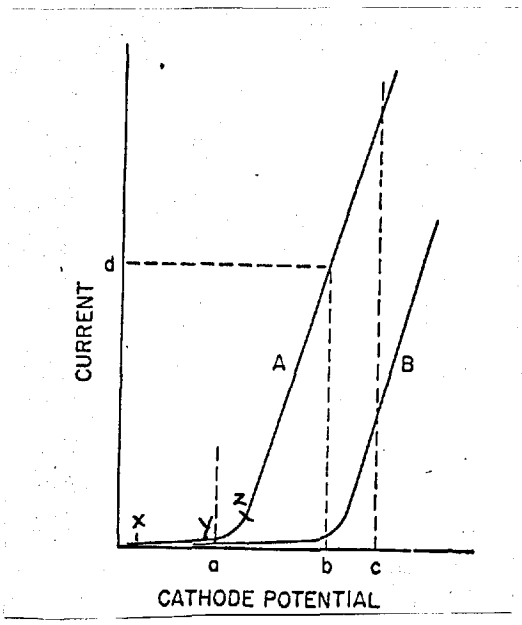
which it is deposited and the stirring efficiency. In each case the limiting value must be determined by trial.

e) Crystal structures of electrodeposits

The relation between brightness of metal deposits and their crystal structures remains a topic of dissension (73). Brightness has been said to depend on either crystal size, crystal orientation or the surface being smooth enough for specular reflection.

Fig 1.1

Current-cathode potential curves



Chapter II

Apparatus

1) Circuit

The essential circuitry for controlled-potential electrolysis is shown in fig2.1. The cathode potential is monitored against a suitable reference electrode with a potential measuring device. The electrodes are connected to a suitable D.C. source via a voltage adjustor which can be regulated, in either direction to counteract the drift in potential of the cathode. The electrolysis circuit also contains an ammeter which can help to determine the completion of the electrolysis.

2) Potentiostat

Manual control of the electrolysis current is tedious as constant attention is needed throughout the electrolysis until the minimum current has been reached. Potentiostats or automatic potential control machines were first introduced in the early Forties. A good review is given by Lingane (41). Most, but not all, potentiostats are based on the following principles : (a) the e.m.f. of the cell formed by the working electrode and the reference electrode is connected in series-opposition with the required e.m.f. set on a potentiometer, (b) the resulting 'error voltage' is amplified and (c) the amplified signal is used to actuate a motor that alters a variable transformer or resistance in the circuit supplying the

electrolysis current and thus alters the voltage applied to the electrolytic cell.

A design of fairly recent date by Herringshaw and Halfhide (20) was used in this work. In this instrument the 'error voltage' is fed into a D.C. amplifier based on two cathode-coupled pairs, thus avoiding the need for a high degree of stabilization of the high-tension supply. The amplified signal operates a relay system controlling a motor that alters a variable transformer in the circuit supplying the electrolysis current.

Special features include (i) a sensitivity of ±2.5mV, (ii) high zero stability, (iii) high ~~impact~~ input impedance, (iv) the relay-controlled motor is stopped 'dead' as soon as the signal ceases and (v) a high degree of smoothing and 'discrimination' in the electrolysis supply circuit.

The general plan of the instrument is shown in fig 2.2.

3) Electrodes

a) Cathodes

Platinum gauze electrodes were used exclusively. These were supplied by Messrs Johnson Matthey & Co. Ltd. and were of their usual design, consisting of a half-round wire frame supporting a 48-mesh woven wire gauze. Three sizes were used whose dimensions are given in Table 2.1.

b) Anodes

Helical platinum wire anodes, also supplied by Johnson Matthey, were used. There were two sizes whose dimensions are given in Table 2.1.

c) Reference electrode

A calomel reference electrode was used and this was of the saturated potassium chloride type, although for a short time at the beginning of this work an N-KCl type was used. As constructed it consisted of a small electrode vessel of approximately 10ml capacity to which was attached a side-arm of approximately 13cm length. The end of the side-arm was curved at right angles and drawn to a point at its tip. This was to ensure that the current density at the tip was altered as little as possible and that the tip could be brought as close as possible to the cathode surface to minimize any iR effects. The electrode was made up by filling the side-arm with a hot 3 per cent solution of agar in saturated KCl (or N-KCl when appropriate) by suction, allowing it to cool and solidify, cleaning any excess of agar gel from the electrode vessel and then placing successively in the electrode vessel 1 to 2 ml of mercury, a few mg of calomel and about 5ml of saturated potassium chloride (or N-KCl). External connection was via a short length of platinum wire sealed into a glass tube which dipped into the mercury pool. The glass tube contained a few drops of mercury into which was placed a copper wire, the end of which had been amalgamated to improve connection. The glass tube had a ground-glass collar which fitted tightly in a

ground-glass socket in the top of the electrode.

d) Arrangement of electrodes in the electrolysis vessel

Lingane (42) advocates that the anode should be placed concentrically inside the cathode to provide a uniform electric field. Otherwise, if the anode is much off-centre, the resistance between the electrodes will not be uniform, the current will concentrate in the region where the electrodes are closest, and correspondingly the metal deposit will tend to build up on the part of the cathode closest to the anode. This occasionaly encourages unfavourable deposits, notably with cadmium in sulphuric acid in the absence of brighteners.

We used a concentric arrangement and placed the reference electrode so that its tip was as close as possible to the outside of the cathode. The solution was normally stirred by an L-shaped stirrer, the arm of which was just longer than the radius of the cathode and which rotated in the space between the electrodes and the bottom of the beaker.

4) Use of Platinum Electrodes

a) Cleaning

Before each determination the cathode was cleaned free of grease and previous deposits by immersing it in a beaker of warm diluted (1 + 2) nitric acid for a few minutes. It was rinsed thoroughly with distilled water to remove all traces of acid and

ignited to red heat in a fully oxidizing bunsen flame. The cathode was used as soon as it was cool to avoid the accumulation of dust etc. Whenever possible it was held in a stand to keep the surfaces to be used for plating free from contact with possibly greasy surfaces.

Anodes were similarly treated, but less frequently.

b) Washing and weighing

After every determination the deposit was washed, first with distilled water, then with acetone, and dried in an oven at 105-110°C, cooled and weighed.

As the nature of the first water wash is of the utmost importance, this is dealt with at length in Chapters V and VI. After the water wash, it was found best to place the wet electrode, previously shaken, in a dry beaker and pour acetone rapidly down the stem until the gauze was covered. The electrode was then removed to the oven and dried. To determine the optimum conditions of drying, cooling and weighing, the following experiments were made on a cleansed platinum gauze electrode of 120 sq cm area.

i) Electrode dried in electric oven at 105-110°C for 5 minutes. Removed, placed in a desiccator containing no desiccant for 10 minutes. Removed to the balance pan and weighed immediately and after various time intervals.

Weight (g)	Time on balance pan (mins)
30.59728	0
30.59720	2
30.59730	5
30.59735	7
30.59740	10
30.59740	15

ii) As (i) but electrode cooled in desiccator for 15 minutes.

Weight (g)	Time on balance pan (mins)
30.59730	0
30.59735	2
30.59740	5
30.59740	10

Even when cooled in the desiccator for 15 minutes the electrode required at least 5 minutes on the balance pan before constant weight was obtained. The temperature of the electrode was measured approximately to see if it would be safe to put it directly into the balance case. Immediately on removal from the oven it could just be held in the hand and after 5 minutes felt quite 'cool'. Approximate temperatures of the electrode during cooling were measured

by holding the bulb of a sensitive mercury thermometer against the gauze.

Time (mins)	Temperature ^{o}C
1	60^{o}
2	35^{o}
5	25^{o}
10	18^{o}
15	18^{o}

As it took at least 1 minute to transfer the electrode from the oven to the balance case it was concluded that it would be quite safe to put the electrode straight into the balance case. The case was left slightly open so that the air inside and outside were in equilibrium.

(iii) The electrode was weighed at given time intervals after drying for 5 minutes and transferring straight to the balance case.

Weight (g)	Time on balance pan (mins)
30.59728	5
30.59739	10
30.59740	15

The longer time needed to reach equilibrium when the

dessicator was used is attributed to the presence of a moisture film of appreciable weight on the electrode. Electrodes cooled in the dessicator would have a smaller film on account of the restricted atmosphere inside the dessicator. Cooling is also probably slower.

Lingane advocates drying for only two minutes, so this was tried to see if a reduction in time was possible.

(iv) Electrode dried for 2 minutes, placed in balance case and weighed at given time intervals.

Weight (g)	Time on balance pan (mins)
30.52729	5
30.52738	10
30.52741	15

As these figures are virtually identical with those after longer drying, it is concluded that 2 minutes was quite sufficient.

We, therefore, used the following drying and weighing procedure. The electrode from the acetone wash was shaken to remove excess of acetone, placed in an electric oven at 105-110°C for 2 minutes, removed to the balance case and allowed to cool for 15 minutes and weighed.

With a larger electrode of 160 sq cm surface area it was felt advisable to cool for 20 minutes. No drying and weighing experiments were done but duplicate weighings always agreed within $\pm$0.02mg.

Fig 2.1

Essential circuitry for controlled-potential electrolysis

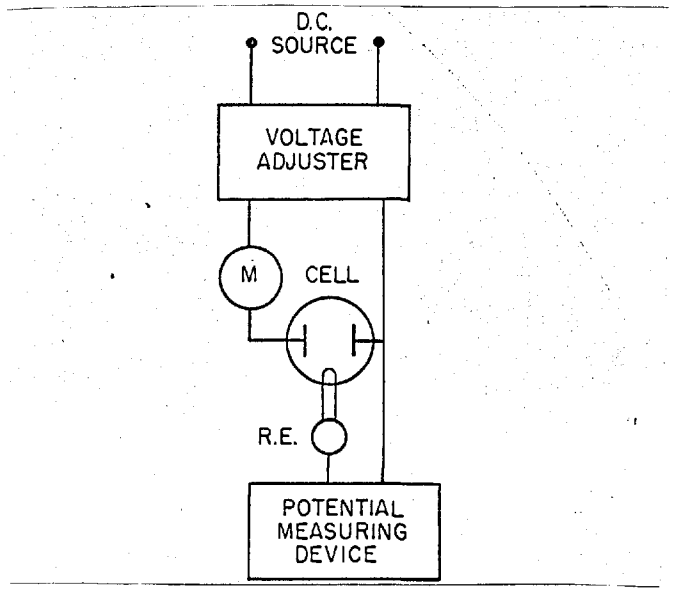


Fig 2.2

Schematic diagram of the general arrangement of the potentiostat

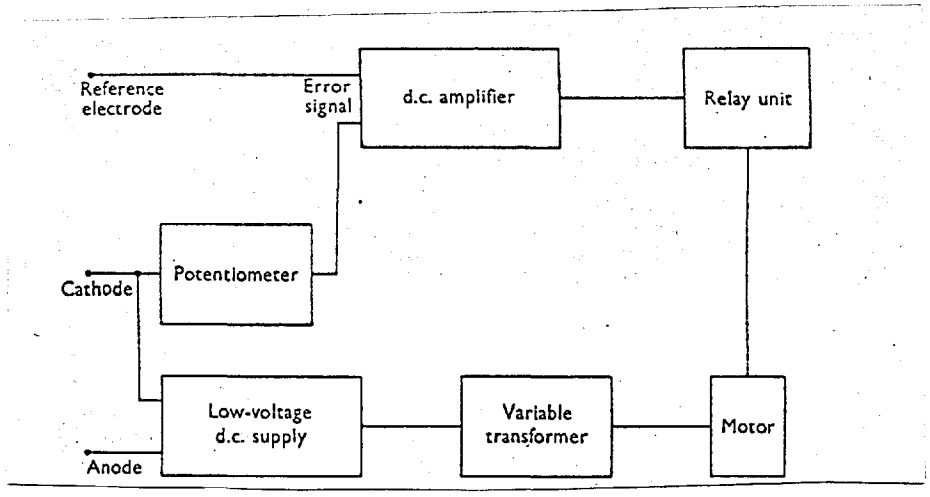


Table 2.1

Sizes of platinum electrodes

Type	Diameter (cm)	Height (cm)	Stem length (cm)	Approximate area (sq cm)
Small gauze	3.0-3.2	3.1	10.8	60
Medium gauze	4.4-4.6	4.4	10.5	120
Large gauze	5.0-5.2	5.0	10.5	160
Small spiral	1.2	3.3	10.7	-
Large spiral	3.0	3.0	10.7	-

Chapter III

Previous Work

This is not intended to be a comprehensive review. Only those methods which offer separations of bismuth, lead and cadmium in the presence of tin electro-gravimetrically have been examined. Indium is dealt with separately in Chapter IV.

Considerable work has been done in acid solutions which offers some scope for the separation of these metals. However, it should be borne in mind that, in general, deposits from acid solutions have poorer physical properties. In nitric acid, bismuth has been determined at controlled potential by Sand (60) in the presence of anodic depolarizers and lead can be deposited anodically at constant current as 'PbO_2', but cadmium cannot be deposited in the presence of free nitric acid, since the overpotential of hydrogen on platinum is much lower than the deposition potential of cadmium. Tin precipitates as metastannic acid and this entails a tedious separation as the precipitate adsorbs appreciable quantities of the other metal ions which must be separated subsequently and returned to the main solution.

The deposition of 'PbO_2' from nitric acid is one of the most popular gravimetric methods for lead, but is accompanied by a number of difficulties. The deposit is hydrated and the water present cannot be completely removed by heating before decomposition of the peroxide to the monoxide begins (37). The peroxide cannot

be completely reduced to the monoxide by further heating as PbO is appreciably volatile at the temperature required for complete conversion (37). This necessitates the use of empirical factors and rigorous control of experimental conditions. By this process lead can be separated from cadmium but bismuth peroxide contaminates the 'PbO_2' deposit. The interference of bismuth and precipitation of tin can be avoided by adding fluoride (48). However the PbO_2 deposit is then contaminated with fluoride and must be dissolved and re-deposited. Collin (10) suggested the separation of bismuth at controlled potential by Sands' method with hydrazine hydrate as anodic depolarizer to prevent the deposition of bismuth and lead peroxides. After the determination of bismuth, the depolarizer was destroyed by the addition of caustic soda and sodium peroxide. Lead was then deposited as 'PbO_2' after re-acidification with nitric acid.

In sulphuric acid, bismuth can only be determined with difficulty and in the presence of a large excess of acid (32). Lead precipitates as sulphate. The deposition of cadmium is retarded by much acid and there must be sufficient cadmium ion present in the solution to cover the cathode completely at the start of the electrolysis (6). Otherwise there is simultaneous deposition of hydrogen gas and loose deposits are formed. The overpotential of hydrogen is much greater on cadmium than on platinum so that once a layer of cadmium has been deposited the remaining cadmium can be deposited without the deposition of hydrogen. Osborn (52) found deposits were always powdery and the last traces of cadmium difficult to remove unless gelatin was added.

In hydrochloric acid, Schoch and Brown (64) reported good results for the deposition of bismuth, lead, tin and cadmium individually at controlled potential in the presence of hydroxylamine hydrochloride as anodic depolarizer. They obtained clean separations of bismuth from the other three metals and of tin from cadmium. The potentials for the complete deposition of lead and tin were too close for them to be separated electrolytically. Engelenburg (16) following Schoch and Brown's method, confirmed the good results for lead, tin and cadmium, but was unable to obtain good deposits for bismuth. He obtained a clean separation of tin from cadmium, but was unable to separate completely bismuth from tin or tin plus lead from cadmium. Kny-Jones (31) found that poor bismuth deposits resulted from the precipitation of bismuth oxychloride in the cathode layer and this could be prevented by the addition of oxalic acid. A major objection to hydrochloric acid as electrolyte is that tin is deposited before cadmium. This is best avoided as tin is more accurately determined volumetrically.

In phosphoric acid, Aylward and Bryson (13) deposited lead at controlled potential in the presence of tin which was too complexed to deposit. The procedure involved a special washing method to remove the contamination of phosphate from the lead deposit. Bismuth and cadmium are insoluble in phosphoric acid.

Although some separations can be accomplished in these acid media, a simple general scheme involving bismuth, lead, cadmium and tin is unlikely to be evolved. In addition, the deposits of bismuth

from acid solution are poor in character, cadmium is obtained only with difficulty and lead when deposited cathodically is prone to considerable loss by aerial oxidation during washing. The separation of lead as peroxide cannot be recommended as too much empiricism is involved.

It is clear that a solution containing a complexing agent is required to keep these metals in solution, to separate the deposition potentials and to improve the physical properties of the deposits.

Alkaline cyanide is the most common medium for the deposition of cadmium. However Diehl (14) in experiments using potential control found that the deposit was often darkened, causing high recoveries. Kny-Jones (33) deposited bismuth from cyanide solution but found considerable attack on the platinum electrodes. Tanaka (68) found that bismuth deposits were contaminated with cyanide and unsuitable for its determination. Lead and tin do not deposit.

Tanaka has studied a variety of complexing solutions for the deposition of large numbers of metals at controlled potential. In EDTA (69) , bismuth and lead are deposited but are considerably contaminated with co-deposited EDTA. Only copper and cadmium from the large number of metals studied were deposited free of EDTA. However Hayakawa (19) has reported successful constant-current determination of bismuth and lead from EDTA solution. Among other media suggested by Tanaka have been alkaline pyrophosphate at

pH7 (70) for the determination of cadmium and at pH10 for the determination of lead and cadmium, alkaline triethanolamine (71) for bismuth and ammoniacal triethanolamine for lead and cadmium, formic acid-formate buffer at pH4.1 (72) for cadmium and the separation of cadmium from lead, acetic acid-acetate buffer at pH5.3 (73) for cadmium and the separation of cadmium from lead.

However, none of these methods shows the apparent versatility of deposition at controlled potential from a tartrate medium at carefully controlled pH. This was first proposed by Lingane and Jones (44) who reported excellent results for the separation and determination of bismuth and lead at pH4 to 5. In such a solution tin is too complexed to deposit. Ishibashi et al (27), Tanaka (67) and Alfonsi (1) have also used similar tartrate electrolytes.

Alfonsi (2) suggested that cadmium could be deposited, after the separation of lead, at pH6.8 to 7.2, but as the buffer capacity of the solution is very small at this pH, constant attention to the adjustment of the pH must be made throughout the electrolysis. Lingane (43), however, found that good deposits of cadmium were obtained from an ammoniacal solution in the presence of gelatin. This solution was formed after the deposition of lead in a tartrate solution simply by adding concentrated aqueous ammonia.

For this work we chose to follow Lingane and Jones for the deposition of bismuth and lead and Lingane for the deposition of cadmium.

Principle of Lingane and Jones' Method

a) Determination of Bismuth

Lingane and Jones successively plated copper, bismuth, lead and tin onto a platinum gauze cathode.

Polarography of copper and bismuth in tartrate solution (39) had shown the great dependence of their half-wave potentials on pH, i.e. $E_{\frac{1}{2}}$ became increasingly negative with increasing pH, and had indicated that the optimum pH for their separation lay between 4 and 6. Because the amalgam formation involved in polarography creates a different thermodynamic situation than in reduction to solid metals, and because deposition of the solid metals proceeds less reversibly than reduction to amalgams, it was necessary to verify this prediction by determining the deposition potentials under the actual conditions extant in electrolysis with the platinum cathode. This was done by recording current-voltage curves for copper and bismuth deposition separately in tartrate solutions of various pH using a platinum micro-electrode. The results are summarised in fig 3.1. The deposition potential of bismuth increased regularly from -0.10V vs SCE at pH1.5 to -0.80V at pH7.5. At a given pH the bismuth deposition potential on a copper-plated cathode was the same as on platinum and it was also the same with or without hydrazine present. The great increase in deposition potential with increasing pH resulted from increasing stability of the tartrate complexes. Below pH3.3 in the presence of hydrazine and below pH2.2 in its absence, the deposition of bismuth proceeded

at a more positive potential than that of copper. These results showed that the optimum pH range for the copper-bismuth separation was 5 to 6. They suggested that the complexation of metal ions with tartrate involved the replacement of the hydrogens of the tartrate hydroxyl groups by the metal ion, i.e. hydrogen ion was a product of the complexation reaction and that this was the fundamental reason why the stabilities of tartrate complexes, and consequently their electrochemical behaviour were so greatly dependent on pH. They dismissed methods using tartrate in acid solution as futile, since in the presence of free strong acids complexation would be impossible.

In trial depositions of bismuth on copper-plated cathodes from 0.5M tartrate at various pH, Lingane and Jones found that deposition was rapid at pH less than 4.5 but that the deposit tended to be loose with danger of loss on washing and at pH4.5 to 5.5 very smooth deposits of bismuth were obtained when the cathode potential was controlled at -0.40V to -0.50V vs SCE.

They decided that the optimum pH for depositing bismuth was 5.2 to 5.4 at a potential of -0.40V vs SCE. The deposition of bismuth on a platinum or copper cathode at this pH was highly irreversible and proceeded autocatalytically as shown by the current-time curves in fig 3.2. At $25^{o}C$ the current was initially small but gradually rose to a maximum, then finally underwent a normal exponential decrease. Maximum current coincided with the complete coating of the cathode with bismuth. With increasing

temperature the 'induction period' decreased until at 50°C the current-time curve corresponded to a normal diffusion-controlled electrode reaction. Deposition on a bismuth electrode was found to be much more reversible. On a platinum or copper electrode at pH5.2 to 6.0 no deposition of bismuth occurred, even after several hours electrolysis, at a potential of -0.30V vs SCE. However under the same conditions bismuth deposited on a bismuth coated cathode without an 'induction period'. The actual mechanism of the electrode process is obscure, though it is possibly a several-step process.

For actual determinations of bismuth Lingane and Jones dissolved a weighed amount of pure metal in diluted (1 + 2) nitric acid (or in hydrochloric acid if tin was likely to be present) in a 300ml tall-form beaker to which were added 1g of urea to remove the oxides of nitrogen, 50ml of M sodium tartrate, 2g of hydrazine dihydrochloride and 1g of succinic acid if copper was to be separated beforehand. The solution was diluted to 190ml and the pH adjusted to 5.2 to 5.4. The final volume was 200ml. The deposition onto a copper-plated platinum gauze cathode of 160 sq cm area required about 45 minutes for completion, the minimum current being about 10mA. The cathode was washed with a jet of water, then a small volume of acetone, dried for 2 minutes at 110°C, cooled in air and weighed.

They found that bismuth could be satisfactorily separated and determined in the presence of 1g of tin, cadmium and nickel, 200mg of magnesium, zinc and manganese, 50mg of lead and 40mg of iron. Larger amounts of manganese, zinc and lead precipitated as

tartrates and larger amounts of magnesium caused a powdery bismuth deposit. Iron, present as ferric tartrate complex, underwent cyclic reduction increasing the residual current and decreasing the current efficiency of the bismuth deposition. Aluminium inhibited the reduction of bismuth and necessitated the use of a more negative potential for its deposition. However, up to 200mg of aluminium could be tolerated, provided the cathode potential was increased to -0.60V vs SCE for the deposition of bismuth. No explanation was offered for this effect. Selenium and tellurium had to be absent, but moderate amounts of nitrate and sulphate were not objectionable.

Details of our work on this method for bismuth are given in Chapter V.

b) Determination of Lead

As with bismuth, pH affects the deposition potential of lead but to a much lesser extent. Deposition of lead is very much more reversible. Lingane and Jones found that lead completely deposited from tartrate at pH4 to 5 at a potential of -0.60V vs SCE. Polarographic investigations of residual solutions showed only traces of lead, but considerable losses of lead occurred on washing. The problem of minimizing this loss has been given special attention in Chapter VI.

c) Determination of Cadmium

Up to pH6, cadmium shows very little tendency to complex formation ($pK_a \cong 1$) and above pH8 weak complexes ($pK_a \gtrsim 4$) are formed. This suggests that deposition of cadmium would be better from a solution of pH greater than 8. Alfonsi obtained satisfactory deposits in the range 6.2 - 8.0 but in this pH range tartrate has very little buffer capacity, so constant attention is needed to adjust the pH throughout the electrolysis.

However, Lingane developed the following method for the determination of cadmium (see Chapter VI). After the deposition of lead onto a copper-plated platinum gauze cathode of 160 sq cm area from 175ml of 0.25M tartrate at pH4.5 to 5.0 containing in addition 20ml of an 0.1 per cent gelatin solution, the solution was made ammoniacal by the addition of 25ml of concentrated aqueous ammonia. The lead coated cathode was replaced, after weighing the lead, 1g of hydrazine dihydrochloride was added and the deposition of cadmium started at -1.0V vs SCE, finally increasing to -1.15V after most of the cadmium had deposited.

Lingane found that in the presence of about 0.01 per cent gelatin and when the current density was kept below about 0.01 amp/cm^2 by starting with a relatively small cathode potential during the initial stage of the deposition, an excellent, smooth cadmium deposit was obtained. The deposition potential of cadmium from this ammoniacal solution was close to -0.95V vs SCE. Furthermore, the much smoother cadmium deposit in the presence of gelatin underwent less loss during washing with water than the more coarsely crystalline deposit obtained in the absence of gelatin. No appreciable amount of gelatin was retained in the cadmium deposit.

Fig 3.1

Deposition potentials vs SCE of copper and bismuth from 0.25M tartrate solutions at 25° as a function of pH. (A) Bismuth on either platinum or copper with or without hydrazine. (B) Copper without hydrazine. (C) Copper in presence of 0.1M hydrazine dihydrochloride. The data were determined from current-cathode potential curves recorded polarographically with a platinum microelectrode. [Lingane and Jones (44)]

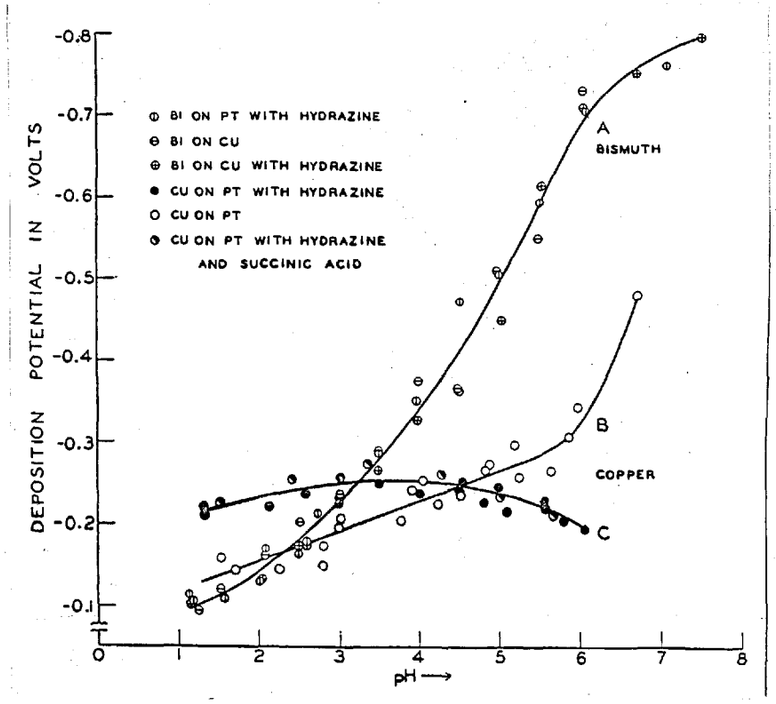
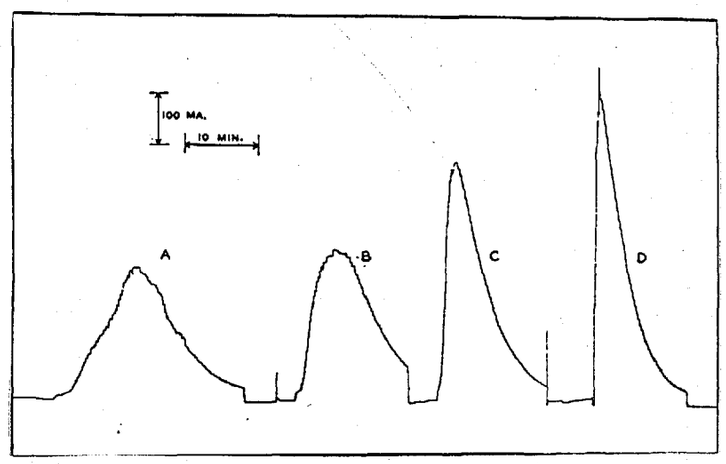


Fig 3.2

Automatically recorded current-time curves for deposition of 100mg of bismuth onto a platinum cathode (area 160 sq cm) from 200 cc of a solution of pH = 5.25 containing 0.25M total tartrate and 0.05M hydrazine dihydrochloride. Cathode potential -0.40V vs SCE. Temperature was (A) 25°, (B) 30°, (C) 35°, (D) 50°C. [Lingane and Jones (44)]



Chapter IV

Current-Cathode Potential Curves for Indium

As many of the alloys for which this scheme of analysis is intended contain indium, some knowledge of the behaviour of indium in tartrate solutions is required. As very little information is available on the electro-deposition of indium, a complete literature survey has been made to evaluate the possibilities.

1) Literature Survey

Only a few methods, all at constant current, have been published for the electro-gravimetric determination of indium. The earliest is probably that of Thiel in 1904 (77) who used an electrolyte containing a slight excess of sulphuric acid with a silvered platinum dish as cathode. Kollock and Smith (34) used a similar electrolyte and also suggested electrolytes containing cyanide, acetate and Rochelle salt. These latter electrolytes have been variously rejected by Dennis and Geer (13) and by Royer (59) for giving poor quality deposits. Dennis and Geer (13) and later Terry and Thabit (76) recommended a sulphate electrolyte containing formic acid but avoiding an excess of sulphuric acid. Royer (59) has published the only micro-procedure which used ammoniacal oxalate. However, Dennis and Geer (13) had earlier rejected oxalates as electrolytes. Yatagawa (80) used an electrolyte containing borax, sodium formate and formic acid. Bray and Kirschman (4) found the

quantitative deposition of indium very difficult, particularly the removal of the last traces of indium. Thiel and Luckmann (78) found that many apparently quantitative deposits contained appreciable amounts of water and concluded that electro-gravimetry was of no use for the determination of indium.

The mercury cathode has been used for the separation of indium, always with sulphuric acid electrolytes. Kollock and Smith (34) were the first to publish a method and more recently Bock and Hackstein (5) included indium in their study of the effects of sulphuric acid concentration on the rate of deposition on the mercury cathode at constant current. They found as with thallium, tin, bismuth and iron that increasing the acid concentration markedly decreased the rate of deposition.

The only method published with potential control is the coulometric method of Mountcastle et al (51) with a mercury cathode and an M potassium chloride - 0.25M hydrochloric acid electrolyte. This method is fairly unspecific (a feature of indium analysis). Electrolysis is carried out at -0.66V vs SCE which is the same as the potential for the deposition of cadmium and is close to the deposition potential of lead. They suggested, without offering any evidence, that the use of a tartrate medium might increase specificity. Matsumae et al (47) separated lead from indium at controlled potential before the polarographic determination of indium in 0.25M sodium tartrate at pH4.2 to 4.3.

2) Behaviour of Indium in Tartrate Solution

Only two methods have been published in which indium is deposited on a solid cathode from a solution containing tartrate. Kollock and Smith's method using Rochelle salt for which very little information is available and an internal electrolysis method by Chernikov and Shtutser (8) with a zinc anode and platinum cathode and an electrolyte containing sodium tartrate and hydrochloric acid at pH3.5 to 3.8. This method appears to be inadequate for mosre than very small amounts of indium.

A number of papers have been published on the use of tartrate in the polarographic determination of indium. Clear and measurable waves were obtained by Jentzch et al (28) from a solution made by dissolving indium hydroxide in aqueous 10 per cent tartaric acid, for which the half-wave potential was -0.63V vs SCE. Reinacker and Hoschek (55) confirmed this and found that the tartaric acid concentration had little effect on the position of the half-wave potential. Matsumae et al (47) obtained a typical reduction wave in 0.25M sodium tartrate at pH4.2-4.3 containing 0.01 per cent gelatin. Siniyakova (66) found a greatly extinguished wave in 0.25M tartrate with $E_{\frac{1}{2}}$ = -0.68V vs NCE. The effect of pH on the reduction of indium was not studied. Zuman gives a value of -0.8V vs NCE for $E_{\frac{1}{2}}$ in 0.5M sodium tartrate (81).

The most extensive polarographic study has been made by Cozzi and Vivarelli (12). They measured the polarograms obtained from solutions containing 5 x 10^{-4}M In^{3+} and 0.1 tartaric acid at

intervals over the pH range 0.5 to 6. At low pH values, i.e. 0.5 to 1.0, only poorly developed waves are obtained probably corresponding to the highly irreversible reduction of the aquo indic ion. From pH1.5 to 2.6 very well developed waves are obtained with $E_{\frac{1}{2}}$ = -0.58V vs SCE. These correspond to the reduction of the complex In $(C_4H_4O_6)$ $(C_4H_5O_6)$ for which pK_a = 6.8 ± 0.1. With increasing pH the half wave potential shifts to more negative values and the waves are gradually extinguished until at pH6.0 virtually no wave is obtained. At pH greater than 2.6 the complex ion In OH $(C_4H_4O_6)^{2-}$ becomes the predominant species with pK_a = 18.5 ± 0.1. This follows the same pattern as bismuth, showing that pH has a major effect on the formation of tartrate complexes and on the electrochemical behaviour of ions in tartrate solution.

To investigate the behaviour of indium at solid electrodes, current-cathode potential curves as described in Chapter I were determined at various pH with platinum, copper-plated platinum, and lead micro-electrodes. Some curves for bismuth and cadmium were also measured to provide a comparison.

3) Apparatus

a) Electrolysis cell.

The electrolysis vessel was a 150ml tall-form beaker into the top of which was fitted a large rubber bung. Through the bung passed a glass tube of 5mm diameter, which reached to the bottom of the beaker, to pass nitrogen gas through the solution to remove

dissolved oxygen, and a 15mm diameter glass tube sealed at the bottom with a porous sintered glass disc to act as anode compartment, to keep the products of anodic reaction from interfering with the cathode reaction. The anode was made of platinum foil. The side-arm of the reference electrode and the micro-cathode also passed through the bung. The tip of the reference electrode was placed as close as possible to the micro-electrode, without actually touching it to minimise any iR drop through the solution. The solution was stirred magnetically.

b) Micro-electrodes

i) Platinum

A length of 14 S.W.G. platinum wire was sealed into the end of a 5mm-bore glass tube such that 2-3mm protruded. External connection was made by placing a few drops of mercury in the tube and placing in this a length of copper wire, the end of which had been amalgamated to improve contact.

ii) Copper-plated

Platinum electrodes were plated from a solution of copper sulphate containing a few ml of sulphuric acid with a current of 20 to 40 microamps. When a good deposit was apparent the electrode was removed, washed and used immediately.

iii) Lead

About 0.5g of pure lead was melted in a small porcelain basin over a small bunsen flame and poured free of surface oxidation

products into a second clean porcelain basin. The end of a glass rod of 5mm-bore was warmed in a flame and placed in the lead which had meanwhile been remelted. A length of copper wire was placed down the tube so that it was within about 0.5cm of the end and molten lead was sucked up into the tube until contact had been made with the copper wire. Still under gentle suction, the tube was removed from the basin, whereupon the lead rapidly solidified. After cooling for about 10 minutes the excess lead at the end of the tube was smoothed off with a knife. After use it was cleaned first with a knife and then by etching in 2N nitric acid.

c) Circuit

The electrolysis current was provided by a 4V battery which was connected across a potential divider R_1. The arm of the divider was connected through a resistance R_2 in series with a microammeter to one electrode. The other electrode was connected to one end of the potential divider; cf fig 2.1. The cathode potential was measured against a normal calomel electrode with a 'Pye Universal' pH meter. The values of R_1 and R_2 were varied to obtain steadier readings.

d) Preparation of solutions

Materials: Indium: 99.95 per cent electrolytically refined indium supplied by Mining and Chemical Products Ltd.

Bismuth: 99.99 per cent refined bismuth supplied by Mining and Chemical Products Ltd.

Cadmium: Spectrographically analysed cadmium supplied by Johnson Matthey.

100mg each of indium, bismuth and cadmium were dissolved separately in 10ml of diluted (1 + 2) hydrochloric acid containing 0.5-1ml of concentrated nitric acid in the electrolysis beaker. Oxides of nitrogen were removed by boiling gently for a few minutes. The sides of the beaker were washed down, 50ml of M sodium tartrate added and the pH adjusted with 2N hydrochloric acid or 2N sodium hydroxide as appropriate. The final volume was 100ml. A few ml of this solution were placed in the anode compartment such that its level was lower than that of the main solution.

e) Method

With the electrodes, etc, in place and the circuit set up, but not connected to the electrodes (to prevent any changes which may be caused by back e.m.f.), the solution was de-aerated for 10 minutes with oxygen-free nitrogen gas. The nitrogen was then switched off, the stirrer started and the circuit connected. The applied voltage was increased in steps and the current and cathode potential values read for each step. A short time was allowed for the readings to reach a steady value. At certain applied voltage, readings were very unsteady. R_1 and R_2 were altered to try and compensate for this. Best results were obtained when R_1 was 250 ohms and R_2 was 1000 ohms.

f) Results

i) pH5.1

Fig 4.1 shows the results for solutions of indium, bismuth and tartrate alone at pH5.1. For the indium and tartrate curves a copper-plated cathode of 2mm length was used. R_1 was 25,000 ohms and R_2 zero; the readings were rather unsteady. The curve (a) for bismuth was determined with a copper-plated cathode of 3mm length; R_1 was 250 ohms and R_2 was 1000 ohms. The curve (b) for bismuth was determined with a bright platinmu cathode of 3mm length; R_1 was 250 ohms and R_2 was 20,000 ohms. Readings for (a) were steadier than for (b).

ii) pH5.1

Fig 4.2 shows curves for indium, cadmium and tartrate alone using the lead micro-electrode at pH5.1. R_1 was 250 ohms and R_2, 1000 ohms.

iii) pH3.5

Fig 4.3 shows curves for indium and tartrate alone at pH3.5

iv) pH2.1

Fig 4.3 shows curves for indium and tartrate alone at pH2.1.

g) Conclusions

These curves show that no deposition of indium occurs at pH5.1 or 3.65 on platinum, copper or lead electrodes. Close inspection of the electrodes revealed no deposit of indium. At pH2.1 indium deposits, but the small height of the current plateau indicates that deposition is very irreversible. A bright coating of indium was apparent. Thus the deposition of indium is unfeasible in tartrate solution. It is possible that, if the solution were made highly acidic with hydrochloric acid, indium might deposit quantitatively, as indium deposits reversibly from chloride solution at the dropping mercury electrode. However, cadmium will almost certainly co-deposit as happened in the experiments of Mountcastle et al

We therefore decided not to attempt any work on the deposition of indium. However, as it does not deposit in the pH range 4 to 5, it should be possible to determine bismuth and lead in the presence of indium under these conditions.

Fig 4.1

Current-cathode potential curves for indium, bismuth and tartrate at pH5.1

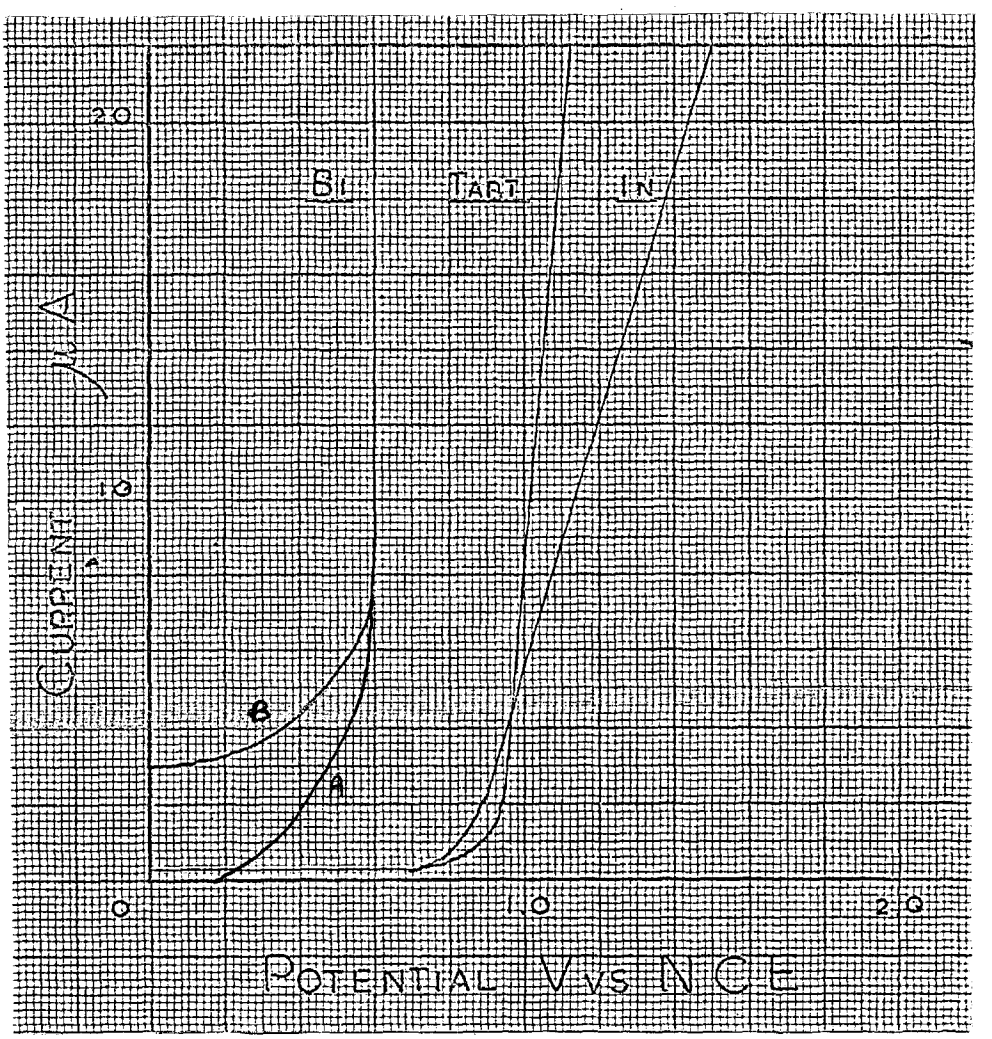


Fig 4.2

Current-cathode potential curves for indium, cadmium and tartrate at pH5.1 using a lead micro-electrode

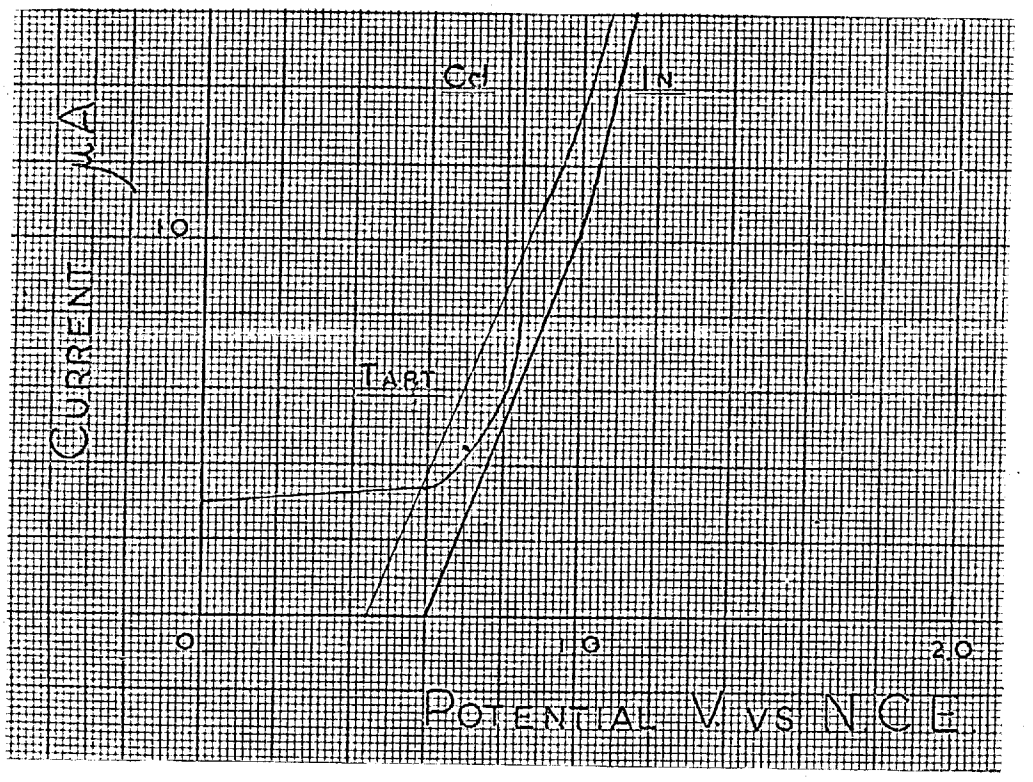
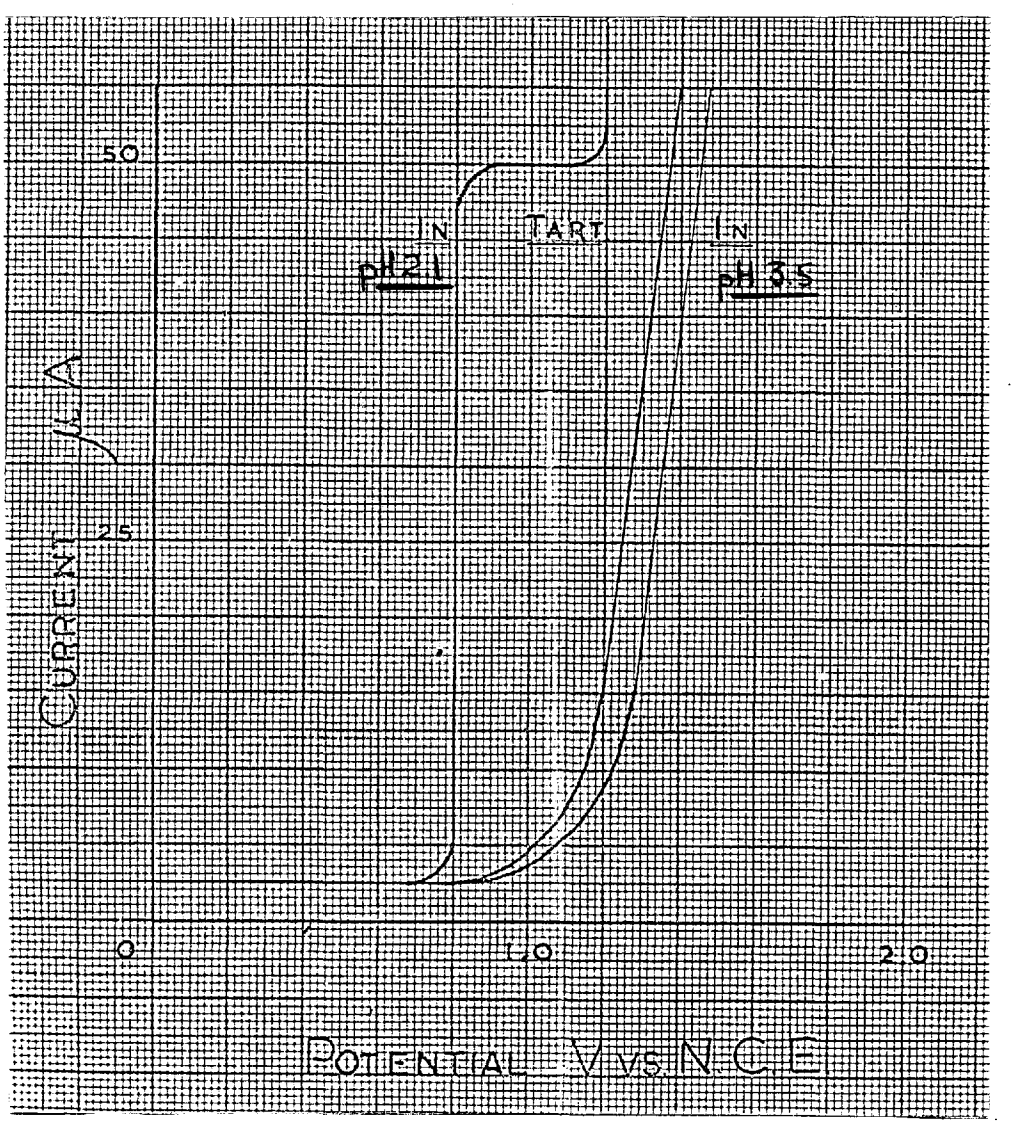


Fig 4.3

Current-cathode potential curves for indium and tartrate at pH3.5 and 2.1



Chapter V

Bismuth

1) Experiments on Lingane and Jones' Method

a) Preparation of sample for analysis

100 to 300mg of pure bismuth metal were weighed into the electrolysis beaker and dissolved in 10ml of diluted (1 + 2) hydrochloric acid containing 0.5 to 1ml of concentrated nitric acid by warming on a steam bath. The solution was boiled gently for a few minutes to remove oxides of nitrogen, then the sides and cover of the beaker were washed down with distilled water. M sodium tartrate was added and 1.5 to 2g of hydrazine dihydrochloride. The solution was diluted and the pH adjusted with a 'Pye Universal' pH meter, with 2N hydrochloric acid or sodium hydroxide as appropriate. The final volume was made up to 50 to 200ml with distilled water.

b) Experimental details

The electrolytic solution was warmed to the required temperature and the electrodes, stirrer, etc. were placed in the solution. The cell was covered with a 'perspex' cover. With the stirrer rotating at constant speed, and the potentiostat set to give the required cathode potential, the electrolysis circuit was connected. Readings of current and temperature were taken at regular intervals and note was taken of the rate of stirring. At the finish of the electrolysis, the cathode was slowly raised from the

solution without interruption of the current and washed simultaneously with a jet of distilled water directed round the upper rim of the electrode. The current was then switched off and the cathode removed and rinsed once in a beaker of water. It was then rinsed in acetone, dried, and weighed as given in Chapter II. Some time before the finish of each electrolysis the sides of the beaker and cover were washed down with a few ml of water. Where indicated, a small volume was pipetted from the solution just before the finish of the electrolysis and analysed for traces of bismuth. The residual solution and washings were saved after each electrolysis and analysed for traces of bismuth (p. 64).

c) Copper-plated cathodes

Copper was most conveniently deposited by Lingane and Jones' method. The electrolysis cell was set up as above with an electrolyte containing 10 to 100mg of copper in 0.25M tartrate with 2g of hydrazine dihydrochloride. The pH of the electrolyte was adjusted to 5.5-5.8; above pH 6 cuprous oxide, etc., precipitate. The solution was electrolysed with the cathode potential at 0.30V vs SCE and the cathode was removed and washed down when a good coating of copper was apparent.

d) Observations and results. (See Table 5.1), page 71).

I) Deposition from solutions containing bismuth alone

In the determinations described, all depositions were carried out at a controlled cathode potential of -0.40V vs SCE.

In experiments 1 and 2, Lingane and Jones' instructions were followed except that the cathode area, 120 sq cm, and the volume of solution, 150ml, were smaller (cf 160 sq cm and 200ml respectively). The volume was kept as small as possible to obtain a maximum cathode area to volume ratio. A 250ml pyrex beaker was used as electrolysis vessel. The deposition of bismuth was studied on a platinum gauze cathode in the presence of 1.5g of hydrazine dihydrochloride at room temperature, approximately 17°C, from 0.5M tartrate at pH5.2. Stirring was mechanical with an L-shaped glass rod stirrer. Very poor recoveries of bismuth were obtained; even after three and a half hours electrolysis the plating was patchy and the current much lower than those observed by Lingane and Jones. No current maximum was observed.

We then studied the effect of altering cathode surface, rate of stirring, pH and temperature to establish the conditions necessary for obtaining quantitative recovery of bismuth.

Cathode Surface

As the deposition of bismuth is highly irreversible, it may be affected by the nature of the cathode surface. Lingane and Jones' results show no difference between platinum or copper surfaces. In experiment 3, the cathode was copper-plated, all other conditions being as in 1 and 2. A slight improvement was noted, sufficient to warrant the continued use of a copper cathode throughout the rest of the depositions.

Stirring

As shown in Chapter I, the thickness of the diffusion layer and hence the size of the current under diffusion-controlled conditions depends greatly on the efficiency of the stirring. In experiment 4, magnetic stirring replaced mechanical stirring. However, it was found to be less efficient and at higher stirring speeds the bar of the stirrer tended to get 'lost'. In experiment 5, the rate of stirring with the mechanical stirrer was kept as high as possible. However, the residual current was considerably increased ($\sim$ 50mA). The solution was very 'churned-up' and it seemed that a secondary reduction was taking place through the introduction of air. It was concluded that stirring should be as fast as possible, but just slow enough to prevent 'churning'. Another danger at high speeds is that droplets of solution tend to get thrown from the top of the solution.

pH

Recoveries were still poor, so the next parameter considered was pH. Lingane and Jones found that the deposition of bismuth became considerably more rapid as the pH was reduced. However, below pH4.5 deposits tended to be loose. In experiment 6, the pH was reduced to 4.5 and the solution electrolysed with a copper-plated cathode. An improvement was noted, but recovery was still low.

Concentration of Tartrate

In 7, the concentration of tartrate was reduced to 0.25M. The improvement in recovery continued, but was still too low for the quantitative determination of bismuth.

Temperature

None of the previous changes had succeeded in making bismuth deposit quantitatively. Deposits were hard but patchy, and at no time did the bismuth deposit completely cover the cathode. Currents observed were low and current maxima were not formed. Lingane and Jones had stressed the importance of temperature and the fact that current maxima coincided with the complete covering of the electrode. It was clear that at our room temperature of approximately 17°C, deposition was too irreversible to give a satisfactory rate of deposition.

In 8, the temperature was raised to 25°C and in 9, to 30°C. The concentration of tartrate was 0.25M in each and in 9, the volume was increased to 200ml as in previous experiments the top rim of the cathode had tended to become uncovered as the solution was stirred. Recoveries were apparently well within 0.1mg, the deposits were hard, and even the length of time taken acceptable. The current maximum described by Lingane and Jones was observed and this did correspond to the complete coverage of the electrode. It was reached more quickly at the higher temperature in 9 (5 as against 10 minutes), so it was decided that a temperature of at least 30°C was advisable. A normal diffusion-controlled type of decay was noted after the

maximum had been passed. Residual current was 10 to 15mA and electrolysis was continued for about ½ hour or more at the residual current. This was thought to be somewhat excessive, so in experiment 10 electrolysis at the residual current was reduced to 15 mins. However, recovery was incomplete and colorimetric analysis of an aliquot just before the finish of the electrolysis showed the presence of 0.4mg of undeposited bismuth.

In experiments 11 to 13, all the changes described previously were included with good recoveries (within 0.3mg) of bismuth, colorimetric analysis at the finish of the electrolyses revealing not more than 0.1mg of undeposited bismuth. The conditions arrived at were that 100mg of bismuth were deposited onto a copper-plated platinum gauze cathode of 120 sq cm area from 200ml of solution in a 250ml beaker, 0.25M in sodium tartrate at pH4.5 and at a temperature of 30°C.

In experiments 11, 12 and 13 the loss of bismuth on removing the electrode from the solution and during washing was studied. The deposits were hard and adherent and examination of wash solutions revealed no solid particles of bismuth. Residual solutions after washing showed up to 0.3mg of bismuth, but the water wash solutions failed to show any traces of bismuth. (See Table 5.2). Hence there is a loss of 0.2 to 0.3mg of bismuth on washing (after subtracting the 0.1mg remaining undeposited) and this takes place entirely during the time the electrode is being removed from the solution. Hence completeness of recovery depends on the efficiency and speed of

washing of the cathode as it is removed from the electrolyte. This is exactly the same behaviour, to a lesser extent, as that noted for lead by Lingane.

The difference by weight is always less than the loss shown by analysis of the residual solutions and is rarely greater than 0.3mg. Hence it is concluded that the deposit probably contains some oxygen or occluded electrolyte.

In addition, determinations 14 and 15 were conducted with a cathode of larger area (160 sq cm) under the conditions arrived at above, to note the effect of cathode area to volume ratio. Maximum currents were somewhat higher, otherwise no difference was noted.

Deposition of less than 100mg of bismuth

Following the conditions arrived at in experiments 11 to 13, a series of determinations was carried out with amounts of bismuth less than 100mg. Determination 16 shows results for 50mg of bismuth. Recovery was within 0.3mg, but the plating was very patchy. In determination 17 the effect of increasing cathode area to volume ratio was tried by reducing the volume of electrolyte to 100ml and using a 150ml beaker as electrolysis vessel. The cathode area was 120 sq cm. The recovery of 50mg of bismuth was within 0.3mg and the electrode was well covered. In determination 19, 10mg were recovered to within 0.3mg, but the deposit did not completely cover the electrode. In determination 20, the deposition of 5mg failed utterly to give a reasonable recovery. However, in 21, recovery of 5mg of bismuth within 0.3mg was obtained by using a 50ml beaker, 40ml of electrolyte

and a cathode of 60 sq cm area. Stirring was magnetic as there was no room in the beaker for a mechanical stirrer.

(ii) Deposition of bismuth in presence of lead

According to Lingane and Jones only about 50mg of lead can be present in solution at pH5 owing to the low solubility of lead hydrogen tartrate. To test the separation of bismuth from lead, varying amounts of lead were dissolved with bismuth and electrolysed at -0.40V vs SCE in tartrate at pH4.5.

Preparation of sample

Matthey spectrographically analysed lead rod supplied by Messrs Johnson, Matthey & Co. Ltd. containing 0.0003 per cent bismuth was purified from surface oxide coatings by melting a few grams in a small porcelain basin over a bunsen flame and pouring the melt onto a porcelain-glazed tile. The button obtained was cut with steel pincers into pieces small enough to weigh.

The weighed sample of lead was dissolved with the weighed sample of bismuth in hydrochloric/nitric acid mixture as given previously in section (i).

In the experiments detailed in Table 5.3, perfectly clear solutions were obtained prior to electrolysis. The solutions contained 0.25M tartrate and 1g of hydrazine dihydrochloride. However, in all determinations, except 5, a white crystalline deposit initially forms at the cathode which is followed by general precipitation throughout the solution. At the end of the electrolysis, crystals

were still attached to the cathode which were not removed even by the most vigorous washing. It seems that up to 200mg of lead can be obtained in tartrate solution at pH4.5 but that the solution is supersaturated. It is probable that lead hydrogen tartrate is precipitated in the cathode layer, either because of a local change in pH on electrolysis or a local concentration of tartrate ions, and this precipitate furnishes nuclei for further precipitation. It is clearly impossible to determine bismuth accurately in the presence of precipitated lead hydrogen tartrate which means the maximum tolerable amount of lead is about 60mg as given by Lingane and Jones.

(iii) In presence of lead, cadmium and tin. (Table 5.4)

Lingane and Jones state that bismuth can be determined in the presence of 1g each of cadmium and tin.

In determination 1 (Table 5.4), 1g each of 'Analar' tin and 'spectrographically' analysed cadmium metal were dissolved without prior purification or cleaning with 300mg of bismuth and 50mg of lead in hydrochloric/nitric acid mixture as given in section (i). The solution was electrolysed with a copper-plated cathode of 120 sq cm area under the conditions arrived at in section (i). The electrolysis followed its normal course, except that the current maximum was somewhat higher than expected (600mA). Recovery was slightly high (+0.12mg) but within acceptable limits. In the second determination 30mg of bismuth were deposited onto a copper-plated cathode of 120 sq cm area from 100ml of solution in a 150ml beaker containing 20mg of

lead and 0.5g each of cadmium and tin. Again the current maximum was somewhat high and recovery a little high but within the 0.3mg which was considered quite acceptable in this rather abnormal circumstance.

iv) In presence of indium. (Table 5.5)

As shown in Chapter IV, indium was not deposited from tartrate solution at pH4.5. Hence a separation of bismuth seems feasible under the conditions arrived at in section (i).

In determinations 1 and 2, 100mg amounts of indium metal were dissolved with 100mg of bismuth in hydrochloric/nitric acid and electrolysed at -0.40V vs SCE under the conditions given in section (i). The bismuth deposition apparently followed its normal course but was incomplete. Even reducing the amount of indium to 20mg in determination 3 failed to improve the recovery.

It had been observed by Lingane and Jones that aluminium hindered the reduction of bismuth necessitating an increase in the cathode potential for the deposition of bismuth to -0.60V vs SCE. Since indium is in the same periodic group as aluminium, it was thought that perhaps a similar phenomenon was occurring with indium. In experiments 4 and 5, the cathode potential was increased to -0.50V and satisfactory recoveries were obtained. Colorimetric determination of traces of bismuth in residual solutions showed that not more than ~0.3mg of bismuth was lost on washing, as previously. No explanation is given for this curious effect. Experiments 6, 7 and

8 show the same behaviour when a cathode of larger area (160 sq cm) was used. The loss of bismuth at the less positive potentials, however, appears to be greater.

The use of a more negative cathode potential raises the possibility of considerable co-deposition of lead. Results in Table 5.6 show that in the presence of 50mg of lead, and up to 1g each of cadmium and tin, the positive error for the recovery of bismuth is nearly always within +0.4mg. Thus bismuth may be satisfactorily determined in the presence of indium, lead, cadmium and tin.

V) Depositions on a mercury cathode at controlled potential

On account of the difficulties encountered in the deposition of bismuth on solid copper-plated cathodes, particularly in the presence of indium, a short study was conducted on the separation of bismuth at a mercury cathode from tartrate solution at a controlled potential of -0.40V vs SCE, as bismuth deposits more reversibly at the mercury cathode. The conditions followed here correspond to those given by Lingane for the separation of bismuth from lead and cadmium prior to the polarographic analysis of lead (39).

Apparatus

The electrolysis cell was a 250ml pyrex beaker. The mercury cathode consisted of a pool of approximately 20ml of mercury which completely covered the bottom of the beaker. This was connected to the external circuit by means of a short piece of platinum

wire sealed in a glass tube. A spiral platinum anode was used with its end close to the level of the mercury. The saturated calomel reference electrode was placed so that the tip of its agar-filled side arm was just above the level of the mercury. The electrolyte and mercury surface were stirred simultaneously by a propeller-shaped stirrer, placed at the mercury solution interface driven mechanically. In one case a magnetic stirrer was used, but this was thought to be less efficient.

The bismuth sample was prepared as given on p53 and the electrolysis solution contained 0.25M tartrate in a volume of 100ml with 1g of hydrazine dihydrochloride at pH4.5. Mercury was added down the side of the beaker and the anode stirrer and reference electrode were placed in the beaker after it and the external circuit was connected. At the end of each experiment, the electrolyte was sucked from the cell into a small suction flask fitted with a side arm , the cell was washed with a few ml of water and this was sucked off also. Any small globules of mercury accidently sucked into the flask were immediately removed by filtering the solution through a small filter paper. This solution was then analysed colorimetrically by dithizone in presence of bismuth alone or diethyldithiocarbamate in the presence of bismuth and indium. In experiment 5, 25ml of electrolyte were pipetted from the solution just before the finish of the experiment and analysed for bismuth colorimetrically by dithizone. The results are given in Table 5.7.

In experiment 1 separation was very slow with approximately 50mg of bismuth remaining in solution after one hour. In experiments 2 to 5, mechanical stirring was used, the electrolyte and mercury being stirred as vigorously as possible without the solution splashing out of the beaker. As seen in experiment 2 this by itself was insufficient to completely separate bismuth within a reasonable time. By raising the temperature to over 30°C all but 0.3mg were removed at the mercury cathode after electrolysis for 75 minutes. The analysis of the 25ml aliquot in experiment 5 revealed that 0.2mg of bismuth remained undeposited after 75 minutes; a further 0.1mg redissolved during washing.

On adding 100mg amounts of indium it was found that as with the solid cathode incomplete deposition of bismuth occurred. The figures obtained for residual amounts of bismuth in 6 to 9 were all low on account of an error in the determination of bismuth by diethyldithiocarbamate which was corrected for later determinations.

These experiments show that bismuth is never completely separated at a mercury cathode under the conditions given. Although the deposition of bismuth is more reversible (no current maxima are observed), the very much smaller surface area of mercury means that the current densities will be much lower. Thus efficient stirring is needed to ensure reasonable times of deposition. Magnetic stirring is not fast enough, but by using the propeller-shaped mechanical stirrer and a temperature of 35°C all but 0.2mg of bismuth can be deposited within 75 minutes. However, these results

are poorer than those given by Lingane. Presumably he must have used excessively high stirring rates. In the presence of indium incomplete recovery is obtained; the indium seems to prevent the reduction of bismuth on the mercury cathode in the same way as on the copper-plated cathode. With these results which show no positive advantages for the mercury cathode, it was decided not to continue the investigation.

VI) Analysis of residual solutions for bismuth

It was thought that residual amounts of bismuth could be determined polarographically by Lingane's method (39). In order to get solutions sufficiently concentrated to be amenable to polarographic investigation, evaporation was necessary. However it was found that evaporated tartrate solutions produced spurious reduction waves which completely obliterated the bismuth waves. It was found also that hydrazine dihydrochloride, added as depolarizer in the electrolysis, interfered with the polarographic determination of bismuth. Thus colorimetric methods were used.

a) Dithizone

For bismuth in the absence of other metals, the method described by Sandell (61) was used. The residual solution was made up to 250ml in a graduated flask and an aliquot, usually 25ml, depending on the concentration of bismuth thought to be present, was transferred to a 125ml separating funnel. The aliquot was diluted to 50ml and the pH adjusted to about 9 with concentrated ammonia

solution by noting the first faint red tinge of phenolphthalein indicator. Bismuth was extracted by shaking with successive 5ml portions of a solution of dithizone in chloroform (5mg of dithizone per 100ml of chloroform) for one minute. The last portion showed no colour change after shaking for one minute. The aqueous solution was then shaken with a small portion of chloroform and the latter was added to the chloroform extracts collected in a second 125ml separating funnel. The aqueous solution was then discarded. The combined extracts were washed once by shaking with 25ml of distilled water, then drawn off into another 125ml funnel where they were shaken for one minute with 25ml of diluted (1 + 100) nitric acid. The chloroform layer was drawn off and shaken with a second 25ml portion of diluted (1 + 100) nitric acid. The acid extracts were combined and the chloroform extracts discarded. To the combined acid extracts were added 20ml of concentrated ammonia solution (S.G.0.88), 2ml of potassium cyanide solution (1g potassium cyanide in 100ml of water) and 15 ml of dithizone solution in chloroform (as given). The mixture was shaken for one minute, then the chloroform extract was drawn off through a cotton-wool plug in the stem of the funnel into a 1-cm adsorption cell. The optical density was measured against a pure chloroform reference solution on a Helger 'Spekker' adsorptiometer using Ilford Spectrum Violet No 601 filters.

A calibration curve was constructed by extraction from portions of standard bismuth solutions made up from dissolved bismuth metal. The completeness of the extraction of bismuth was tested by

adding aliquots of standard bismuth solutions to aliquots of the residual solution and extracting as above.

The accuracy of the determination of less than 1mg of bismuth in 250ml of solution is about 5 to 10 per cent.

b) Diethyldithiocarbamate

Lead and indium are extracted by dithizone under the conditions given above. To separate bismuth from the large amounts of indium present, hydrogen sulphide precipitation from a strongly acid solution was attempted. Without a collector, precipitation was incomplete. Cadmium (5mg as sulphate) was tried as a collector, as it is claimed that indium is less easily co-precipitated with cadmium sulphide. However, on dissolving the sulphides in acid, making alkaline and extracting in the presence of tartrate with dithizone in chloroform, the cadmium interfered. Extracting a solution of the sulphide precipitates with diethyldithiocarbamate in the presence of EDTA was tried with varying success.

It was then found that bismuth could be separated from the residual solution by direct extraction with diethyldithiocarbamate and carbon tetrachloride in the presence of EDTA. In an attempt to increase sensitivity, the diethyldithiocarbamate extracts were decomposed with acid and the resulting solution extracted with dithizone. However, indium, although it gave no interfering coloured solution with diethyldithiocarbamate, was extracted in sufficient amount to give serious interference in the dithizone determination. Thus the following method was used, although it is rather insensitive.

According to Sandell (61) , provided the pH is at least 11 to 12, in the presence of EDTA, bismuth should be effectively extracted from all other metals by diethyldithiocarbamate. The residual solution was made up to 250ml and an aliquot containing 0.1 to 0.3mg of bismuth was taken. To the aliquot were added 10ml of a complexing solution (5g of EDTA + 5g of potassium cyanide in 100ml of diluted (1 + 10) ammonia solution), 1ml of reagent solution (0.2 per cent colution of sodium diethyldithiocarbamate in water) and exactly 10ml of carbon tetrachloride. The mixture was extracted for one minute, then the carbon tetrachloride layer was run through a cotton-wool plug in the stem of the funnel into a 1-cm adsorption cell. The optical density was measured immediately against a carbon tetrachloride reference solution on the 'Spekker' using Ilford Spectrum Violet No 601 filters. The accuracy of this method is not better than ten per cent at the levels of bismuth determined.

SUMMARY

Over 50mg of bismuth can be determined electro-gravimetrically from tartrate solution under the following conditions:

1) Cathode potential, -0.40V vs SCE;
2) Concentration of tartrate, 0.25M;
3) pH4.5;
4) Volume, 200ml, when using 120 sq cm area cathode;
5) Temperature, at least 30°C;

6) Vigorous stirring;

and 7) Cathode, copper-plated.

Less than 50mg can be deposited by reducing the volume of electrolyte and the area of the cathode. Bismuth can be determined in the presence of up to 50mg of lead, 1g of cadmium and 1g of tin. In the presence of indium, the cathode potential must be raised to -0.50V vs SCE for quantitative recovery, and this can be done without fear of co-deposition of lead.

Table 5.1

Cathodic deposition of bismuth from tartrate solution

	Weight Bi Taken (g)	Weight Bi Found (g)	Difference (mg)	1*	2*	Current Max (mA)	Current Min (mA)
1.	0.11051	0.10592	-4.95	-	4.25	-	8.1
2.	0.10046	0.09970	-0.76	-	0.75	57	8
3.	0.10060	0.09935	-1.25	-	1.0	65	4
4.	0.11088	0.10559	-5.29	-	5.0	54	7
5.	0.10370	0.10185	-1.85	-	1.5	150	50
6.	0.10614	0.10478	-1.41	-	1.6	115	8
7.	0.10849	0.10761	-0.88	-	0.8	200	10
8.	0.10559	0.10560	-	-	0.2	220	10
9.	0.10730	0.10730	-	-	0.2	190	10
10.	0.10392	0.10337	-0.55	0.40	0.6	170	10
11.	0.10312	0.10300	-0.12	0.1	0.3	200	10
12.	0.10132	0.10123	-0.09	0.1	0.3	160	12
13.	0.27147	0.27157	+0.10	0.1	0.3	350	10
14.	0.10222	0.10229	+0.07	0.1	0.4	200	10
15.	0.10241	0.10229	-0.12	0.1	0.4	160	10
16.	0.05270	0.05248	-0.22	-	-	150	10
17.	0.05289	0.05258	-0.31	-	-	175	10
18.	0.01040	0.01913	-0.27	-	-	90	10
19.	0.01067	0.01043	-0.24	-	-	50	10
20	0.00502	0.00269	-2.33	-	-	60	10
21.	0.00511	0.00485	-0.26	-	-	65	10

1* Weight of bismuth in electrolyte just before finish of electrolysis (mg)

2* Weight of bismuth in residual solution and washings (mg)

Temperature Max °C	Temperature Min °C	Time hr	Time min	pH	Concentration of Tartrate (M)	Volume of Solution (ml)
	17	2	15.	5.2	0.5	150
	17	3	35	5.2	0.5	150
	17	2	47	5.2	0.5	150
	17	3	30	5.2	0.5	150
	17	1	30	5.2	0.5	150
	17	1	30	4.5	0.5	150
	17	1	30	4.5	0.25	150
25	23.8	1	40	4.5	0.25	150
30	30	1	32	4.5	0.25	200
32	32	1	0	4.5	0.25	200
30	30	1	10	4.5	0.25	200
31	31	1	15	4.5	0.25	200
31	31	1	15	4.5	0.25	200
38	31	1	15	4.5	0.25	200
40	29	1	15	4.5	0.25	200
40	29	1	10	4.5	0.25	200
40	29	1	0	4.5	0.25	100
40	29	1	0	4.5	0.25	100
40	29	1	0	4.5	0.25	100
40	29	45	0	4.5	0.25	100
40	29	45	0	4.5	0.25	40

Table 5.2

Loss of weight of deposited bismuth on washing

	Weight Bi Taken (g)	Weight Bi Found (g)	Difference (mg)	1*	2*	Water Wash Solution
10.	0.10392	0.10337	-0.55	0.4	0.55	NIL
11.	0.10312	0.10300	-0.12	0.1	0.30	"
12.	0.10132	0.10123	-0.09	0.1	0.30	"
13.	0.27147	0.27157	+0.01	0.1	0.30	"

1* Weight of Bi in electrolyte just before finish of electrolysis (mg).

2* Weight of Bi in residual solution and washings (mg).

Table 5.3

Deposition of bismuth in presence of lead

	Weight Bi Taken (g)	Weight Bi Found (g)	Difference (mg)	Current Max mA	Current Min mA	Temperature Max °C	Temperature Min °C	Time Taken hr	Time Taken min	Pb Added (mg)
1.	0.10382	0.10376	0.06+	200	9	33	29	1	15	100
2.	0.10823	0.10609	2.14+	210	9	32	27	1	10	200
3.	0.10093	0.10012	0.81+	210	7	33	29	1	0	100
4.	0.09958	0.10140	+1.82	130	8	32	29	1	15	100
5.	0.30100	0.30126	+0.26	500	9	38	30	1	15	60

+ AFTER VIGOROUS WASHING.

Table 5.4

Deposition of bismuth in presence of lead, tin and cadmium

Weight Bi Taken (g)	Weight Bi Found (g)	Difference (mg)	Current Max	Current Min	Time hr	Time min	Temperature °C	Volume (ml)
0.29935	0.29947	+0.12	500	10	1	15	40	200 *
0.03075	0.03102	+0.27	120	10	1	15	40	100 **

* + 1g Cd + 1g Sn + 50mg Pb.

** +0.5g Cd + 0.5g Sn + 25mg Pb.

Table 5.5

Deposition of bsimuth in presence of indium

	Weight Bi Taken (g)	Weight Bi Found (g)	Difference (mg)	Bi in Residual Solution (mg)	In (mg)	Time hr	Time min	Temperature °C	Potential V vs SCE
1.	0.10049	0.09966	-0.83	0.6	100	1	15	29	-0.40
2.	0.09953	0.09894	-0.59	0.6	100	1	30	35	-0.40
3.	0.19949	0.19807	-1.42	1.3	20	1	70	31	-0.40
4.	0.09970	0.09951	-0.19	0.25	60	1	30	37	-0.50
5.	0.33229	0.33264	+0.35	0.25	60	1	30	35	-0.50
6.	0.10320	0.10142	-2.78	-	100	1	20	35	-0.40
7.	0.10469	0.10359	-1.10	-	100	1	15	35	-0.45
8.	0.10320	0.10310	-0.10	-	100	1	20	35	-0.50

Table 5.6

Deposition of bismuth in presence of indium, lead, tin and cadmium

	Weight Bi Taken (g)	Weight Bi Found (g)	Difference (mg)	Residual Bi (mg)	In (mg)	Time hr	Time min	Temperature °C	Potential	Pb (mg)	Cd (mg)	Sn (mg)
1.	0.12758	0.12779	+0.21	0.35	60	1	30	35	-0.50	40	-	-
2.	0.10070	0.10079	+0.09	0.35	60	1	30	35	-0.50	40	-	-
3.	0.10649	0.10679	+0.30	-	100	1	10	40	-0.50	50	100	-
4.	0.10089	0.10133	+0.44	-	100	1	15	40	-0.50	50	100	-
5.	0.10168	0.10206	+0.38	-	100	1	15	40	-0.50	50	1.0g	1.0g

Table 5.7

Deposition of bismuth at mercury cathode

	Weight Bi Taken (g)	Weight Bi in Residual Solution (mg)	In Added (mg)	Time hr	Time min	Temperature °C	Current Max (mA)	Current Min (mA)
1.	0.10471	50	-	1	0	20	100	12
2.	0.10080	0.75	-	1	15	26	200	12
3.	0.09987	0.3	-	1	5	35	300	9
4.	0.31048	0.45	-	1	30	25	200	6
5.	0.21662	0.3	-	1	15	35	320	6 *
6.	0.10062	(0.2)	100	1	25	35	200	15
7.	0.10130	(0.7)	100	1	15	39	300	6
8.	0.10000	(0.4)	100	2	0	38	230	10
9.	0.10000	(0.5)	100	2	0	38	400	15
10.	0.10000	0.3	-	2	0	38	300	8

* + 0.2mg before finish of electrolysis

Chapter VI

Lead and Cadmium

Cathodic deposition of lead has never been popular for the determination of lead, owing to the ease of oxidation of the cathodic deposits on washing. From tartrate solution, Lingane (40) found that deposition was virtually complete as polarographic analysis of residual solution showed only traces of lead, but considerable redissolution took place during washing. This redissolution occurred entirely whilst electrolyte was being washed off the electrode. Dried lead deposits, when washed with water, showed no change in weight and wash liquids revealed no traces of lead. Lingane and Jones (44) found that lead deposited virtually completely onto bismuth or copper-coated cathodes at pH4 to 5 at a potential of -0.50V to -0.60V vs SCE from tartrate solution and again found that a loss was always incurred on washing. They obtained a mean error of 1.5±0.6mg and stated that this error was "sufficiently reproducible so that it can be added as a correction to obtain lead results which generally will be correct to well within 1mg".

To test the truth of these statements we deposited lead following as closely as possible Lingane and Jones' conditions.

1) Lingane and Jones' Method

50mg of Matthey spectrographically analysed lead were weighed into a 250ml electrolysis beaker and covered with a watch glass. The lead was dissolved in hydrochloric/nitric acid mixture

in the usual way. 50ml of 0.5M sodium tartrate and 2g of hydrazine dihydrochloride were added, the pH adjusted to 5 and the volume made up to 200ml with distilled water. The lead was deposited on a copper-plated gauze cathode of 120 sq cm area at a potential of -0.60V vs SCE at room temperature using fairly vigorous stirring. The current underwent a normal diffusion-type decay and electrolysis was continued for about 15 minutes at the residual current ($\sim$10mA). Total electrolysis time was about 45 minutes. At the finish of the electrolysis, without breaking the current, the cathode was raised and washed simultaneously with a jet of water. It was then removed, rinsed successively in beakers of water and acetone, dried at 110°C for 2 minutes, cooled and weighed. Results given in Table 6.1 (p.95) show very low recoveries of lead. In determination 1, stirring was fairly slow and the deposit did not completely cover the copper coating. In 2, stirring was vigorous and plating was uniform, hard, and dull grey in colour.

We consider the correction of Lingane and Jones too imprecise for use in accurate analysis. The loss on washing must depend largely on manner of washing which will vary considerably. In our opinion, even their own results do not wholly support it.

Assuming with Lingane and Jones that the loss occurred entirely during washing, we examined the literature to find other answers to this problem. A time-honoured method is to neutralize the solution with ammonia prior to washing. Results using this technique are described on p 80 However, Alfonsi (1), finding

this tedious and open to the danger of changing the conditions by adding an excess, found it sufficient to deposit lead from ammonium tartrate solution just acid at pH5.2-5.4. His work closely followed that of Lingane and Jones merely substituting ammonium hydroxide and ammonium salts for caustic soda and sodium salts. His results are remarkable. In addition he used his own washing procedure. This consisted of just removing the reference electrode at the finish of the electrolysis with the current still flowing, then washing the electrode as it was removed from the solution with a jet of water containing one drop of concentrated ammonia (0.88) per litre, and finally washing with a spray of acetone, i.e. the rinse in a beaker of water was omitted.

2) Alfonsi's Method

Lead was determined following Alfonsi's conditions and washing procedure (results in Table 6.2). The solution was prepared by dissolving 50mg of lead in hydrochloric/nitric acid mixture, adding 0.5M tartaric acid and adjusting the pH with diluted (1 + 1) ammonium hydroxide to 5.2. The final volume was made up to 200ml. The solution was electrolysed with a copper-plated cathode of 120 sq cm area at a potential of -0.60V vs SCE at room temperature. The current followed the normal diffusion-controlled pattern and electrolysis was continued for 15 minutes at the residual current ($\sim$ 10mA). At the finish of the electrolysis according to Alfonsi's method, the reference electrode was first removed, then the cathode, with simultaneous washing with a very slightly ammoniacal water solution.

The cathode was finally washed in a beaker of acetone, dried and weighed. Before the finish of each electrolysis an aliquot (say 25ml) was pipetted from the solution and analysed polarographically for traces of lead. Residual solutions and washings were saved and also analysed for lead.

In determinations 6, 7 and 8 (see Table 6.2), lead was deposited in the presence of 100mg of indium at -0.60V vs SCE. No adverse effects of the type encountered with bismuth were noted, the separation being clean and the results for lead unaffected.

The results given in Table 6.2 clearly support Lingane's contention that lead is completely deposited to within 0.1mg during the electrolysis and that a loss occurs during washing. In this instance the loss was up to 1mg. However, the loss by weight was always considerably less, often to within 0.5mg. The weighed deposits must contain oxygen or electrolyte to account for the weight difference. The large amount of lead found in residual solutions after washing suggests that the type of electrolyte has very little effect on the rate of loss. To confirm this we determined lead from sodium tartrate solution as in section (1), but used Alfonsi's washing procedure. Table 6.3 shows practically identical results were obtained. Hence the good results that Alfonsi obtained must be due to the presence of unwashed electrolyte or perhaps slight oxidation of the deposit during drying, from the action of this trace of electrolyte in air. We are strengthened in this belief by the fact that some of Alfonsi's results show slightly high recoveries and

although other reasons might be found for this, e.g. slight co-deposition of other metals, 'insufficient' washing is probably a major cause.

In general, our results were not nearly as good as Alfonsi's; hence 'good' recovery depends on the operator. We therefore feel we cannot recommend this method for work with any pretensions to accuracy.

3) Making Solution Ammoniacal

In a final effort to improve recovery, we tried the time-honoured method of neutralizing with ammonia to pH7 prior to the completion of electrolysis. Lingane (39) found the polarographic half-wave potential for lead in tartrate at pH4.5 to be 0.48V vs SCE and this changed by only -0.02V to -0.50V at pH9. Under the more irreversible conditions involved in the deposition of lead onto a copper-plated cathode, it is possible that the deposition potential will increase in a negative direction more rapidly with pH. Thus it is advisable to keep the pH below 9.

The electrolysis solution was made up as in section (1). The amount of ammonia required was found by adding 4N ammonium hydroxide to 200ml of an 0.25 tartrate solution at pH4.5. We found this to be about 2ml. Lead was electrolysed in tartrate at pH4.5 as described previously at -0.60V vs SCE at room temperature, but just prior to the end of the electrolysis 2ml of 4N ammonium hydroxide were added. The cathode was removed immediately with simultaneous washing, the current was switched off and the electrode washed in acetone, dired and weighed. Measurement of the pH of residual

solutions showed it to be less than 7.5.

Results given in Table 6.4 show that in our hands this modification effected no improvement in recovery.

We decided to investigate the possibility of plating a protective coating of a known weight of another metal onto lead. Work was done on the deposition of cadmium and of copper.

4) Plating with Cadmium

Lingane (43) had reported excellent results for the determination of cadmium when depositing it onto a lead-coated cathode from a strongly ammoniacal solution containing gelatin. As many of the alloys for which this work is intended contain cadmium, the possibility of protecting the lead deposit with a deposit of cadmium was, naturally, first investigated. If quantitative recovery of cadmium was obtained, it might be possible to deposit cadmium onto lead without interruption of the electrolysis and subsequently determine one or the other by an alternative method. Thus it was with this in mind that this investigation of the deposition of cadmium was conducted.

i) Plating of cadmium onto copper-plated electrodes

To investigate Lingane's method we first studied the deposition of cadmium onto copper-plated cathodes.

Procedure

100mg of Matthey spectrographically analysed cadmium were weighed into a 250ml beaker and dissolved in hydrochloric/nitric acid in the usual way. 50ml of M sodium tartrate, 1g of hydrazine dihydrochloride and 20mg of gelatin (in aqueous solution) were added and

the pH adjusted to about 5 with 2N sodium hydroxide. 25ml of concentrated aqueous ammonia (0.88) were added and the volume made up to 200ml with water. The solution was electrolysed using a copper-plated cathode of 120 sq cm area. Fairly vigorous stirring was maintained with a mechanical stirrer. Lingane states that the current density should not exceed 0.01 amp per sq cm to avoid formation of loose deposits and does this by limiting the potential at the beginning of the deposition to -1.0V vs SCE. However, when using copper-plated cathodes it was found that no deposition of cadmium started when the potential was set to give an electrolysis current of 1.2 amps. It was necessary to raise potential sufficiently to give a current of 1.5 amps to induce the deposition of cadmium. At this current a uniform layer of cadmium, completely covering the electrode, is quickly formed and the rate of hydrogen evolution decreases owing to the greater overpotential of hydrogen on cadmium than on copper. Immediately this cadmium layer had been formed (about 1 minute's electrolysis) the potential was reduced to -1.0V vs SCE which gave a current of about 1 amp. The current then followed a normal diffusion-controlled pattern, but residual currents were very high, about 400mA. On reading the residual current the potential was raised to -1.15V vs SCE and electrolysis continued for a further 15 to 30 minutes. Throughout the deposition there was considerable simultaneous evolution of hydrogen.

At the finish of the electrolysis, the cathode was removed from the solution with simultaneous washing, rinsed in acetone, dried

at 110°C for 2 minutes, cooled and weighed (i.e. Alfonsi's procedure). The electrolyte and washings were examined colorimetrically (p.91). for traces of cadmium. Results are given in Table 6.5.

As can be seen, apparent recoveries of cadmium are nearly always very good, but analysis of washings reveal a considerable loss. This led us to suspect that the weighed deposit contained appreciable amounts of gelatin, particularly as the electrolyte becomes very frothy during the electrolysis and this froth requires much rinsing with a strong jet of water to remove completely from the electrode. After determination 3 to 5, the dried cathodes were stood in boiling water for about 10 minutes. The water was then evaporated to small volume on the steam-bath and the presence of gelatin tested with tannin. Significant amounts of gelatin were found. Hence cadmium, though it is deposited completely, undergoes considerable dissolution during washing as in the case of lead. Apparently good recoveries are probably accounted for by the presence of appreciable amounts of gelatin in the deposit.

In determination 5, the electrolysis was allowed to continue overnight. Often electrolysis over a long period of time gives a harder deposit (cf 'slow' method for copper); however, in the case of cadmium under these conditions no differences were noted.

ii) Deposition of cadmium on lead. (Table 6.6)

To study the effects of depositing cadmium on lead, solutions were made up by dissolving 50mg of lead and 100mg of cadmium in hydrochloric/nitric acid in 250ml beakers. After the addition

of tartrate and hydrazine dihydrochloride, the pH was adjusted to 4.5 with 2N sodium hydroxide. The volume was made up to 200ml. Gelatin was added to the solution at the beginning of the determinations so that lead was depsoited in its presence. Lead was deposited at a potential of -0.60V vs SCE. After about 45 minutes, when the residual current (about 10-20mA in the presence of gelatin) had remained steady for about 15 minutes, 25ml of 0.88S.G. aqueous ammonia were added and the potential simultaneously raised to -1.0V vs SCE. The potentiostat was altered to accommodate the new current which was about 0.8 to 1 amp. Cadmium deposited immediately upon the lead deposit giving a bright and even coating. As before there was considerable evolution of hydrogen. Electrolysis continued for about half an hour at -1.0V whence the current had fallen to a residual value of about 400mA, then the potential was raised to -1.14V vs SCE and electrolysis continued for a further half-hour. Aliquots of the residual solution were analysed colorimetrically before and after washing. The deposits were washed, dried and weighed as given.

In determinations 10 and 11 (see Table 6.6), the deposited metals were stripped with diluted (1 + 2) nitirc acid and the lead content determined subsequently by EDTA titration. These titrations showed that virtually all the lead had been deposited on the cathode and that none was lost during the deposition of cadmium.

The results for these determinations (Table 6.6) show exactly the same behaviour as when copper-plated cathodes were used. Although recoveries were apparently good, losses of up to 0.7mg of

cadmium occurred during washing. This difference in weight was probably made up by gelatin. In determination 11, the electrode was rinsed thoroughly in a beaker of water to attempt to remove all traces of electrolyte. The result obtained shows a much closer correspondance between loss by weighing and loss determined colorimetrically.

In our opinion, the loss of cadmium is too great for this method to be recommended for the protection of lead or for the determination of cadmium in accurate analyses. However, the method would be quite suitable in routine work.

iii) Deposition of cadmium in the presence of indium

Results in Table 6.7 show recoveries of cadmium deposited in the presence of 100mg of indium from 200ml of solution onto a lead-coated cathode of 120 sq cm area. The apparent weight of cadmium was always high (1 to 8mg). The deposits were stripped with nitric acid and analysed colorimetrically for indium. Sufficient indium was found in each case to account for nearly all of the increase in weight. As indium itself does not deposit under these conditions, some alloy formation must occur.

5) Plating the Lead with Copper

Following the relative lack of success with cadmium, the possibility of protecting lead with a deposit of copper was investigated.

We first added a solution of cupric chloride containing about 10mg of copper at the end of a deposition of lead at -0.60V vs SCE.

The current rose sharply to over 200mA and black dust, found to be mainly cupric oxide was deposited at the cathode. This could be easily brushed off the cathode and much of it fell spontaneously to the bottom of the electrolysis beaker. Copper deposited in a similar manner when a tartrate solution at pH4.5 was electrolysed at -0.60V vs SCE using a platinum cathode.

A search of the literature showed that Diehl and Craig(15) had deposited copper onto platinum from M ammonium hydroxide at -0.73V vs SCE. We decided to attempt the deposition of copper onto lead from ammoniacal solution. Lingane had shown that the polarographic half-wave potential for lead became only -0.02V more negative when the pH was altered from 4.5 to 9, and according to Alfonsi, at pH6.3 to 8, cadmium starts to deposit at -0.80V vs SCE. Thus the potential for the deposition of copper can be up to -0.70V without fear of co-deposition of cadmium at these pH. At higher pH there may be a danger of co-deposition of copper and cadmium, since the deposition potential of lead rises sharply with pH beyond 9. Hence the potential for the deposition of copper would have to be raised.

In determination 1 (see Table 6.8), lead was deposited as usual from tartrate at pH4.5 at -0.60V vs SCE onto a cathode of 120 sq cm area. At the end of the lead electrolysis a solution containing 10mg of copper and sufficient ammonium hydroxide to bring the pH of the electrolyte to 8 was added from a tap funnel. The potential was simultaneously raised to -0.70V vs SCE. Although the copper deposit was very much improved in appearance, it was still

very dark, powdery and could be wiped off with a finger. The recovery by weight was high. In determination 2, a similar result was obtained at pH9.

Since gelatin markedly improves the character of the cadmium deposit, its effect on the deposition of copper was studied. In the first trial deposition (see Table 6.9) 10mg of gelatin were added to the lead electrolyte before the deposition of lead. At the finish of the lead deposition, a solution containing 10mg of copper and sufficient NH_4OH to bring the pH of the electrolyte to 8 was added from a tap funnel. The cathode potential was raised simultaneously to -0.75V vs SCE. The electrolysis current for the copper followed a normal diffusion-controlled decay, reaching a residual current of about 40mA after 15 minutes. After a further 15 minutes' electrolysis, the cathode was removed from the solution with simultaneous washing. During the depositions the solution becomes very frothy and care was taken to see that all the froth was washed off the electrode in this first wash. The current was then switched off and the electrolysis beaker replaced by a beaker of distilled water. The stirrer was rotated at high speed to scour as far as possible all electrolyte from the electrode. The electrode was then rinsed in acetone, dried and weighed in the usual manner. The deposit was hard, with a deep bronze colour, but recovery was about 0.7mg high. Most of this increase in weight was probably due to the deposition of some oxide, as special care had been taken to remove gelatin as completely as possible. In the

second trial deposition, copper was deposited at -0.70V and 10mg of gelatin were added with the copper solution. However, the deposit was soft and powdery. Clearly gelatin must be added well in advance of the deposition of copper.

To reduce the deposition of oxide, the effect of changing pH was studied. In determination 3, copper was deposited at 0.70V at pH4.5, i.e. without altering the pH after the deposition of lead. A very much improved recovery was obtained. In 4, deposition of copper was at -0.65V and pH4.5 with a further slight improvement. The deposits were hard, even and bronze coloured. In 5, deposition of copper was started at -0.60V vs SCE. No increase in current was observed and after 10 minutes the cathode showed black specks on the lead surface. On increasing the potential to -0.65V the durrent increased to 120mA and decayed normally. The recovery of lead plus copper was very low (about 3mg short). However, colorimetric analysis of the residual solution showed only traces of copper (0.2mg). Hence at a potential -0.60V vs SCE in tartrate solution at pH4.5 lead will tend to dissolve off the electrode in the presence of copper ions. Thus it is essential for good recoveries that the potential of the cathode be raised to the required value as soon as or just before the addition of copper ions.

Determinations 6 and 7 show results taking the precaution outlined, depositing copper at -0.65V from 0.25M tartrate at pH4.5 in the presence of 10mg of gelatin. Results were rarely greater than 0.3mg high. We consider this to be quite acceptable.

Analysis of the residual solution after washing from determination 6 showed only traces of copper ($\sim$ 0.2mg).

We can offer no explanation as to why gelatin should have this beneficial effect. Possibly gelatin is adsorbed on the lead surface increasing the overpotential of the copper deposition or perhaps a copper-gelatin complex is formed in the cathode layer.

i) Deposition of copper in the presence of cadmium and tin

Table 6.10 shows recoveries for lead plus copper under the conditions used in determinations 6 and 7 showing little or no interference from the presence of cadmium and tin.

ii) Deposition in the presence of indium

Table 6.11 shows results for the deposition of lead plus copper in the presence of indium. Recoveries are over a milligram or more high. Since it was shown that indium did not affect the deposition of lead, some alloy formation must occur during the deposition of copper. Thus this method cannot be used in the presence of indium.

SUMMARY

Lead can be coated in the presence of cadmium and tin with a deposit of copper, recovery for lead plus copper being within +0.3mg, provided that

1) at least 10mg of gelatin are added to 200ml of the electrolyte well before the addition of copper, preferably

before the deposition of lead;

2) the cathode potential is increased to -0.65V vs SCE and no further immediately before the addition of copper solution;

3) deposits are washed thoroughly to remove gelatin as completely as possible;

and 4) indium is absent.

Chapter VI : Appendix 1.

Determination of traces of lead, cadmium, indium and copper

i) Lead

As with bismuth, it was found impossible to determine lead in residual solution directly with the polarograph. However, successful polarograms in the presence of indium were obtained using Jones and Basher's (29) method. In this, organic matter is destroyed by wet oxidation in the presence of sulphuric and perchloric acid and lead is determined in the resulting sulphate solution. The half-wave potential and the size of the diffusion currents depend on the viscosity of the solution. The original method involves a titration procedure to determine viscosity. We felt it was sufficient for our purposes to eliminate this. Lead was determined polarographically at pH3 from the sulphate solution, the concentration of sulphate being kept as constant as possible. 2ml of sulphuric acid were added for the oxidation of organic matter and fuming was kept to a minimum. The lead waves obtained were nearly swamped by a large and diffuse wave for indium, but a sufficiently large limiting diffusion current plateau was obtained for lead to enable measurements to be made.

ii) Cadmium

At pH13 only cadmium is extracted by dithizone in carbon tetrachloride. The method of Fischer and Leopoldi (17) as given by Sandell (61) was used.

iii) Indium

Indium was extracted free from cadmium by ether from iodide solution. It was then subsequently determined colorimetrically by extraction with 8-hydroxyquinoline in chloroform by the method of Irving et al (26).

iv) Copper

Copper was determined with bis-cyclohexanone oxalyldihydrazone. The method given in "Organic Reagents for Metals" published by Messrs Hopkin and Williams (25) was followed. Only very small aliquots of the electrolyte could be taken, otherwise the amount of tartrate present greatly extinguished the colour. This made the method rather insensitive, but it was considered sufficient for the need here.

Chapter VI : Appendix 2.

Determination of lead in the presence of cadmium and copper by EDTA titration

A method supplied by Dr J.A. Clements (9) was used. To a solution of lead, cadmium and copper in nitric acid were added 2ml of 60 per cent perchloric acid. The solution was taken to fumes of perchloric acid, cooled and diluted to 75ml. 0.5g of Rochelle salt was added and the pH adjusted with 5M NaOH to neutral (litmus). 2ml of an ammonia-ammonium chloride buffer, made by dissolving 65g of ammonium chloride in water, adding 570ml of 0.88S.G. aqueous ammonia and diluting to 1 litre, were added, followed by 2g of solid potassium cyanide and 2.5g of solid ammonium chloride. The solution was diluted with a further 25ml of water. 10 to 12 drops of a 3 per cent solution of magnesium sequestrate in water were added and 5 to 6 drops of Eriochrome Black-T indicator. This was prepared by dissolving 0.2g of the dye in 5ml of dry isopropyl alcohol and 15ml of triethanolamine.

The following observations were made:

1) The concentration of copper must be kept as small as possible, otherwise the yellow colour from $Cu(CN)_4^{3-}$ ions will mask the end-point. This colour can be removed to a certain extent with ascorbic acid.

2) The concentration of cyanide does not affect the sharpness of the end-point.

3) The concentration of tartrate must be kept to the minimum necessary to keep lead in solution, otherwise the sharpness of the end-point is seriously diminished.

4) It was found necessary to have a comparison solution to determine the colour change, mauve to blue, accurately.

5) The indicator lasts only about one day when made up in water. Indicator made up as described with perfectly dry reagents was found to be stable for at least three months.

Table 6.1

Deposition of lead at pH5.1 : Lingane and Jones' method

	Weight Pb Taken (g)	Weight Pb Found (g)	Difference (mg)	Time hrs	Current Max (mA)	Current Min (mA)	Temperature
1.	0.05133	0.04948	1.85	1	400	40	20
2.	0.05457	0.05263	1.94	1	400	15	20

Table 6.2

Deposition of lead at pH5.2-5.4 : Alfonsi's method

	Weight Pb Taken (g)	Weight Pb Found (g)	Difference (mg)	1*	2*	Time hr	Time min	Potential V vs SCE	
3.	0.05907	0.05869	-0.38	0.1	-	1	0	-0.60	
4.	0.05907	0.05847	-0.60	0.1	-	1	0	-0.60	
5.	0.05081	0.05009	-0.72	0.1	0.9	0	45	-0.60	
6.	0.06146	0.06105	-0.41	0.1	0.6	0	45	-0.60	**
7.	0.05377	0.05301	-0.76	0.1	0.9	0	45	-0.60	**
8.	0.05599	0.05560	-0.39	0.1	0.7	0	45	-0.60	**

1* Weight Pb found before finish of electrolysis (mg).

2* Weight Pb found in residual solution and washings (mg).

** + 100mg In.

Table 6.3

Deposition of lead at pH4.5 : washing by Alfonsi's procedure

	Weight Pb Taken (g)	Weight Pb Found (g)	Difference (mg)	Time mins	Potential V vs SCE
9.	0.04960	0.04914	0.46	45	-0.60
10.	0.05099	0.05047	0.52	45	-0.60
11.	0.05369	0.05312	0.57	45	-0.60

Table 6.4

Deposition of lead : neutralization with ammonia

	Weight Pb Taken (g)	Weight Pb Found (g)	Difference (mg)	Time mins	pH	Potential V vs SCE
12.	0.05282	0.05214	0.68	45	4.5	-0.60
13.	0.04991	0.04949	0.42	45	4.5	-0.60

Table 6.5

Deposition of cadmium on copper by Lingane's method

	Weight Cd Taken (g)	Weight Cd Found (g)	Difference (mg)	1*	2*	Time hr min	
1.	0.10109	0.10059	-0.50	0.01	0.7	1 0	
2.	0.12100	0.12106	+0.06	0.01	0.6	1 15	
3.	0.11709	0.11608	-1.01	0.01	1.4	1 30	
4.	0.10059	0.10043	-0.16	0.01	0.5	1 30	
5.	0.11791	0.11768	-0.23	0.01	0.5	16 0	Overnight

1* Weight of Cd before finish of electrolysis (mg).

2* Weight of Cd found in residual solution and washings (mg).

Table 6.6

Deposition of lead and cadmium by Lingane's method

	Pb Taken (g)	Cd Taken (g)	Cd and Pb Taken (g)	Cd and Pb Found (g)	Difference (mg)	1*	2*	Time Hr min	Pb by EDTA
6.	0.05671	0.10879	0.16550	0.16501	-0.49	0.01	0.75	1 30	-
7.	0.05907	0.13642	0.19549	0.19492	-0.57	0.01	0.6	1 30	-
8.	0.05730	0.11548	0.17278	0.17208	-0.70	0.01	0.7	1 30	-
9.	0.05437	0.05469	0.10906	0.10895	-0.11	0.01	0.7	2 00	-
10.	0.05670	0.05035	0.10705	0.10721	+0.16	0.01	0.5	2 00	0.05663
11.	0.05288	0.05035	0.10323	0.10258	-0.65	0.01	0.7	2 00	0.05287

1* Weight Cd before finish of electrolysis (mg).

2* Weight Cd in residual solution and washings (mg).

Table 6.7

Deposition of lead and cadmium in presence of indium

	Weight Pb Taken (g)	Weight Cd Taken (g)	Weight Cd and Pb Taken (g)	Weight Cd and Pb Found (g)	Difference (mg)	1*	2*	Time hrs	Weight In Taken (mg)	Weight In Found in Cd Deposit (mg)
12.	0.05391	0.11640	0.17031	0.17126	+0.95	0.05	0.3	2	100	0.8
13.	0.05978	0.11354	0.17332	0.18153	+8.21	0.05	0.2	$2\frac{1}{2}$	100	7.7
14.	0.05759	0.09990	0.15749	0.16412	+6.63	0.05	-	16	100	5.2

1* Weight Cd before finish of electrolysis (mg).

2* Weight Cd in residual solution and washings (mg).

Table 6.8

Deposition of copper on lead at pH8 to 9

	Weight Pb Taken (g)	Weight Cu Taken (g)	Cu and Pb Taken (g)	Cu and Pb Found (g)	Difference (mg)	pH
1.	0.05035	0.01040	0.06075	0.06260	+1.85	8
2.	0.05171	0.01012	0.06183	0.06472	+2.89	9

Table 6.9

Deposition of copper on lead in presence of gelatin

	Weight Pb Taken (g)	Weight Cu Taken (g)	Cu and Pb Taken (g)	Cu and Pb Found (g)	Difference (mg)	pH	Potential of Cu Deposition	
1.	0.05029	0.00989	0.06018	0.06090	+0.72	8	-0.75V	
2.	0.04908	0.01140	0.06048	0.06110	+0.62	8	-0.70V	
3.	0.05360	0.01048	0.06408	0.06449	+0.41	4.5	-0.70V	
4.	0.04750	0.01013	0.05763	0.05780	+0.17	4.5	-0.65V	
5.	0.05610	0.01070	0.06680	0.06372	-3.08	4.5	-0.60V to -0.70V	0.2mg Cu in residual solution
6.	0.05480	0.00968	0.06448	0.06438	-0.10	4.5	-0.65V	0.2mg Cu in residual solution
7.	0.00980	0.01078	0.02058	0.02080	+0.22	4.5	-0.65V	

Table 6.10

Deposition of copper on lead in presence of cadmium and tin

	Weight Pb Taken (g)	Weight Cu Taken (g)	Cu and Pb Taken (g)	Cu and Pb Found (g)	Difference (mg)
9.	0.04910	0.00951	0.05861	0.05888	+ 0.19 *
10.	0.05060	0.00970	0.06030	0.06057	+ 0.27 **

* + 100mg Cd.

** + 300mg Cd + 300mg Sn.

Table 6.11

Deposition of copper on lead in presence of indium

	Weight Pb Taken (g)	Weight Cu Taken (g)	Cu and Pb Taken (g)	Cu and Pb Found (g)	Difference (mg)	Weight Sn (g)
11.	0.05382	0.01068	0.06450	0.06638	+1.88	100
12.	0.05629	0.01140	0.06769	0.06870	+1.01	100

PART II

ANODIC DISSOLUTION OF CADMIUM FROM AN AMALGAM

1) Introduction

In Part I methods have been evolved for the accurate determination of bismuth and lead. However, the results obtained for cadmium by cathodic deposition were acceptable only for routine determinations. The loss on washing precluded results of the highest accuracy. It might be possible to protect cadmium with a coating of another metal, as in the case of lead, e.g. by deposition of copper from cyanide solution, but the co-deposition of indium would limit its applicability. It was decided, therefore, to make a different approach to the problem.

The mercury cathode is less prone to loss of deposited metals on washing, principally on account of its smaller surface area. Theoretically it is possible to determine the amount of deposited metal by weighing the amalgam, but the practical difficulites are very great. However, dilute amalgams can be decomposed electrolytically. Thus it should be possible either to remove metals successively at controlled cathode potential and then dissolve them individually in an appropriate solution for their determination, or to deposit metals simultaneously without cathode potential control and dissolve them successively at controlled anode potential.

The latter course was chosen for cadmium, first because it is simpler and faster to deposit metals without potential control at the mercury cathode, and second because cadmium is the most electronegative of the metals studied and dissolves first at controlled-anode potential. The separation of cadmium from bismuth, lead, tin and indium by this means has been studied.

2) Previous Work

Although the mercury cathode has been used to a considerable extent for the separation of metals by electro-deposition, much less use has been made of the amalgams formed for the subsequent analysis of the separated metals.

Direct measurements on amalgams include electro-gravimetry which has not been popular since the early years of the century for practical reasons. More recently, the concentration of metals in amalgams has been determined by electrical-resistance measurements and fission products have been determined by measuring the radio-activity of the amalgam formed at a dropping mercury electrode, the drops being collected for a suitable period of time and then 'counted' (46). Voltammetric methods, etc. for measuring the concentration of amalgams are considered separately below.

Various procedures have been suggested for the non-electrolytic decomposition of amalgams, e.g. decomposition with oxidizing agents, acid leaching, dissolution of the amalgam in nitric acid and precipitation of elementary mercury with formic acid, and removal of mercury by distillation (53). The metals recovered by such procedures were determined either from the amount of oxidizing agent used for the decomposition or by standard analytical procedures such as absorptiometry, polarography and titration. Objections have been raised to decomposition with oxidizing agents or acids by Bricker who found that either there was incomplete removal of the metal or sufficient mercury was introduced to make subsequent determinations

difficult. Cadmium and mercury cannot be separated by distillation, as cadmium is appreciably volatile.

The electrolytic decomposition of amalgams received little attention until the early fifties. Up to that time some polarographic studies had been made on dropping amalgam electrodes, notably by Lingane (38), Heyrovsky (22), and Furman and Cooper (18) They found that the currents obtained were controlled by the rate of diffusion of the metal in the amalgam to the amalgam-solution interface. Although it was theoretically possible to determine the concentration of amalgams by polarographic measurement of the anodic currents, the practical difficulties involved in setting-up a dropping amalgam electrode precluded the development of the method as a means of analysis. However, much useful information was obtained, such as anodic half-wave potentials, degree of reversibility of electrode reactions, diffusion coefficients and diffusion layer thicknesses in mercury, and the condition of the metals in simple and multicomponent amalgams.

Kozlovskii et al(35,36)published the first papers in 1950 on the electrolytic decomposition of amalgams formed at mercury pool electrodes and have since published a series of studies on amalgams containing copper, bismuth, tin, indium, thallium, cadmium and zinc, individually and in various combinations. For cadmium amalgams they found that the reversible electrode potential became more negative with increasing acidity and concentration of the amalgam and determined a relationship between the amalgam potential and the current

density for the anodic decomposition of cadmium amalgams in sulphuric acid. Procedures were published for the separation of up to 16mg of cadmium by deposition at a mercury cathode and subsequent electrolytic decomposition of the amalgam at constant current (79).

Rogers (56) has derived a set of equations for equilibrium distribution of a metal between the aqueous and mercury phases as a function of the amalgam potential, the polarographic half-wave potential and the volume ratio of the phases. Rogers and Merritt (57) have tested these equations for the separation of thallium from cadmium. Coriou et al (11) have made a study of the anodic decomposition of various dilute ($< 10^{-3}$M) amalgams in sulphuric acid with particular attention to the completeness of decomposition and the behaviour of the anode potential as a function of current density at currents which are low compared with the limiting diffusion current. Hickling and Maxwell (23) have studied diffusion currents in various amalgams over a wide range of metal concentrations and with Shennan (24) have evolved an anodic polarographic method for determining the concentrations of amalgams (10^{-4} to 10^{-6}M) by measuring the limiting diffusion currents obtained at a small mercury pool electrode. Porter and Cooke (54) have studied the nature of the electrolytic decomposition of dilute (10^{-4}M) amalgams (a) at constant current and (b) at constant potential. It was found that the decomposition of a cadmium amalgam at constant current under the conditions of their experiments was not reversible in that there was a "non-polarization contribution to the overpotential". Losev and Khopin (45), using radio-active

indicators, found an exponential relationship between the rate of the anodic process for a cadmium amalgam and the potential. A number of workers (54, 63) have found that passive metals such as cobalt and nickel cannot be completely extracted from dilute amalgams before the onset of mercury dissolution.

Taylor and Smith (75), Schmidt and Bricker (63), and Scacciati and D'Esti (62) have each published procedures in which dilute amalgams were decomposed electrolytically at controlled-anode potential into acid solution and the separated metals (up to 5mg) subsequently determined polarographically.

Meites (50) has suggested that very small amounts of metal ($\sim 0.1\mu g$) are more accurately determined coulometrically by electrolytic decomposition of an amalgam at controlled potential as the 'background' corrections involved are smaller. Mountcastle et al (51) determined up to 10mg of indium coulometrically with a mean error of $\pm$0.01mg by decomposing an indium amalgam in hydrochloric acid at -0.50V vs SCE.

Within recent years a large amount of work has been done on the determination of metals in very dilute solutions (down to 10^{-8}M) by electrolysis with a Hanging Mercury Drop Electrode and subsequent electrolytic stripping of the amalgam using a variety of techniques, particularly chronopotentiometry.

Comprehensive reviews are given by Shain (65), and Kemula and Kublik (30). However, this work lies well outside the scope of the present study, as the amalgams formed are very much more dilute, the techniques used for measuring the concentration apply only to very

dilute amalgams and the small size of the electrode usually necessitates 'non-stoichiometric' deposition of the metal ions in the pre-electrolysis step.

In the present study the aim has been to prepare and decompose quantitatively amalgams having a cadmium concentrations of about 5 x 10^{-2}M. This is very much more concentrated than in most previous work. Only Hickling and Maxwell (23) have determined limiting diffusion current densities in amalgams of this concentration. Hence this is a novel application of this technique and conditions have been evaluated for handling such concentrated amalgams.

3) Preliminary Cathodic Deposition

i) Apparatus

The cathodic deposition of bismuth, lead, cadmium, tin and indium was carried out at constant current without applied stirring. The electrolysis vessel was a 250ml beaker, covered with a perspex cover. The volume of mercury used for the cathode was kept to the minimum required to cover the bottom of the beaker (15-20ml) and surface area of the cathode was about 20 sq cm. External connection was via a short length of platinum wire sealed in a glass tube. The anode was a platinum wire helix of 3 cm diameter. The electrolysis current was supplied from the mains via a simple power pack or the electrolysis current supply circuit of the potentiostat. The beaker was normally mounted on the magnetic stirrer in readiness for the redissolution. The arrangement is similar to that encountered in Chapter V without stirring bar or reference electrode.

ii) Effect of current density and temperature

Herringshaw and Kassir (21) have shown that there is a considerable increase in the rate of deposition of a metal over the rate obtained in controlled-potential electrolysis when the current density is sufficiently high to cause simultaneous evolution of hydrogen. They attribute this increase almost entirely to a stirring effect by the hydrogen gas bubbles, i.e. to a much greater rate of diffusion. Applied stirring was found to have little effect on rate of deposition at controlled current when there was vigorous hydrogen evolution. Their results show that continued increase in the rate of hydrogen evolution has progressively less effect on the rate of metal deposition as would be expected for a stirring effect. Thus there is little advantage in increasing the current density beyond 10^{-1} amp/cm^2 when electrolysing a solution of about 10^{-2}M at a cathode of 1.13 sq cm area. The rate of metal deposition was found to be dependent on the cell geometry, as hydrogen was preferentially evolved round the circumference of the electrode, i.e. the rate of metal deposition per unit area decreased with increasing surface area for a circular cathode as the ratio of circumference to area decreases with increasing area. Thus for a circular cathode of about 20 sq cm, as used in this work, the rate of metal deposition per unit area was about 2 to 3 times slower than the rate on the cathode of 1.13 sq cm at the same current density. Thus considerably higher current densities would have to be used with the larger cathode to obtain an 'optimum' rate of metal deposition. However, it is impractical to

increase the current much above 5 amp under the experimental conditions of this work, i.e. electrolyte volume 100ml, cathode area 20 sq cm, otherwise there would be excessive heating of the electrolyte.

It was decided to use an electrolysis current of 3.5 amp. Since the concentrations of the electrolytes were up to 5×10^{-2}M, this is somewhat less than that required for an 'optimum' rate of metal deposition at the beginning of the electrolysis according to Herringshaw and Kassir's figures. However, as the electrolysis proceeds, the rate of hydrogen evolution will increase until an 'optimum' rate is reached. The time to reach this 'optimum' rate can be considerably reduced by increasing the temperature of the electrolyte. An initial temperature of about 60°C was used and this was kept fairly constant by the heating effect of the current.

iii) Effect of concentration of acid

The acids most widely used in constant current depositions at the mercury cathode are sulphuric and perchloric. Bock and Hackstein (5) have studied the separation from sulphuric acid of 20 elements, the concentration of the acid being varied over the range 0.05 to 3M. In general it was found that faster and more complete separations were achieved from solutions of low acidity (0.2M) and this has been confirmed by others (55) in investigations with one element or another.

In this work it was decided to use perchloric acid to keep lead in solution. In preliminary experiments with 100mg of high purity cadmium, lead and bismuth, as used in Part I, were dissolved

individually in dilute (1 + 2) nitric acid. The solutions were evaporated with 2ml of 60 per cent perchloric acid to fumes of perchloric acid, then diluted to 100ml with water to give solutions about 0.2M with respect to perchloric acid.

After electrolysis of the cadmium solution for 1 hour at 3.5 amp and 60°C, the residual electrolyte was found, by colorimetric analysis on an aliquot removed before breaking the current, to contain less than 0.1mg of cadmium. However, lead, and to a certain extent bismuth, was found to deposit in appreciable quantities as 'peroxide' on the anode. This is undesirable as it may occlude cadmium ion and it entails cleaning the anode before the redissolution of the amalgam. To prevent this hydrazine dihydrochloride was added as anodic depolarizer. The addition of 5g was necessary to prevent the evolution of chlorine during an electrolysis of 1 hour's duration at 3.5 amp. The addition of this amount of depolarizer introduces a considerable concentration of hydrochloric acid (1M) and hence a risk of decreasing the rate of metal deposition. However, trial deposition of cadmium from 0.2M perchloric acid containing 5g of hydrazine dihydrochloride at 3.5 amp and 60°C for 1 hour were complete to within 0.1mg.

Although it is best to strip the amalgam into the same electrolyte as used for the cathodic deposition, the presence of hydrazine dihydrochloride makes this undesirable. At the end of the deposition the electrolyte was removed by suction with the current still passing. The current was then switched off and the electrolysis

vessel and cathode washed once with a few ml of water. Colorimetric analysis of the residual electrolyte plus washings showed the presence of not more than 0.3mg of cadmium. This was just within the limits of accuracy desired. No doubt this could have been improved by modifications to the electrolysis cell, but it was desired that the apparatus should be as simple as possible and that the volume of mercury used should be kept to a minimum.

Similar results for cadmium were obtained in trial depositions from electrolytes containing in addition 100mg of lead, bismuth, tin and indium. No tests were made for the completeness of deposition of bismuth, lead, tin and indium as the electrolyte was removed at the end of the electrolysis.

Thus the following cathodic deposition procedure was used throughout this work:

The metals were dissolved in 10ml of diluted (1 + 1) hydrochloric acid containing 1 to 2ml of concentrated nitric acid in the electrolysis beaker covered with a watch glass. When dissolution was complete, the cover and sides were washed down and the mixture was evaporated with 1ml of perchloric acid to fumes of perchloric acid on a hot plate. The sides of the beaker were washed down with water and 5g of hydrazine dihydrochloride were added. After gentle warming the basic metal salts dissolved and the volume was made up to 100ml with water. The solution was then warmed to 60° to 70°C and about 20ml of mercury were added down the side of the beaker. External connections were made, the anode placed in the solution near the

cathode, the beaker covered and the electrolysis commenced at 3.5 amp. After about 45 minutes the cover and sides of the beaker were washed down with a few ml of water. After one hour, the electrolyte was removed by suction without interruption of current, the current switched off, and the amalgam and beaker washed once with a few ml of water, also removed by suction. The amalgam was then ready for the redissolution process.

4) Electrolytic Dissolution of Cadmium from an Amalgam

i) Apparatus

After the removal of the electrolyte used for deposition, 50 to 100ml of fresh electrolyte were added immediately for the electrolytic dissolution of cadmium. A stirring bar was added and a saturated calomel electrode with a vertical side arm. The cell arrangement was the same as in Chapter V. The tip of the reference electrode was placed so that it was just above the surface of the stirred amalgam. The potential of the amalgam differs from the potential set on the potentiostat on account of the iR drop between the tip of the reference electrode and the amalgam. However, in such a well-conducting electrolyte, this error was too small to be significant. The amalgam was stirred vigorously during the dissolution at about 300 r.p.m. At higher speeds the stirrer tended to get 'lost'. In a few determinations, mechanical stirring was tried with a 'paddle' type of stirrer as advocated by Lingane (42), but the solution and mercury became very 'churned up'. The magnetic stirrer gave very much smoother stirring.

A slight modification was needed to the potentiostat. If the amalgam was connected as a cathode at a potential more positive than the reversible amalgam potential, the potentiostat always reduced the electrolysis current to zero and attempted to decrease it further. This was because the potential of the amalgam was always attempting to attain its reversible value. Thus the 'error' voltage reduced the current and the current continued to decrease until the amalgam potential was equal to the reversible value. Conversely when the amalgam was connected as an anode, the current increased continuously. However, by reversing the leads between the potentiometer and the relays when the amalgam was connected as an anode, i.e. by changing the sign of the 'error voltage' as received by the potentiostat, the electrolysis current could be made to decrease to counteract any increase in the amalgam potential and control of the potential was possible. To facilitate this a reversing switch was incorporated in the leads between the potentiometer and the relays.

ii) Electrolyte

In preliminary experiments on the decomposition of 5×10^{-2}M cadmium amalgams, 100ml of 0.3M perchloric acid were used as electrolyte. The potential was controlled at about 0.05V more positive than the reversible amalgam potential. However, it was found that cadmium always deposited on the platinum cathode in a loose form. It was noted that drops of mercury were often thrown up from the amalgam surface, by the action of the stirring, and attached themselves to the cathode. It was thought that these may have had the effect

of increasing the cathode potential to a more negative value and although this may be so, cadmium still deposited on the platinum even when great care was taken to see that the cathode was kept completely free of mercury. Clearly in solutions of this composition the potential of the cathode was negative enough to allow the deposition of cadmium. It was decided to prevent this by increasing the acidity of the solution. An alternative would have been to isolate the cathode in a separate compartment, in contact with the main solution via a sintered disc. However, this would greatly increase the resistance of the cell and such compartments usually cause practical difficulties.

Perchloric acid was discarded as greatly increasing its concentration could lead to difficulties in removing the excess of acid in later stages of the analysis (see below). The most satisfactory acid for preventing cathodic deposition of cadmium is nitric acid. However, nitric acid would undoubtedly attack the mercury anode bringing mercuric and possibly other salts into solution which would interfere with the EDTA titration of cadmium. Hence it was decided to use hydrochloric acid. There was no possibility of attack on the platinum cathode as its potential was too negative for chlorine evolution. However, it has been reported that hydrochloric acid slightly attacks mercury in the presence of oxygen (49). In some determinations, where no precautions were taken to guard against this, small amounts of mercury salts were found ($\sim$ 1mg) in residual solutions. However, if the acid was boiled beforehand to remove

dissolved oxygen, no traces of mercury were detectable in the residual solutions.

Experiments were made to determine the minimum acid strength required to give electrolytic dissolution of 5×10^{-2}M amalgams at a reasonable rate without cathodic deposition of cadmium. 100ml of acid of various strengths were taken and approximate maximum tolerable electrolysis current densities found. At a current of about 100mA (current density 5mA/cm^2) redissolution of a 5×10^{-2}M cadmium amalgam took about 30 minutes. Results are summarized in Table 7.1.

Table 7.1

Normality of HCl	Current
2N	2.5mA/cm^2
3N	2.5 "
4N	5 "
6N	10 "
6N	5* "

* Volume of electrolyte, 50ml.

These results show clearly that a high acidity is needed to prevent the cathodic deposition of cadmium if the amalgam was to be decomposed at a reasonable rate. However, for a reasonable end-point in the titrimetric determination of cadmium with EDTA, the concentration of anions must not exceed 0.5M (see later). Hence it was necessary to remove excess of acid by evaporation. Clearly this would be impractical with perchloric acid.

To keep the time of analysis to a minimum it was decided to keep the volume of the dissolution electrolyte at a minimum. With the 250ml beaker cell, containing about 20ml of amalgam, this was found to be 50ml. With smaller volumes, there was insufficient volume of electrolyte to accommodate the platinum cathode. In this work, 50ml of 6N hydrochloric acid were used as the dissolution electrolyte.

iii) Current-time and completeness of dissolution

Current-time curves for the electrolytic dissolution of 5×10^{-2}M cadmium amalgams at controlled potential had the general form given in fig 7.1. The control potential was set to give an electrolysis current of 100mA. This was usually -0.74V vs SCE. The electrolysis current remained steady for about 25 to 30 minutes, stirring being kept vigorous and steady. The current then dropped sharply at a rate faster than the potentiostat could follow, i.e. faster than 0.5mA per sec. Attempts were made to follow the current, by reducing the applied e.m.f. by hand, but it fell too fast, reaching zero after about 0.5 to 1 minute. When there was no current flowing there was no control of potential. The final potential measured with the potentiometer on the potentiostat was usually about -0.65V vs SCE. When the current reached zero, the electrolyte was removed by suction, the sides of the beaker and the mercury anode were washed a number of times with small quantities of water and the washings also removed by suction. The electrolyte plus washings were then evaporated in a 250ml squat-form beaker to dryness on a hot plate. This took about

1 hour. The residue was moistened with a few drops of concentrated hydrochloric acid to make soluble any oxide residues, then 50ml of water were added. The solution was warmed to dissolve the residue. At this stage, if no precautions had been taken to de-aereate the dissolution electrolyte, there was a slight precipitate of mercurous chloride. This was removed by filtering the solution through a 7cm No 40 filter paper. There was never any precipitate if the hydrochloric acid was boiled beforehand. Cadmium was then determined in this solution by titration with EDTA.

Results for the electrolytic dissolution of cadmium amalgams are given in Table 7.2 which shows that recoveries are within 0.3mg of the amount taken. Since this amount is lost during the change of electrolyte at the end of the preliminary deposition of cadmium, these results show that cadmium amalgams are virtually completely decomposed to within $\pm$0.1mg.

Table 7.2

Cadmium Taken	Cadmium Found
0.10202g	0.10170g
0.10045g	0.10019g
0.02009g	0.02009g
0.09961g	0.09963g*
0.10058g	0.10083g*

* No precautions against mercury attack.

iv) Discussion

The current for the dissolution of a metal Q from an amalgam to give ions Q^{n+} according to the reaction

$$Q(Hg) + ne \rightleftharpoons Q^{n+}$$

can be expressed as a function of the concentration in the bulk of the electrolyte and at the electrode surface by applying similar considerations as in diffusion-controlled cathodic deposition of Q^{n+} (see Chapter I), i.e. the current i_t at a given time t will be given by the expression

$$i_t = n\,FAD\,\frac{(C_E - C)}{\delta_s} \qquad (i)$$

where C_E is the concentration of Q^{n+} at the electrode surface as C is the bulk concentration at time t. The other symbols have their usual significance. However, for anodic dissolution, diffusion in the electrolyte is not rate-determining. In many cases, the potential is rate-determining because it more or less fixes the value of C_E.

If, initially, the potential of the amalgam is set about 50mV more positive than the reversible amalgam potential, C_E will be approximately 10^{+2}M for a 2-electron oxidation. This is the case with the dissolution of a cadmium amalgam. When the initial potential was about -0.74V vs SCE it was about 50mV more positive than the measured half-wave potential (see Table 7.3) which is close to the reversible amalgam potential. There is undoubtedly an activation overpotential, but this will not be more than a few mV. Hence C_E, initially, will not be less than molar. If, initially, the rate

of diffusion in the amalgam is not rate-determining, C_E and the electrode potential will remain constant until the concentration of the amalgam reaches that for a limiting rate of diffusion. In our experiments, the bulk aqueous concentration was never greater than 10^{-2}M. Thus C_E is at least 100 times greater than C and the current cannot alter by more than 1 per cent. Hence until limiting conditions are reached, the current is virtually constant and its magnitude depends on the concentration C_E which, in turn, depends on the potential. This is shown by the plateau ab in fig 7.1 which, in our experiments, extended over about 25 minutes.

When limiting conditions are reached, the current will be controlled by the limiting rate of diffusion of cadmium in the amalgam and should decay exponentially, i.e.

$$i_t = i_o e^{-\frac{DAt}{V\delta_A}} \qquad \text{(ii)}$$

where i_t is the current after time t, D is the diffusion coefficient of cadmium in mercury, δ_A is the thickness of the diffusion layer in mercury, and A and V are the surface area and volume of the amalgam respectively.

The current, after the plateau, decreases to its final value in 30 to 60 seconds and if the decrease is linear or faster (i.e. exponential), the limiting conditions are not reached until the dissolution of cadmium is at least 98 per cent complete (point B, fig 7.1). After this, diffusion in the amalgam is rate-determining. Calculation shows that the thickness of the diffusion layer in the amalgam, δ_A, is about 8×10^{-4}cm which is surprisingly small.

For unstirred amalgams, Hickling and Maxwell found δ_A to be about 2×10^{-2}cm, i.e. much the same as for a diffusion-controlled cathodic reaction. However, they were able to reduce δ_A by a factor of 8 simply by stirring the amalgam with a stream of hydrogen bubbles. With the more efficient stirring used in our experiments, a further reduction in δ_A would be expected, and so considering the approximations involved, a calculated value of 8×10^{-4} is not unreasonable.

Thus, the current-time curve is composed of two parts. First a plateau (ab) in which the potential is rate-determining, during which about 98 per cent of the cadmium is stripped, followed by a presumed exponential decrease (bc) where diffusion in the mercury is rate-determining.

Rogers derived an approximate equation for dilute amalgams:

$$E_A \quad E_{\frac{1}{2}} - \frac{0.059}{n} \log \frac{\frac{1-x}{V_{ox}}}{x/V_{red}} \qquad \text{(iii)}$$

where E_A is the potential of the amalgam, $E_{\frac{1}{2}}$ the polarographic half-wave potential, x the fraction of element in mercury, V_{ox} and V_{red} the volumes of the aqueous and mercury phases respectively. For 99.99 per cent dissolution $E_A - E_{\frac{1}{2}} = 0.11V$ for $n = 2$ where $V_{red} = 20ml$ and $V_{ox} = 50ml$, i.e. for cadmium, the amalgam potential for 99.99 per cent dissolution will be -0.78 + 0.11V or -0.67V vs SCE. Since the final potential of the amalgam was about -0.65V vs SCE, it is probable that dissolution was complete to within this limit. This is confirmed by the results in Table 7.2.

v) Separation of cadmium from bismuth, lead, tin and indium

The half-wave potentials of cadmium, lead, tin and bismuth were measured polarographically in 6N hydrochloric acid.

Table 7.3

Cadmium	-0.78V vs SCE
Lead	-0.58V vs SCE
Tin	-0.59V vs SCE
Bismuth	-0.25V vs SCE
Indium	-0.68V vs SCE

Applying equation (iii) for lead and tin (assuming stannous) not more than 0.01 per cent dissolution should occur at 0.11V more negative than the half-wave potential, i.e. at about -0.70V. Thus, provided the potential for the dissolution of cadmium does not fall much below this value, it should be possible to separate cadmium from lead and tin. The potential of bismuth is very much more positive and should cause no bother. Results for trial dissolutions of 10 to 100mg of cadmium for separation from 100mg of lead, tin and bismuth are given in Table 7.4. The dissolution of cadmium was started at about -0.74V vs SCE and the final potential after the current decay was about -0.68V vs SCE.

Table 7.4

Cadmium in the presence of lead, tin and bismuth

Cadmium Taken	Cadmium Found	Other Metals
0.09882g	0.09869g	lead
0.09528g	0.09520g	lead
0.01242g	0.01248g	lead
0.09548g	0.09525g	lead + bismuth
0.10045g	0.09999g	tin
0.10045g	0.10014g	lead + tin + bismuth
0.02009g	0.02014g	lead + tin + bismuth

These results are very satisfactory, showing little or no interference from bismuth, lead and tin.

The half-wave potential for indium as found from the literature is very much closer to that of cadmium. From equation (iii) at the potential for 99.99 per cent dissolution of cadmium, i.e. -0.70V vs SCE, about 10 per cent of indium will also dissolve. However, as equation (iii) is very approximate, ignoring activity coefficients and assuming complete reversibility, it may be just possible to separate cadmium and indium in 6N HCl. Table 7.5 shows results for the recovery of 20 to 100mg of cadmium in the presence of 100mg of indium.

Table 7.5

Dissolution of cadmium in presence of 100mg of indium.

Cadmium Taken	Cadmium Found	Difference
0.10181g	0.08640g	15.41mg
0.10120g	0.08555g	15.65mg
0.10240g	0.08723g	15.17mg
0.05231g	0.05184g	0.47mg
0.02009g	0.01944g	0.53mg

In each case dissolution was started with a current of 100mA at a potential of about -0.74V vs SCE. The current followed the course described earlier and immediately it had fallen to zero, the electrolyte was removed by suction and treated in the normal way. The final potential was about -0.70V. In some experiments the current started to fall much earlier than previously, i.e. after about 15 minutes, when 100mg of cadmium were taken. Results for 100mg of cadmium are very low, but fairly reasonable for less than 50mg. Since nearly quantitative recoveries were obtained when smaller amounts of cadmium were taken, there was unlikely to have been any intermetallic compound formation in the amalgam. However, in one determination, after the current had decreased to zero, the potential was reduced to -0.65V vs SCE and electrolysis continued until the current had again fallen to zero. After evaporating the excees of acid, the indium present was precipitated with ammonia, filtered and dissolved in acid, re-precipitated, filtered and the second filtrate

added to the first. The combined filtrates were titrated for cadmium with EDTA. However, no increase was found in the amount of cadmium recovered and tests on the indium precipitate showed no traces of cadmium. This suggests that indium does in some way hold back cadmium in the amalgam.

Although it would seem quite possible to separate small amounts, up to 50mg of cadmium, from 100mg of indium, we feel these results are too uncertain to justify the recommendation of this separation.

vi) Titration of cadmium with EDTA

A brief investigation was made of the use of two indicators, Xylenol Orange at pH5 to 6 in the presence of hexamine and Eriochrome Black T at pH10 in the presence of ammonia/ammonium chloride buffer, since these were readily available.

a) Xylenol Orange

It was found essential to keep the pH above 5, otherwise the end-point was indistinct. The best end-point was obtained from a solution containing 100mg of cadmium as sulphate, 5g of hexamine and the pH adjusted to 5 to 5.4 with 2N sodium hydroxide. The titre was about 35ml of 0.025M EDTA. The end-point was sharp, changing from pink to orange-yellow; however, it was not nearly so distinct as that obtained with Eriochrome Black T.

b) Eriochrome Black T

This indicator was used exclusively in the determinations of cadmium after the dissolution from an amalgam. The indicator

was prepared as given on p93. A very sharp end-point, purple to blue, was obtained when a solution containing ammonia/ammonium chloride buffer, 0.1M with respect to chloride, at pH10 and at 60°C was titrated with 0.025M EDTA. However, the sharpness of the end-point fell seriously when the concentration of chloride or of any anion present was increased. Table 7.6 shows approximate sharpness of end-point with increasing concentration of chloride.

Table 7.6

Concentration of chloride	End-point
0.1M	good
0.2M	fairly good
0.5M	poor, just discernible using a comparison
1M SO_4^{--}	no end-point
1M ClO_4^-	no end-point

Clearly the free acid in the electrolyte must be removed by evaporation before titration. An alternative would be to take an aliquot of the electrolyte and dilute, but this would give results of reduced accuracy.

SUMMARY

10 to 100mg of cadmium have been successfully separated from 100mg of lead, tin and bismuth by electrolytic dissolution of an amalgam of these metals at controlled potential into 6N hydrochloric

acid. After removal of the excess of acid by evaporation, cadmium was determined by titration with EDTA using Eriochrome Black T as indicator. Results indicate that dissolution is virtually complete and that any loss of cadmium occurs during the change of electrolyte after the preliminary deposition. The separation of cadmium from indium is uncertain.

This is a novel application of the principle of quantitatively removing a metal from an amalgam at controlled anode potential, as earlier methods have dealt exclusively with smaller amounts of material. The apparatus required is simple, since the pre-electrolysis is carried out at constant-current and as dissolution is virtually at constant current a simple manually operated controlled potential circuit will suffice. The total time for the determination of cadmium from the beginning of the preliminary deposition was about $2\frac{1}{2}$ to 3 hours, though attention was not needed for more than half an hour.

There is no reason why this principle should not be extended to the determination of other elements, such as zinc. With little modification to the apparatus, it could be used for a coulometric determination at controlled potential as carried out by Mountcastle et al for the determination of indium.

Appendix

The methods evolved for the determination of bismuth, lead and cadmium were tested for their successive determination in mixtures similar to those found in the commercial alloys 'cerrobend' and 'cerrobase'.

Table A1

	Bi	Sn	Pb	Cd
Cerrobend	50.0%	13.3%	26.7%	10.0%
Cerrobase	55.5%	-	44.5%	-

For the determination of bismuth and lead by cathodic depsoition a 400ml tall-form beaker was used as electrolysis vessel. Bismuth was deposited from 200ml of electrolyte onto a cathode of 120 sq cm area. After the bismuth determination, lead was deposited onto a cathode of 160 sq cm area. The washings after the bismuth deposition were kept to a minimum so as to keep the volume of electrolyte as small as possible for the lead determination. For the determination of bismuth in a mixture similar to 'cerrobend', 100mg of bismuth were taken and for 'cerrobase', 50mg of bismuth. The weights of the other metals were adjusted accordingly.

Table A2

	Bi Taken	Bi Found	Difference	Pb Taken	Pb Found	Difference	
1.	0.10830g	0.10833g	-	0.05600g	0.05652g	+0.52mg	*
2.	0.10730g	0.10739g	-	0.05500g	0.05546g	+0.46mg	
3.	0.10410g	0.10412g	-	0.05480g	0.05494g	+0.10mg	
4.	0.05568g	0.05542g	-0.26mg	0.05360g	0.05354g	-0.06mg	**
5.	0.05568g	0.05578g	+0.1 mg	0.05630g	0.05632g	-0.08mg	**

* + cadmium and tin

** bismuth and lead only

The results for bismuth are within 0.3mg, which is what is expected. The first three results for lead are up to 0.5mg high, which is reasonable, though the results for lead were low in 4 and 5.

For the determination of cadmium in a mixture similar to 'cerrobend', 100mg of cadmium were taken and the weights of the other metals adjusted accordingly (Method as in PART II).

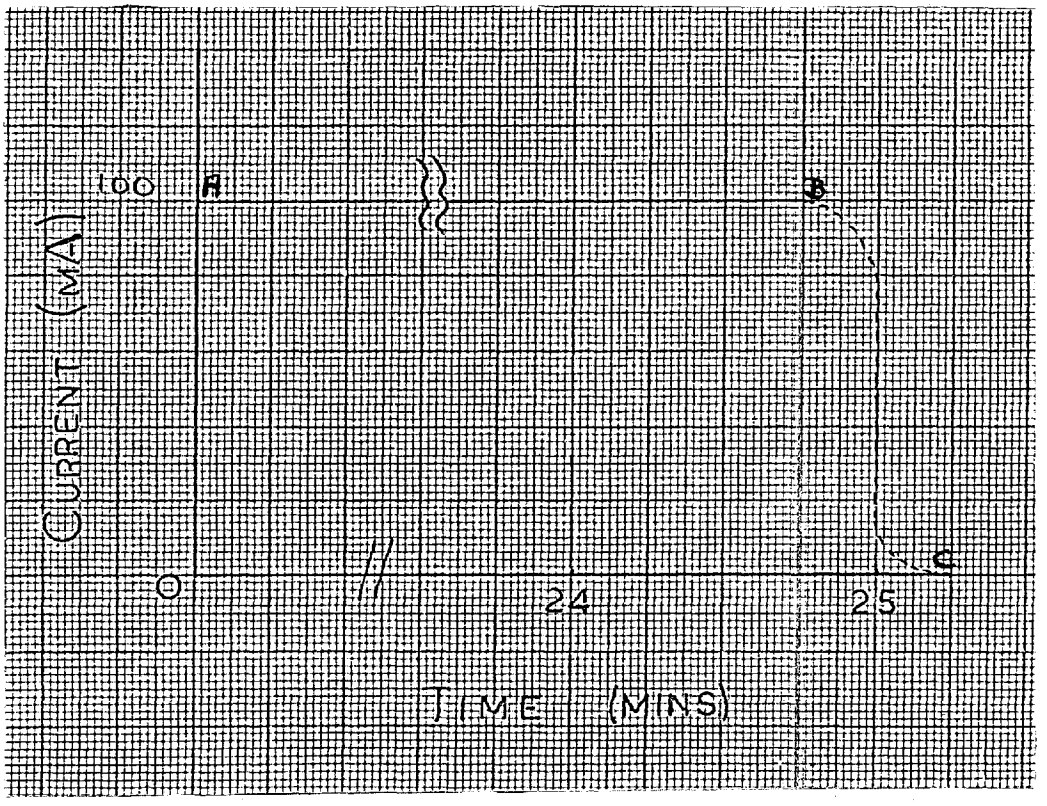
Table A3

	Cd Taken	Cd Found	Difference
1.	0.10308g	0.1032g	+0.12mg
2.	0.10277g	0.10290g	+0.13mg
3.	0.10471g	0.10470g	-

The results for cadmium are up to 0.1mg high. There is probably slight dissolution of lead and tin on account of their high concentration. All of these results are satisfactory.

Fig 7.1

Current-time curve for the controlled-potential electrolytic decomposition of cadmium amalgam



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