INORGANIC ANALYTICAL POLAROGRAPHY IN ORGANIC SOLVENTS

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A thesis submitted for the degree of

Doctor of Philosophy

in the University of London

Department of Chemistry,
Imperial College of Science
and Technology.

September 1966.

For their patient understanding, thoughtfulness, and financial support over the past years, I dedicate this Thesis to my _parents_.

ABSTRACT

The direct application of polarography to the examination of organic phases following solvent extraction has been investigated as a means of extending the fields of both polarography and solvent extraction.

Experimental factors such as, the choice of suitable solvents, supporting electrolytes and electrode systems were studied first by examining the reductions of simple metal ions in various organic solvents.

The extraction of cadmium, cobalt (11), iron (11), manganese (11), nickel and zinc as their pyridine-thiocyanate complexes in toluene was next examined. The results showed that the sensitivity is increased by the concentration effect of the extraction system and a sequential analysis can be achieved without, as in aqueous solution, searching for a suitable supporting electrolyte.

A procedure involving the solvent extraction of the molybdenum (V)-thiocyanate complex in diethyl ether, offers a selective method for the determination of molybdenum down to 0.5 ppm. Of 21 elements examined, only molybdenum showed a reduction wave under the chosen conditions. The method has been evaluated with respect to various experimental factors and is applied to the analysis of molybdenum in mild and alloy steels.

Selective methods for the determination of indium, iron and palladium have also been developed. Acetylacetonate complexes of these metals are extracted into toluene and the polarographic reduction waves measured. Using the above methods concentrations of the respective metal ions

can be determined to as low as 0.05 ppm.

The reducibility of various metal-oxinates after extraction into iso-butylmethyl ketone, chloroform and ethylacetate, has also been studied. Preliminary investigations showed the feasibility of developing analytical methods for other metal ions such as bismuth, lead, uranium, etc.

ACKNOWLEDGEMENTS

The work reported in this thesis was carried out in the Chemistry Department of Imperial College of Science and Technology between October 1964 and October 1966. It is entirely original except where due reference is made and no part has been previously submitted for any other degree.

I am greatly indebted and grateful to my supervisor, Professor T.S. West, for his advice; and in particular to Dr. R.M. Dagnall for his immediate guidance, continual encouragement and constructive criticism throughout the course of this work. Thanks are also due to other staff members of analytical chemistry for their helpful discussion during the course of this work.

Typing of this manuscript was undertaken by Miss C. Delaney, who is thanked for her ever willing help.

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INTRODUCTION

Polarography is an important technique with application both in analysis and in fundamental research. It can be used to detect and estimate electro-reducible substances in solution at concentrations from 10^{-2}M to 10^{-8}M. Normal d.c. polarography with a dropping mercury electrode is suited best to the determination of concentrations between 1 x 10^{-5}M and 2 x 10^{-3} M. A percentage standard deviation of the order of 2 - 3 is obtained under these conditions.

Fundamentally, the method involves the study of current/voltage curves obtained when solutions are electrolysed in a cell, using a polarizable dropping mercury electrode as cathode and an anode reference electrode. The use and scope of the dropping mercury electrode arises as a result of its convenient properties. Mercury can readily be purified and a fresh electrode surface is continually available. Mercury also forms liquid alloys with other metals and, therefore, not only facilitates the electroreduction of many ions, but also minimises the accumulation of insoluble (metal) products. In addition, it has a very high hydrogen over-potential. Above all else it gives a clear and exactly reproducible surface of known area; this means that under favourable conditions the current/voltage curves are exactly reproducible. The term polarography includes experiments in which the current/voltage curves are measured over a series of drops (as in conventional d.c. polarography) or in one drop (as in cathode-ray polarography[1]) or with a continuous stream of mercury (as in the Heyrovsky-Forejt streaming electrode[2]). Some workers have extended the term to include solid metal micro-electrodes.

Polarography deals with the relationship between three fundamental variables; the composition of the solution in which the dropping electrode is immersed, the potential applied to the dropping electrode and the current flowing through the cell. Under suitable conditions, the half-wave potential ($E\frac{1}{2}$) is characteristic for a given electro-reducible ion and the wave-height is directly proportional to the concentration of reducible substance. The limiting current (I_L) of the polarographic wave is the sum of the residual current (I_R), the migration current (I_M) and the diffusion current (I_D), that is

$$I_L = I_R + I_D + I_M$$

The diffusion-current is directly proportional to wave-height, provided other factors are kept constant and is defined by the Ilkovic equation[3]:

$$i = 607\ n\ D^{\frac{1}{2}}\ Cm^{\ 2/3}\ t_{max}^{\ 1/6}$$

where i is the current (microamperes), n the number of electrons involved in the electrode reaction, D the diffusion coefficient of electro-active material (millimoles/litre), m the weight of mercury flowing through the capillary per second (mg. sec^{-1}) and t_{max} the drop time (seconds). It is evident from this equation that if the other factors are constant then,

$$I_D \propto C$$

The migration current of the reducible ion is supressed by the addition of a sufficient excess of a "supporting electrolyte" to diminish the transport number of the reducible ion to a negligable value. The supporting electrolyte should not be reduced under the conditions of the experiment. In quantitative measurements the limiting current is corrected for the residual current to give the diffusion current. As dissolved oxygen is readily reduced at the dropping mercury electrode, it is frequently necessary to remove it. This can be done most conveniently by passing oxygen free nitrogen or hydrogen through the solution.

Since Heyrovsky[4] devised the method, almost all inorganic polarography has been carried out in dilute solutions in which the concentration of the supporting electrolyte has rarely exceeded 1 M. Only in recent years has increasing attention been paid to the use of other media. These have included concentrated solution, fused salts, and non-aqueous media.

1) Polarography in Concentrated Aqueous Solutions

Khlopin[5] studied the reduction of many metal ions in 30% calciumchloride solution (e.g. 0.72 M) and claimed that good polarographic waves could be obtained. He calculated the diffusion coefficient and measured the half-wave potentials of bismuth, cadmium, copper, iron, lead, manganese, nickel, tin and zinc. Reynolds and his co-workers[6-9] carried out a polarographic examination of cadmium, chromium, copper, iron, manganese and nickel in 5M calcium chloride solutions and suggested that the use of a concentrated solution of the above type has a number of interesting possibilities. From the analytical view point, it allows the determination of traces of impurities in metals such as calcium without chemical concentration and without introducing other reagents.

2) Polarography in Fused Salts

A large number of polarographic studies using fused salt media at elevated temperatures have been reported. The underlying principle of this area of polarography is the use of salt or a mixture of salts as both solvent and supporting electrolyte. A sufficient high temperature, which depends upon the salt or salts chosen, has to be employed to keep the contents of the cell in a fully molten state. Polarographic examination of fused salts can be used to analyse molten salt solutions. However, the ultimate objective of this technique viz., the direct analysis of metallurgical slags, glasses, study of reactions at very high temperatures and corrosion by molten salt solvents, etc., is still far from being achieved.

Several groups of workers have made studies using various salt combinations and electrode systems. Nachtrieb and Steinberg [10, 11] studied the reduction of nickel in a fused salt system of lithium nitrate-ammonium nitrate-ammonium chloride at 125° and of cadmium, cobalt, lead, nickel and zinc in lithium nitrate-sodium nitrate-potasium nitrate at 160°. A dropping mercury electrode was used in both these studies. The current/voltage characteristics were found to obey the Heyrovsky-Ilkovic equation and the diffusion coefficients etc., were calculated. The cobalt (11) ion was observed to give two waves under these conditions and this was attributed to the oxidation of cobalt (11) to cobalt (111) by the nitrate in the melt. The reduction waves were thus due to the reduction of cobalt (111) to cobalt (11) and cobalt (11) to cobalt metal.

The ternary eutectic, magnesium chloride - sodium chloride - potasium chloride (50:30:20 moles percent respectively) with a melting point of 396° has been reported[12] to be a useful solvent for the extraction of fission products in liquid metal fuel reactors. A platinum microelectrode, prepared by sealing a length of 14 mm diameter platinum wire into 6 mm diameter pyrex tubing so that about 1.5 mm^2 projects from the seal, was used. Measurements were made with respect to a platinum/platinum (II) reference electrode.

An equimolar mixture of sodium chloride and potasium chloride (m. pt. 660°) has also been used for polarographic studies in the temperature range 700-740°. Delimarskli and Kuzmovich[13] studied the polarographic behaviour of cadmium, cobalt (11), copper (1), copper (11), nickel, silver, thallium (1) and zinc chlorides using a platinum micro-electrode. Maricle and Hume[14] used tungsten-in-Vycor micro-electrodes (with areas of 7.4 and 1.2 mm^2) and a platinum/platimun (11) reference electrode in the same melt. The limiting currents for the reduction of copper (1), iron, nickel and silver chlorides in the sodium chloride - potasium chloride melt at 740° were found to be proportional to their concentrations. A percentage standard deviation of 5-8 was obtained in this study. Polarography in fused salts has been reviewed by several authors [15-19].

3) Polarography in Non-Aqueous Media

Recently, attention has been given to completely and partially anhydrous non-aqueous solvents. Such media enables electro-chemical preparations to be achieved which cannot be carried out in water. Furthermore, the replacement of water by non-aqueous molecules changes the solution condition of the ion-species and therefore, in principle, changes the value of the half-wave potential or the reversibility of the polarographic reaction. This, in some instances, proves to be of great analytical importance [20-23]. Ions that are extensively hydrolysed in neutral aqueous solution, e.g. beryllium, niobium, zirconium and many others; do not give polarographic waves. Their reductions are so slow that an appreciable current is not obtained at any potential up to the start of the final current rise due to the reduction of the supporting electrolyte. Such aquo-complex ions may often be much more easily reduced if their co-ordinated water molecules are replaced by another ligand. This replacement is facilitated by decreasing the activity of water in the solution. Thus beryllium[24] may be determined after extraction by acetylacetone in dimethyl-sulphoxide using tetraethyl ammonium per chlorate as supporting electrolyte. In aqueous media the hydrolysis of beryllium is so extensive that at acidities low enough to prevent interferences from the reduction of hydrogen ion, its reduction wave is not suitable for analytical use [25].

The non-aqueous studies can be conveniently divided into two classes depending upon whether the solvent is inorganic or organic.

(a) Polarography in Inorganic Solvents

Polarography in inorganic solvents has been mainly concerned with sulphuric acid and liquid ammonia. Vlcek[26] has made a careful study of sulphuric acid and has reported that the concentration of 17 M is the most favourable for the polarographic purposes because the conductivity is similar to that of a solution 1M in potasium chloride. In addition, water can dissociate in it as a base and so act as the supporting electrolyte. The half-cell Hg/ Hg SO_4/ 17M H_2SO_4 was recommended as a reference electrode. Vlcek [27] also reported that the products of the reduction of sulphur dioxide and bromine are reoxidised by sulphuric acid giving a resulting current consisting of the diffusion current together with a kinetic component. Similarly two waves were obtained for molybdenum which were larger than the waves for other ions in the same medium. The behaviour of thallium and cadmium was also studied over a range of sulphuric acid concentrations[26]. The unusual properties of this solvent, especially that of re-oxidation of the reduced species, should have great analytical possibilities.

Laitinen and his co-workers[28] studied the reduction of the alkalimetals in liquid ammonia at -36° (the vapour pressure at this temperature is well below atmospheric pressure) and found that they undergo reversible reductions which obey the Ilkovic equation. The electrodes and cells which may be used in this type of work were also discussed by the workers [29, 30]. In this solvent the half-wave potentials became more positive as the atomic number of the metal increased[31]. The polarography of ammonium, copper, molecular oxygen and thallium has been studied[32] as has also that of aluminium, cadmium, chromium, cobalt, lead, nickel and zinc[33]. Some interesting observations concerning the use of the dropping mercury electrode at -36° have been made by Vecchi[34]. Because this temperature is very close to the freezing point of mercury, he suggested the use of solutions of ammonium nitrate, which can exist at temperatures above 0°. These solutions can be prepared by passing dry gaseous ammonia through dry ammonium nitrate.

Some preliminary investigations and suitable apparatus for use with hydrofluoric acid as solvent were described by Sergent et al[35]. Although not very much work has been carried out, many interesting possibilities appear to exist for this solvent.

Useful reviews on this whole subject have been published recently[36-39].

(b) Polarography in Organic Solvents

Early studies using organic solvents were made by Satori and Giacomellow[40] who investigated the reduction of cobalt and lithium in methanol and methanol/benzene mixtures. At the same time Zanku and Manusova[41] made some studies with a number of common metal ions in several organic solvents, e.g. methanol, ethanol and glycerol. They reported that the half-wave potentials were generally similar to those in aqueous solution, but the step-heights were greatly reduced, although they were still proportional to the concentration of the metal ions.

Kuta[42] analysed many kinds of metal driers in oils using 1:1 benzene/methanol mixture containing 0.3 M sodium acetate as supporting electrolyte. Delimarskii and

Abarbarchuk[43] investigated the reduction of arsenic, cobalt, and silver at a solid platinum micro-electrode in pyridine. Cisak and Elving[44] also used pyridine as a solvent and reported that the silver/silver nitrate electrode is suitable as a reference.

Kolthoff and Coetzee [45] made a comprehensive study of the waves of many metal ions in acetonitrile and observed that the metal ion reductions occured at more positive potentials than those in aqueous solution. Larson and Iwamoto[46] examined the utility of various nitrile solvents viz. acetonitrile, propionitrile, benzonitrile, phenylacetonitrite, and acrylonitrile.

Brown and his co-workers [47,48] used formamide and dimethylformamide for alkali and alkaline earth metal studies. N, methyl acetamide was used as solvent by Sellers and Leonard [49] and also by Knecht and Kolthoff[50] who found it to have no analytical advantages over water and several other solvents.

Gutman, Schober and their associates[51-53] extensively studied polarography in anhydrous dimethyl-sulphoxide. They also investigated ethylenediamine, benzylchloride, acetic anhydride, morpholine and phosphorous oxychloride as polarographic solvents[54].

Bruss and De Vries[55] studied the effect of various solvents and came to the conclusion that the half-wave potential values varied in a regular way, usually becoming more positive as the dielectric constant decreased. Hala[56] studied anhydrous acetic acid and showed that it was a useful solvent and one in which the Ilkovic equation was generally obeyed. Anhydrous formic acid was investigated by Pinfold and Sebba[57] and the conclusion was again made that the half-wave potentials were often more positive than those in aqueous solution. This was attributed to the hydration effect in aqueous solutions.

The increasing importance and use of organic and other non-aqueous solvents in polarography has led to the need for a clarification of the factors affecting the reduction characteristics in such media. The latest review by Reiji Takahashi[58] outlines the progress so far made in investigating the different experimental variables involved, viz., solvents, reference electrodes, supporting electrolytes, comparison of half-wave potentials etc.

The organic solvents so far investigated can be classified as follows:-

1) amphiprotic and
2) inert solvents

Amphiprotic solvents can be further classified:-

a) hydroxylic
b) protogenic (acids considerably stronger than water)
c) protophilic (bases considerably stronger than water)

The use of inert solvents, particularly those which are immiscible with water, is very limited in polarography. However, one general application to inorganic analysis, which has been until now almost completely unexploited, is the polarographic examination of an organic phase following a liquid-liquid extraction. This in fact in keeping with the latest trends of combining polarography with other techniques, for example, chromatography [59, 60] and radiochemistry [61-63].

Extraction-polarography (the combination of solvent extraction and polarography) has been used as a means of concentrating the material under investigation with a subsequent polarographic measurement in an aqueous phase [64-67].

In solvent extraction the aqueous phase is brought into contact with an immiscible organic solvent, which contains either the extractant in solution or else serves as the extractant, in order to transfer one or more of the solutes into the organic phase. The separations achieved are usually rapid and the apparatus needed is only the separating funnel.

Extraction systems can easily be classified on the basis of the nature of the extractable species, for example:

1) chelate complexes
2) ion-association complexes

Metal chelates represent a type of co-ordination compounds in which a metal ion combines with a multidentate reagent capable of occupying two or more positions of the co-ordination spheres of the metal ion to form a cyclic compound. The functional groups of the base must be so situated in the molecule that they permit the formation of stable ring, generally five or six membered. In chelate extraction systems chelating agents, such as 8-hydroxyquinoline, dithizone, cupferron and so on replace co-ordinated water from many metals to form neutral essentially covalent molecules and which are soluble in organic solvents such as hydrocarbons. If the chelating agent possesses only uncharged basic groups, positive metal-chelate compounds are formed, whilst if the reagent has one anionic group, neutral chelates usually result.

In the second category of ion-association extraction systems, the extractable species are formed by the association of ions. They can be further sub-divided into three types. The metal may be incorporated into a very large ion containing bulky organic groups, or it may associate with another ion which is of great size. For example, copper (1) reacts with 2, 9-dimethyl, 1, 10 phenanthroline (neo-cuproine) to form a large univalent cation which associate with a nitrate or perchlorate anion to form a neutral system extractable into chloroform. Again, zinc as Zncl_4^{2-} associates with two tribenzyl-ammonium ions $(C_6H_6CH_2)_3NH^+$ to give an uncharged species soluble in xylene.

In the second type of ion-association system the formation of an extractable species depend upon the combined action of anions such as halides, thiocyanate or nitrate and of oxygen containing organic solvents such as alcohols, ethers, ketones and esters to displace the water of co-ordination of the metal ion. For example, the extraction of the iron (111) complex in hydrochloric acid by ethyl-ether is an instance of such an ion association complex.

A third type of ion-association extraction system exists in which the metal ions are incorporated into salts of high molecular weight which "dissolve" in organic solvents. This seems to be the case in the extraction of uranium, molybdenum and other metals by high molecular weight amines dissolved in kerosene.

The application of solvent-extraction to polarography can be made in the following three ways:-

1) Solvent extraction of an inorganic species, chemical destruction of the organic components and a polarographic examination of the inorganic residue dissolved in water.

2) Solvent extraction of an inorganic species, re-extraction of the desired constitution into an aqueous phase and a polarographic examination.

3) The direct polarographic examination of the extracted inorganic species in an organic phase.

In the first method, the metal ions are extracted into an organic phase, the extract is evaporated to dryness and the organic constituents are destroyed by the addition of concentrated nitric and sulphuric acids and evaporating to dryness. The residue is then dissolved in water containing a suitable supporting electrolyte and polarographically examined.

Zagorski and his co-workers[68-70] developed methods for the determination of traces of thallium in the presence of cadmium, iron, and lead, traces of copper and lead in iron-cadmium mixtures and tin in presence of lead.

The second method has been used by Cyrankowska and Kolodziejczak[71] for the determination of zinc in the presence of excess nickel. Zinc was selectively extracted from an aqueous phase containing potasium cyanide at pH 5.0 to 5.5 by 0.01% dithizone solution in carbontetrachloride. The complex was then re-extracted into a (1:3) hydrochloric acid solution, the organic matter was destroyed by evaporating to dryness followed by digestion with sulphuric and nitric acids. The residue was dissolved in a solution 0. 1 M in acetic acid and 0.025 M in potasium thiocyanate at pH 6.0 and polarographed. The relative error was 6% at a zinc concentration of 0.001%

Zagroski and Cyrankowska[72] similarly determined bismuth in lead-antimony alloys using a cupferron extraction from acidic solution. The extraction of copper was prevented by the presence of thiourea and the extraction of antimony was prevented by prior oxidation of the +5 valency state with potasium permanganate.

The final method, the direct polarographic examination of an organic extract, has not been considered very widely in the past because the solvents which are usually used for solvent extraction purposes, e.g., hydrocarbons, ethers, ketones, alcohols, acetates, etc. are not electrically conducting. Furthermore, it is very difficult to dissolve and achieve sufficient dissociation of supporting electrolytes in these solvents. However, this can be overcome by dissolving the supporting electrolyte in water and adding to it the extracted organic phase together with a third solvent which is able to produce a single homogeneous phase. Another approach is to dissolve the supporting electrolyte in an organic solvent of high polarity and then add this solution to the extracted organic phase.

Fujinaga and Brodowsky[73] determined traces of lead in extra pure sodium chloride using such methods. A solution of sodium diethyldithiocarbanate was added to the sample solution and the chelate formed was extracted with chloroform. Aqueous hydrochloric acid was added to the chloroform solution as supporting electrolyte together with the amount of ethyleneglycol-monomethyl ether (methyl cellosolve), sufficient to bring about a homogeneous solution. An aliquot of this ternary mixture was then directly subjected to a polarographic examination. The essential experimental conditions, for example the composition of the ternary mixture, the behaviour of lead ion in the mixture, the half-wave potential and diffusion current constants, etc., were studied.

Fisher and Thomason[74] developed a rapid method for the determination of uranium and investigated the various experimental parameters. The uranium was extracted with tributyl phosphate in ethylether and the organic extract was diluted with glacial acetic acid. The supporting electrolyte was added and the binary mixture was then polarographed.

This aspect of extraction-polarography has been reviewed recently by Nakagawa[75].

The work reported in this thesis is directed towards establishing the necessary conditions for carrying out a polarographic examination in inert solvents such as benzene, chloroform, diethylether, ethyl-acetate, isobutylmethyl ketone, etc., which are immiscible with water. An attempt has also been made to extend the possibility of combining solvent extraction with polarography by examining the organic phase directly. Extraction-polarography possesses the advantage of simplifying the separation of interfering elements which otherwise would have to be carried out by time-consuming methods such as electrolysis, chromatography, distillation, etc. At the same time it can be used to improve the overall sensitivity by using the extraction system as a means of concentration. The work described also shows that additional selectivity can be obtained as a result of examining the organic phase because, although certain species are reduced at a dropping mercury electrode in aqueous solution, they do not necessarily give polarographic waves in organic solvents [76,77]. Furthermore, this combination of techniques can be used to analyse elements which are readily hydrolysed in aqueous solution, but which can be extracted as a stable complex or chelate. In addition, some theoretical studied such as the determination of stability constants or the reacting ratios of complexes, normally insoluble in aqueous solution, are now possible. Above all else, however, the selection of a suitable supporting electrolyte, which is so time-consuming, for the analysis of a mixture of metal ions in aqueous solution is eliminated.

During these investigations the extracted organic phase, containing the inorganic species, is mixed with a methanolic solution of the supporting electrolyte and the binary mixture is directly introduced without further treatment. The different experimental variables, viz., reference electrodes, removal of dissolved oxygen, effect of concentration of metal ions on diffusion current, etc. are evaluated for each system investigated.

Ion-association systems were investigated before chelate compounds because the former can be extracted in much larger quantities. For example, iron is removed in gram-quantities by extraction from 6-8 N hydrochloric acid in the analysis of ferrous alloys, rocks and ores whilst chelates are extracted generally to a much lesser extent. Also, ion-association complex systems are mostly more selective than those based on chelate formation. Furthermore, it was thought that in reduction of ion-association systems, large shifts in half-wave potentials ($E\frac{1}{2}$) might not occur as would have been expected for most chelate compounds. This may be attributed to the fact that ion-association complexes can be much more easily reduced than chelate compounds because for reduction of ion-association complexes only one mainly electrostatic bond need be broken whereas in chelate complexes two covalent bonds must be broken simultaneously.

In the first instance, the ternary complexes produced by the reaction of metal ion with pyridine and thiocyanate ions were investigated. This ion-association system was chosen because of those reasons outlined above and also because the extractions could be carried out from near neutral aqueous solutions. This greatly reduces the problems associated with catalytic hydrogen waves which might occur if the extractions were carried out from acidic solutions. In addition, ternary complexes can be extracted particularly well into into hydrocarbons such as toluene and it was not anticipated that either pyridine or thiocyanate would interfere polarographically over the potential range to be examined.

Methods[76] for the determination of cadmium, cobalt (11), copper (11), iron (111), manganese, nickel, and zinc have been developed based upon this extraction system. The detection limits for cobalt, copper, iron, manganese, nickel are *ca.* 0.025 ppm and for cadmium *ca.* 0.05 ppm. In addition, an equi-molar mixture of cadmium, cobalt, copper, manganese and zinc can be readily resolved. Furthermore, it was found that these metal/pyridine/thiocyanate complexes are insoluble in an aqueous phase and they do not give polarographic waves even at concentrations as low as 10^{-5}M. Thus, by using extraction-polarography as described it is possible to study polarographically many insoluble substances.

A method[77] which has been evolved for the determination of molybdenum involves the solvent extraction of the molybdenum (V)-thiocyanate complex into diethylether, followed by the direct polarographic examination of the organic phase. In acidic solutions, most metal-thiocyanate complexes were found to give polarographic waves. However, in the organic phase only those due to iron (111), molybdenum (Vl) and molybdenum (V) were observed amongst 21 elements examined. The thiocyanate complexes of gallium, indium, tin (ll), tin (IV), and uranium (Vl) are not reduced in the organic phase, although they gave waves in aqueous solutions and are certainly extracted to some extent (*Ca.* 70%, 70%, 99% and 40% respectively). This clearly indicates the further selectivity, apart from the extraction system itself, which can be obtained using extraction-polarography. This method was applied to the analysis of mild and alloy steels and results with a standard percentage standard deviation of 2.3 were obtained.

The chelate complexes investigated have included metal-acetylacetonates and metal-oxinates. Both have been found to be useful for the determination of many elements depending on the extraction conditions and the nature of the polarographic wave.

SECTION I

Preliminary Investigations Using Organic Solvents

Introduction

During the last decade, the use of organic solvents in polarography has become an attractive proposition. Inspite of the difficulties encountered in experimental techniques and the lack of both theoretical and basic electro-chemical data in this field, this aspect has been extensively developed by many workers.

It would appear from the literature that the organic solvents normally used in "non-aqueous" polarography are limited to organic compounds possessing a high dielectric constant. This property enables an electrolyte to dissolve and dissociate in sufficient quantities to be suitable for d.c. polarographic measurements with a dropping mercury electrode. These solvents have included nitrogen containing compounds, particularly acetonitrile, N, N-dimethyl formamide and ethylene diamine, lower alcohols and acetone. Each of these solvents have also been used in admixture with water to examine certain inorganic depolarisers. Dioxan and dimethyl-sulphoxide have also found considerable application in a similar manner.

The majority of inorganic studies to date have been of a fundamental nature and the practical chemistry involved has merely been to dissolve simple inorganic salts in the appropriate solvent.

The extensive use of solvent extraction in analytical chemistry as a means of separation and subsequent determination of metal ions prompted us to investigate the possibility of using immiscible organic solvents of low dielectric constant such as, benzene, toluene, xylene, chloroform, ethylacetate, diethylether, iso butylmethyl ketone, etc. to analyse the traces of extracted metals.

The work described in this section is divided into two parts as a matter of convenience.

(A) Establishment of Different Experimental Variables

Experimental

Apparatus

The apparatus used in this study was an Elliot Polarograph Model 200 with a dropping mercury electrode. Unless otherwise stated the operating conditions were as follows:

rate of potential increase 0.5/100 secs, drop time 3.4 sec, height of mercury reservior 60 cm, mass of mercury flowing 2.2636 mg/sec, no damping and counter current. An internal mercury pool reference electrode was also employed and deaeration was achieved by bubbling nitrogen (oxygen-free) through a 5 ml. portion of the sample for 5 minutes.

Reagents

All the solvents and the reagents used were of general purpose grade except the metal salts which were of analytical grade.

Standard Solutions

10^{-2}M Cadmium Solution

Dissolve 0.2283 of cadmium chloride in methanol and dilute it to 100 ml by the further addition of methanol.

10^{-2}M Copper Solution

Dissolve 0.1705 g of cupric chloride in methanol and dilute to 100 ml. with methanol.

5×10^{-1}M Lithium Chloride Solution

Dissolve 21.2 g of dried lithium chloride in methanol and dilute to 1 litre with the further addition of methanol.

Results

1. Favourable Solvents

The solvents listed in Table I, which are particularly suitable for solvent extraction purposes, were investigated polarographically with respect to the available potential range before the reduction of the solvent or of the supporting electrolyte employed. In this study each solvent was made conducting by the addition of 5 ml. of a 0.5 M lithium chloride solution in methanol to 15 ml. of the solvent followed by dilution to 25 ml. with methanol. This gives a 0.1 M supporting electrolyte concentration. An instrument sensitivity of 4 uA/full scale deflection was used.

Polarograms were also obtained for each solvent in the presence of cadmium ion. The solutions were prepared as above, but contained in addition 0.5 ml. of a 10^{-2} M solution of cadmium chloride in methanol, i.e., 2×10^{-4}M in cadmium ions. No reduction waves were obtained with tributylorthophosphate and chloroform. In the latter case the solvent reduction wave masks the cadmium wave. However, satisfactory waves were obtained with a similar concentration of cupric chloride.

TABLE I

Solvent	Solvent Reduction Potential (V)	Lithium chloride Reduction Potential (V)	Reduction of Metal Ions		
			Ion	$E_{\frac{1}{2}}$(V)	Limiting current (uA)
Water	–	-2.2	Cu^{2+} Cd^{2+}	-0.18 -0.675	0.0 1.75
Iso Butyl-methyl ketone	-1.4	–	Cd^{2+}	-0.56	1.65
Diethyl Ether	–	-2.0	Cd^{2+}	-0.58	1.8
Tributylortho phosphate	–	-2.0	Cu^{2+}	-0.33	0.80
Ethyl Acetate	–	-2.0	Cd^{2+}	-0.62	1.63
Amyl Acetate	–	-2.0	Cd^{2+}	-0.66	1.45
Butanol	–	-2.0	Cd^{2+}	-0.62	1.42
Chloroform	-0.8	–	Cu^{2+}	-0.29	1.3
Toluene	–	-2.0	Cd^{2+}	$\simeq -0.76$	1.88
Benzene	–	-2.0	Cd^{2+}	$\simeq -0.74$	1.92
Xylene	–	-2.0	Cd^{2+}	$\simeq -0.78$	1.63

The purpose of this experiment was to investigate the nature and position of the metal ion reduction wave. Only with benzene, toluene and xylene was the wave form inferior to that in aqueous solution. In these solvents the wave was spread out over a large voltage range (Ca. 0.3 v).

Toluene was selected for further investigations because it was proposed, in the first instance, to examine the ion association system cation/pyridine/thiocyanate. The solvent was studied, therefore, with respect to the following experimental factors below.

2. Supporting Electrolyte

(a) Methanol content

The effect of increasing methanol concentration on the nature of the polarographic wave was studied. This was carried out by adding to each 25 ml. flask, 1 ml. of 10^{-2}M cadmium chloride solution and 0.1060 g. of dried lithium chloride. The volume was then adjusted with toluene and methanol so that the final composition of the solution with respect to methanol was 10, 20, 40 and 60%. Then a 5 ml. portion of the solution was transfered to the polarographic cell and polarographed.

An emulsion was produced at a methanol concentration of $\leq$ 20% and therefore a concentration of 40% was used in subsequent investigations.

(b) Lithiumchloride content

Table II shows the effect of increasing lithiumchloride concentration on the shape and position of the reduction wave for a 4 x 10^{-4} M cadmium chloride solution in a 3:2 toluene/methanol solvent mixture. An instrumental sensitivity of 10 uA/full scale deflection was used in this instance. The indication of two coincident waves at 0.2 and 0.3 M lithium chloride concentrations could be due to the partial formation of a cadmium chloride complex. A lithium chloride concentration of 0.1 M was chosen as being the most suitable for future studies.

TABLE II

Concentration of Lithium chloride(M)	Half-wave Potential of Cd^{2+}wave(V)	Limiting current of Cd^{2+}wave(uA)	Observations
0.0	-	-	No reduction wave
0.0004	-0.89	-3.90	Elongated wave
0.001	-0.75	4.25	Elongated wave with maximum
0.005	-0.69	4.15	Slightly elongated wave with maximum
0.05	-0.685	3.95	Normal wave with slight maximum
0.1	-0.74	3.84	Normal wave
0.2	-0.83	3.20	Indication of two nearly coincident waves
0.3	-0.83	2.88	Indication of two nearly coincident waves

(c) Other supporting electrolytes

A number of supporting electrolytes commonly used and also soluble in methanol were investigated on a toluene/methanol (3 2) solution containing 4 x 10^{-4} M cadmium chloride. These included lithium perchlorate, lithium hydroxide, tetraethyl ammonium chloride, tetraethyl ammonium iodide, and sodium acetate. A suitable amount of the supporting electrolyte (to give an overall concentration of 0.1 M) was dissolved in the toluene/methanol medium and the solution was polarographed. All the above supporting electrolytes gave satisfactory results except lithium hydroxide. In this instance, no wave was observed and this was thought to be due to the precipitation of cadmium hydroxide. However, satisfactory results were obtained using a similar concentration of cupric chloride.

3. Removal of oxygen

Oxygen can be removed from toluene and other solvents used in this study in the usual manner by bubbling oxygen-free nitrogen through the solution under test. Satisfactory results were obtained after degassing a 5 ml. sample for 5 minutes using a fast a flow rate as possible. Only with more volatile solvents such as diethyl ether was there any noticeable loss of solvent by evaporation and here a bubbling time of two minutes was found to be sufficient. Alternately, a semi-micro condenser was connected to the out-let arm of the polarographic cell.

A mercury seal, instead of the more usual water seal, was found to be essential to prevent the solution under test from re-absorbing oxygen from the atmosphere. The absorption of oxygen by organic solvents is very much more pronounced than with aqueous solutions. The mercury seal also eliminates the risk of water entering the solution under test and producing an emulsion.

An attempt was also made to remove dissolved oxygen by the addition of a few crystals of sodium sulphite. Polarograms were recorded at the intervals of 0, 5, 10, 15 and 30 minutes. The results obtained were unsatisfactory with all of those organic solvents listed in Table I. This could be due to the lower solubility of the salt in these solvent mixtures.

4. Electrode Requirements

The following were investigated using a 3:2 toluene/methanol solution, 2×10^{-4} M in cadmium chloride and 0.1 M in lithium chloride.

(a) Drop time

The droptime of the dropping mercury electrode was regulated, by a forced drop unit, to one, two and three seconds respectively. The results showed a slight increase in limiting current with increase in drop time over the range 1 to 3.4 seconds. This might be due to a corresponding increase in the size of the drop. A drop time of 3.4 sec (natural drop time of the cappillary employed) was used in subsequent studies.

(b) Distance between electrodes

A study was made of the effect, on the polarographic wave, of the distance between the dropping mercury cathode and the mercury pool reference anode. Electrode distance of 0.5, 1, 2 and 3 cm. were examined. The results showed that the polarograms were independent of the distance between dropping mercury electrode and the counter electrode except when the electrodes were very close to each other, i.e., at a distance $\leqslant 0.5$ cm. In this instance erratic results were obtained.

This indicates that the solution is sufficiently conductive and that the ohmic drop in the bulk of the solution is negligible.

(c) Mercury pressure

A linear relationship was obtained between the limiting current and the square root of the height of the reservior (h) between 30.0 and 60.0 cm. This indicates that the limiting current for the cadmium ion reduction wave is diffusion controlled. This is further verified by the fact that a linear relationship is obtained between the concentration of the metal ion and the wave-height produced. A reservior height of 70 cm. produced a maximum on the polarographic wave and as a result a height of 60.0 cm. was set as being the most suitable.

Figure I shows the polarograms recorded under the above optimum conditions using a solution of 4×10^{-4} M in cadmium (curves a, c - i) or of 4×10^{-4} M copper (curves b, j, k).

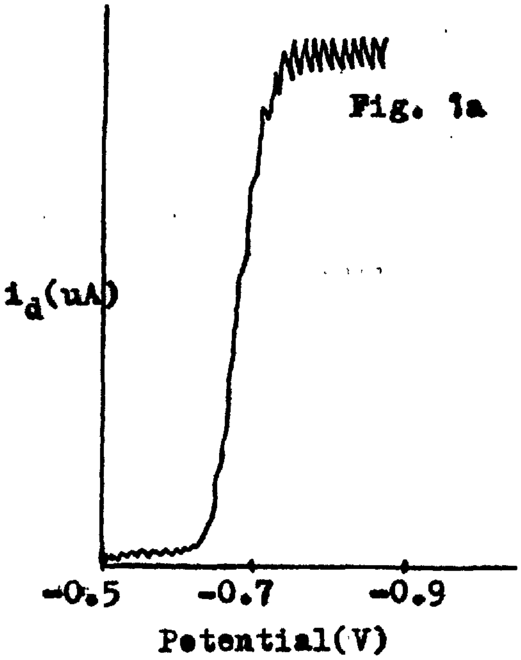


Fig. 1a

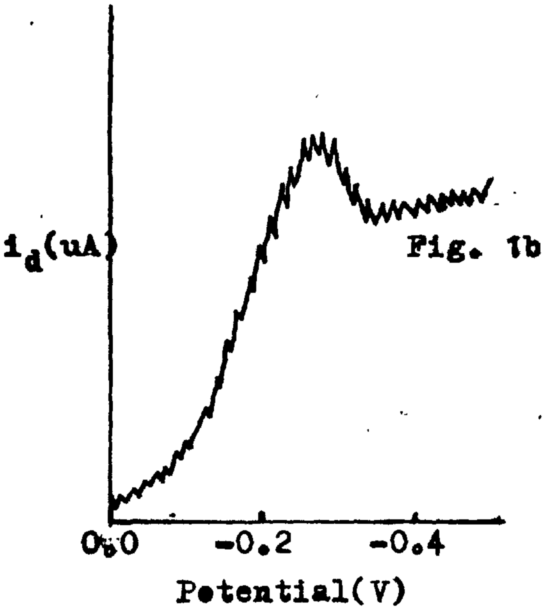


Fig. 1b

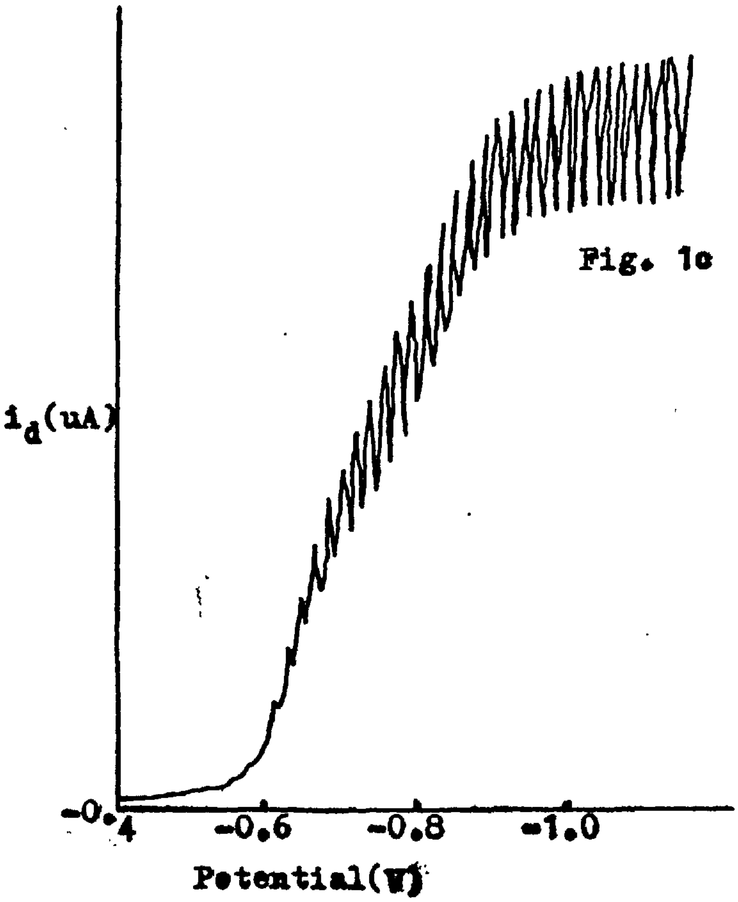


Fig. 1c

Fig. 1a: Cadmium reduction wave in aqueous solution. $2x10^{-4}M$ cadmium chloride in 0.1 M lithium chloride.

Fig. 1b: Copper reduction wave in aqueous solution. $2x10^{-4}M$ cupric chloride in 0.1M lithium chloride.

Fig. 1c: Cadmium reduction wave in 3:2 benzene/methanol mixture. $2x10^{-4}M$ cadmium chloride in 0.1M lithium chloride.

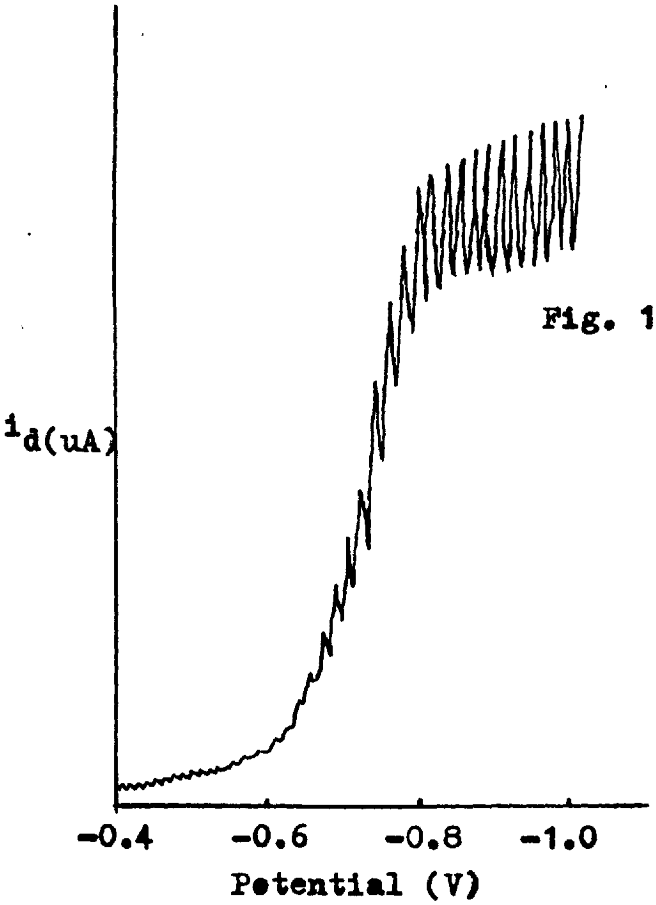


Fig. 1d

Fig. 1d:- Cadmium reduction wave in a 3:2 toluene/methaol mixture. 2x10^{-4}M cadmium chloride in 0.1M lithium chloride.

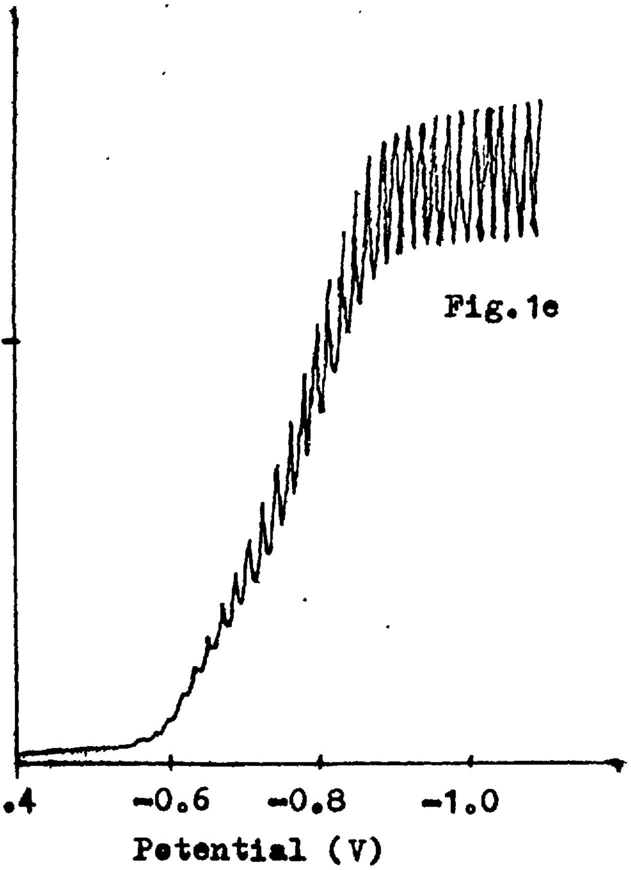


Fig.1e

Fig. 1e:- Cadmium reduction wave in 3:2 xylene/methanol mixture. 2x10^{-4}M cadmium chloride in 0.1M lithium chloride.

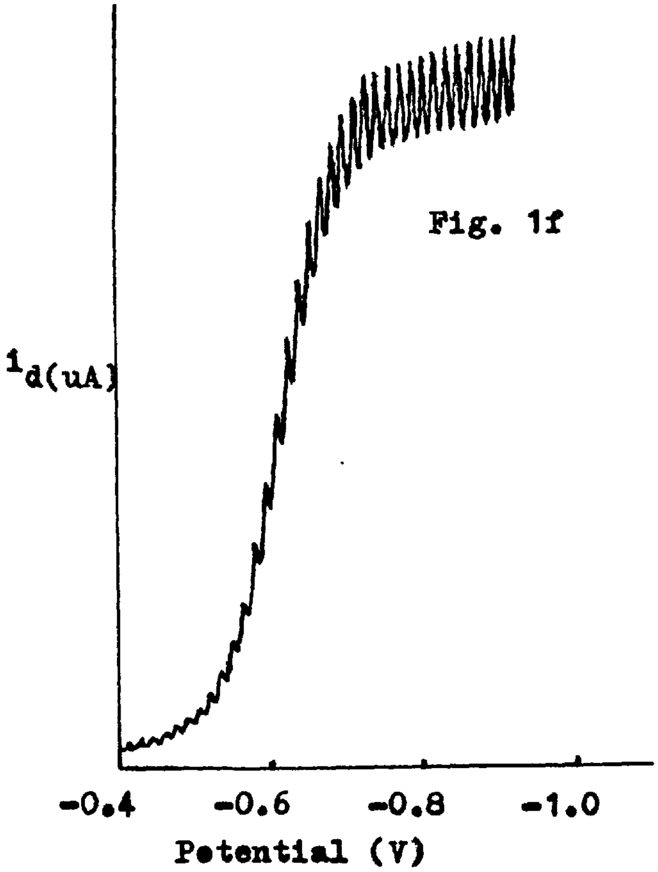


Fig. 1f

Fig. 1f:- Cadmium reduction wave in 3:2 Diethylether/methanol mixture. $2x10^{-4}$M cadmium chloride in 0.1M lithium chloride.

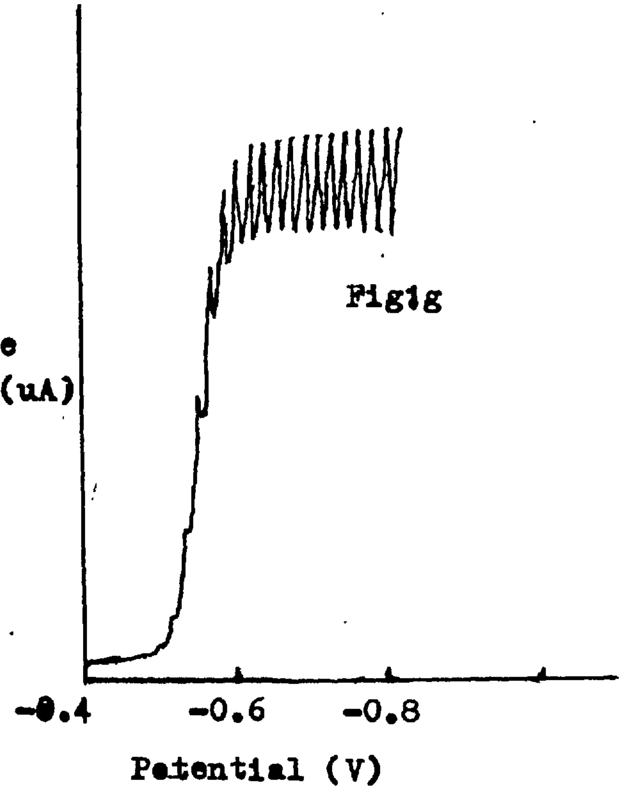


Fig1g

Fig.1g Cadmium reduction wave in 3:2 _iso_-butyl methyl-ketone/methanol. $2x10^{-4}$M cadmium chloride in 0.1M lithium chloride.

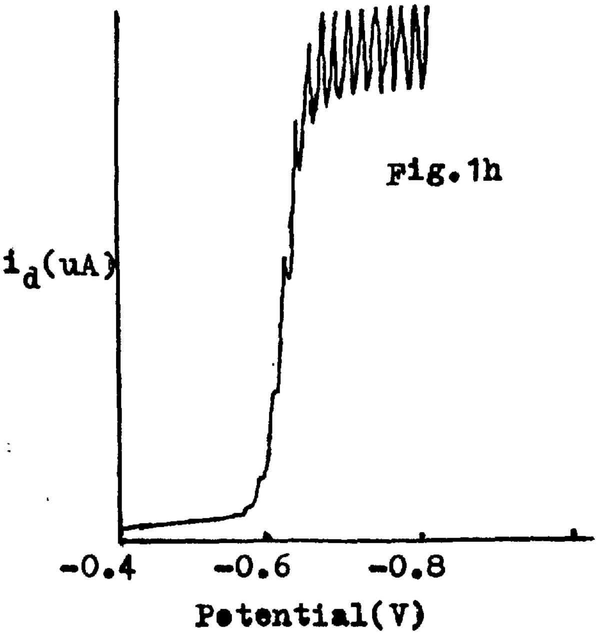


Fig.1h

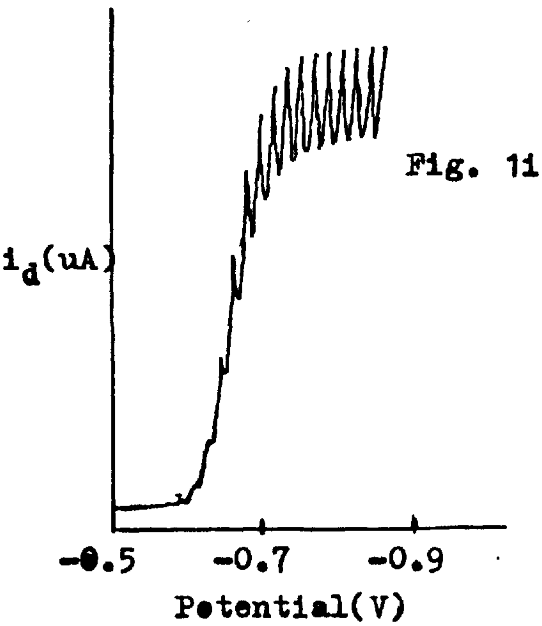


Fig. 1i

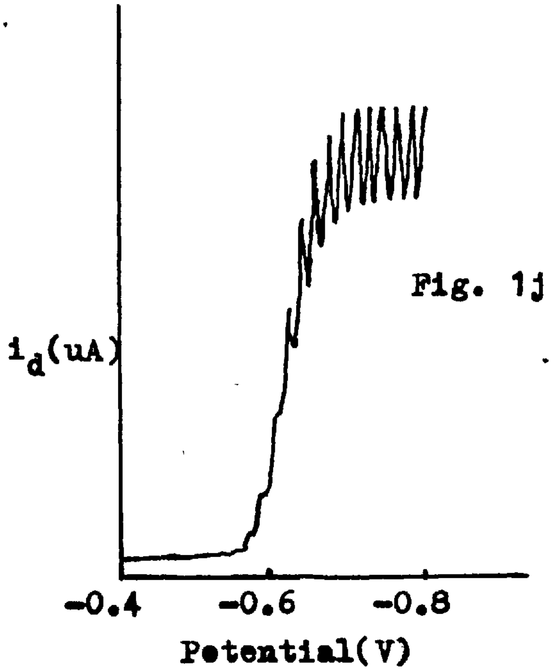


Fig. 1j

Fig 1h:- Cadmium reduction wave in 3:2 ethylacetate/methanol mixture. $2x10^{-4}$M cadmium chloride in 0.1 M lithium chloride

Fig. 1i:- Cadmium reduction wave in a 3:2 amylacetate/methanol mixture. $2x10^{-4}$M cadmium in 0.1M litium chloride.

Fig. 1i:- Cadmium reduction wave in a 3:2 butanol/methanol mixture. $2x10^{-4}$M cadmium chloride in 0.1M lithium chloride.

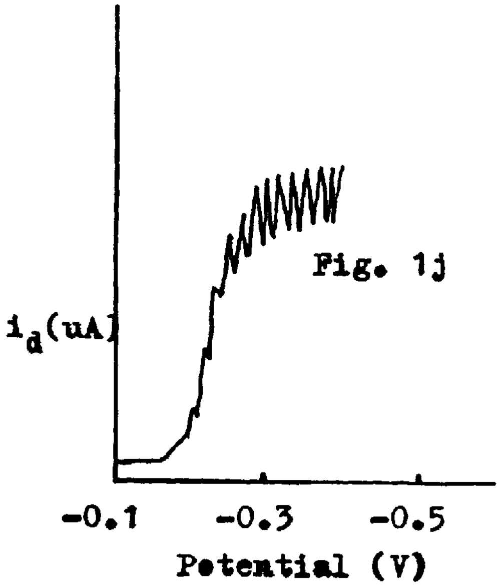


Fig. 1i: Copper reduction wave in 3:2 tributylphosphate/ methanol mixture. $2x10^{-4}M$ cupric chloride in 0.1M lithium chloride.

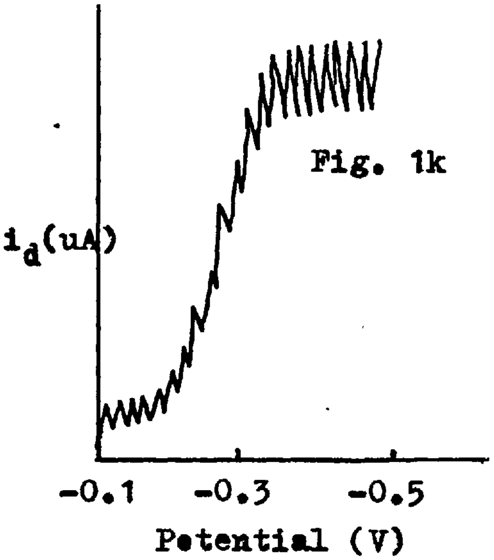


Fig. 1k: Copper reduction wave in 3:2 chloroform/ methanol mixture. $2x10^{-4}M$ cupric chloride in 0.1M lithium chloride.

(d) Reference electrodes

Attempts were made to find some suitable reference electrode for this system which maintains a constant and reproducible potential.

Apart from the mercury pool anode, the following reference electrodes were also studied

1) normal external aqueous saturated calomel electrode with an agar bridge

2) an external reference electrode containing same solvent as in the electrolysis cell

3) internal reference electrode of second order, e.g., silver/silverchloride and a calomel immersed directly in the solution under study.

The aqueous saturated calomel electrode[78] has been extensively used in non-aqueous voltametry for reasons of convenience. Satisfactory results have been obtained because the liquid junction potential is reproducible to an adequate degree. Unfortunately, it was found unsuccessful with the toluene/methanol medium. When the electrode was immersed in the toluene/methanol solvent system, water diffused from the reference electrode into the cell solution through the agar-salt bridge. This formed an emultion which made the determination impossible.

With the second type of external reference electrode, elongated waves were observed which could be due to the high resistance of the experimental set up. Here a cell was employed in which the cathodic and anodic compartments were separated by a sintered glass disc of medium size porosity.

However satisfactory results were given when the silver/silverchloride and calomel electrodes were directly immersed in the electrolysis cell.

The mercury pool anode was eventually chosen as the reference electrode because it was thought that, from analytical purposes, it was the least troublesome.

5. Effect of temperature

The electrolysis cell, containing 2 x 10^{-4} M solutions of cobalt and nickel in a 3:2 toluene/methanol medium and 0.1 M in lithium chloride, was wrapped in a heating tape and the temperature was regulated between 20° and 60° by means of a "Variac". The results showed that not only did the half-wave potential ($E_{\frac{1}{2}}$) of the wave become more positive with increase of temperature, but the slope of the wave became more steep acquiring more the shape of the current/voltage curve theoretically expected for a reversible deposition of a divalent metal ion. An increase in the limiting current was also obtained with the increase in temperature. This could be due to the increase in the activity and diffusion of the ions.

Cobalt and nickel were used in preference to cadmium or copper in this experiment because of their known tendency to give irreversible reductions. Temperature was, as a consequence, more likely to affect these.

(B) Analytical Applications

As a result of the above investigations, it became apparant that inert organic solvents can also be used as suitable media for polarographic studies. In addition, the organic solvents studied appear to possess all the advantages of aqueous solution, e.g. wave height, potential range etc. Therefore, before proceeding to the polarographic examination of organic phases following solvent extraction it was decided to study the essential analytical aspects of some metal ions in organic solvents.

Experimental

Reagents

All the solvents and metal salts used were analytical grade.

Standard Solutions

5×10^{-3} M Cadmium Solution

Weight 0.1142 g. of cadmium chloride in methanol and dilute to 100 ml with the further addition of methanol.

5×10^{-3} M Cobalt Solution

Dissolve 0.1190 g of cobaltous chloride in methanol and dilute to 100 ml by the further addition of methanol.

5×10^{-3} M Copper Solution

Dissolve 0.0853 g of cupric chloride in methanol and dilute to 100 ml.

5×10^{-1} M Lithium Chloride Solution

Dissolve 21.2 g of dried lithium chloride in methanol and dilute to 1 litre.

5×10^{-3} M Nickel Solution

Dissolve 0.1289 g of nickel chloride in methanol and dilute to 100 ml.

Procedure

Add 2.0 ml. of each methanolic solutions of metal salts to separate 25 ml. volumetric flasks containing 5.0 ml. of 0.5 M lithium chloride solution. Add 15 ml of the organic solvent and dilute to the mark by the further addition of methanol. Transfer a 5 ml. portion of the solution to the electrolysis cell and add *ca.* 5 ml. of mercury to serve as the anode. Remove the oxygen by passing oxygen-free nitrogen through the solution for 5 minutes. Divert the flow of nitrogen over the surface of the solution and make recordings between 0.0V and the potential at which the supporting electrolyte begins to reduce.

Results and Discussion

1. Effect of the solvent on the polarographic reduction of cations

The effect of the solvents listed in Table III on the reduction of the cations cadmium, cobalt, copper and nickel was investigated as described above. Solvents not listed in Table III but used for a limited number of experiments included carbontetrachloride, nitrobenzene and cyclohexane. Carbon tetrachloride and nitrobenzene were found to be reduced at too positive a potential (*Ca.* 0.4 and 0.5 V respectively) and therefore could not be used as solvents for polarographic studies. The use of cyclohexane was not encouraged because it was found to be immiscible with methanol.

The data in Table III shows that the reduction order of the metal ions is the same as in aqueous solutions. However, the shifts in half-wave potential is much more pronounced.

TABLE III

Half-wave potentials of cations (V)

solvent	reduction of supporting electrolyte	copper	cadmium	nickel	cobalt
water	2.2	-0.18 (max)	0.68	-1.09	-1.31
iso butyl methyl ketone	-	-0.32 (max)	-0.56	-0.83	-1.08
Diethyl ether	-2.0	-0.30	-0.58	-0.88	-1.08
Tributyl ortho phosphate	-2.0	-0.33	NW		
Ethyl acetate	-2.0	-0.22	-0.62	-0.98	-1.18
Amyl acetate	-2.0	-0.24	-0.66	-1.0	-1.22
Butanol	-2.0	-0.20	-0.62	-0.87	-1.08
Chloroform	-2.0	-0.29	-	-	-
Benzene	-2.0	-0.23	-0.74*	-0.95	-1.1(Ev)
Toluene	-2.0	-0.2 (max)	-0.76 (Ev)	-0.96	-1.12
Xylene	-2.0	-0.24 (max) Ev	-0.78*	-0.98	-1.1(Ev)

Ev indicates elongated wave
max " maximum
NW " no wave obtained
* " appearance of two coincident waves

Cadmium gave a very good wave in all solvents except benzene and xylene in which the two coincident waves which could not be completely resolved were observed. The half-wave potentials of cadmium were more positive in iso-butyl methyl ketone and diethyl ether because of low solvation of the cadmium ion in these solvents. No reduction wave was observed for cadmium in tributylorthophosphate.

Nickel and cobalt exhibited excellent waves in all the solvents except ethyl acetate in which elongated waves were obtained. The half-wave potentials were moved to more positive values in all solvents. This shift was more pronounced in iso-butylmethyl ketone and diethylether than in the other solvents.

In all the solvents the reduction of cupric ion was well-defined and superior to that obtained using aqueous solutions. However, the half-wave potentials were more negative in organic solvents. The reduction wave of cupric ion was characterized by a short residual current and large anodic wave before the cathodic reduction wave. The wave height was about one-half of the value as compared to the other divalent metal ions and hence it might be assumed that the reduction wave measured was that for the reduction of the cuprous ion to the metallic state. The negative potential shift could be explained by assuming that the reduction of the cuprous ion to the metal is more difficult in these solvents, that is, the solvated cuprous ion is more stable in these solvents than in water.

Calibration Curves

Polarographic measurements were made on solutions $2 \times 10^{-4} - 10^{-3}$ M with respect to cadmium, cobalt, copper and nickel. These solutions were prepared as above. The wave height was measured at the half-wave potential, after correcting for the residual current. It was observed that in a few instances (see Table III) polarograms possessed maxima. In these cases the wave height wave was measured at more negative potentials where the plateau of the curve was parallel to the residual current. A plot of the wave height against the concentration of the metal ions was a straight line.

The fact that the relationship,between the diffusion current and the concentration of the metal ions, is linear allows these organic solvents to be used for analytical purposes. Furthermore, it offers the possibility of analysing traces of metal ions following solvent extraction by directly examining the organic phase.

SECTION II

CHAPTER I

Metal - Pyridine - Thiocyanates

Introduction

Ternary complexes formed by the reaction of a metal ion, pyridine, and thiocyanate ions have been used in analysis for the last forty years. The gravimetric determinations are based upon the formation of insoluble products by the reaction of these substances in neutral solutions. Martini[79] has used these complexes for the micro-chemical detection of cadmium, cobalt (11), copper (11) and zinc.

There are a few literature references to the instrumental measurement of the colour of the chloroform extract of the metal ions cobalt (11), copper (11), iron, manganese (11) and nickel. Forsythe, Magee and Wilson[80] have fractionally precipitated cobalt (11) and nickel as their pyridine-thiocyanates by control of pH. The nickel precipitate was then extracted into chloroform and the cobalt (11) precipitate into iso-butylmethyl ketone and both were then determined spectrophotometrically.

G.H. Ayres and S.S. Baird[81] have also determined spectrophotometrically cobalt (11), copper (11), iron, manganese (11) and nickel using the same system extracted in chloroform.

Because of the insolubility of this system in aqueous solution, no polarographic studies have yet been made. It was thought, therefore, worthwhile to investigate this system following its solvent extraction into toluene. This solvent was selected because it is closely related to chloroform in its extracting the above ion association system and offers a much larger potential range. Also it is less toxic than benzene.

(A) Preliminary Study of the Solvent Extraction of Metal-Pyridine-Thiocyanates

Experimental

Apparatus:

1. Elliot Polarograph Model 200 with dropping mercury electrode. Unless otherwise stated the operating conditions were the same as described in the previous section.
2. pH Meter. E.I.L. Vibron pH meter, Model 39A.

Reagents:

All the reagents and the solvents used in this study were of analytical grade purity except *iso*-butylmethyl ketone which was of general purpose reagent grade.

Citric acid	1 percent (W/V) in distilled water.
Hydrochloric acid	Sp. gr. 1.18 and 10 percent (V/V) in distilled water.
Magnesium nitrate	50 percent (W/V) in distilled water.
Potassium thiocyanate	10 percent (W/V) in distilled water.
Pyridine	
Sodiumhydroxide	10 percent (W/V) in distilled water.

Benzene

Iso-butylmethyl ketone

Chloroform

Toluene

Stock Solutions

Metal ion stock solutions

Prepare 100 ml. of 10^{-2} M solutions of metal ions by weighing suitable amounts of the metal salts and diluting them with distilled water.

0.5 M Lithium chloride solution

Dissolve 21.2 g. of dried lithium chloride in methanol and dilute to 1 litre by the further addition of methanol.

1. Effect of pH on extraction of metal-pyridine-thiocyanates

The extraction procedure employed was essentially that recommended by Ayres and Baird [81].

For each metal ion listed in Table IV a series of solutions covering the pH range 2 to 10 were prepared. They contained 2.5 ml. of 10^{-2} M metal ion solution, 2 ml. of 50% magnesium nitrate, 6 ml of 1% citric acid, 2 ml of pyridine and 2.5 ml. of 10% potasium thiocyanate. The pH of the aqueous phase was adjusted to the required value by the addition of ammonium hydroxide or hydrochloric acid, pH measurements being made on an E.I.L. Vibron pH meter. The mixture was then transferred to a separating funnel and extracted with one 15 ml. portion of toluene for 30 seconds. After careful phase separation the organic phase was transferred to a 25 ml. volumetric flask containing 5 ml. of 0.5 M lithiumchloride and the volume was made to the mark with methanol. After deoxygenating the 5 ml. aliquot with nitrogen (oxygen-free) for 5 minutes polarograms were recorded.

Out of the 26 metal ions investigated (listed in Table IV) only cobalt (11), copper (11), iron, manganese (11), nickel and zinc gave waves in the toluene phase after extraction. The extraction of the cadmium-pyridine-thiocyanate complex was incomplete in toluene, benzene and xylene and precipitates collected at the interface of the two phases. A complete extraction could, however, be achieved in iso-butylmethyl ketone. With chloroform, the reduction of the solvent masked the reduction of the cadmium complex.

Furthermore, the complete extraction for cadmium, cobalt (11), copper (11), iron, manganese (11), nickel and zinc was obtained between pH 4 and 10. No variation in the half-wave potential ($E\frac{1}{2}$) with pH was observed which could suggest that the stability of the extracted species was not altered with pH. No waves could be obtained in an aqueous phase for the cadmium, cobalt (11), copper (11), iron, manganese (11), and nickel complexes even at concentrations of 10^{-5} M. It is because of their insolubility in aqueous solutions. Only the zinc complex produced a wave in the aqueous phase (-1.0 V)

The results obtained at pH 7.0 are shown in Table IV.

TABLE IV

Metal ion	Aqueous Phase in 0.1 M LiCl $E_{\frac{1}{2}}$ (V)	Aqueous Phase & Pyridine in 0.1 M Licl $E_{\frac{1}{2}}$ (V)	Aqueous Phase of M-Py-SCN at pH 7.0 in 0.1M LiCl $E_{\frac{1}{2}}$ (V)	Organic Phase after extraction $E_{\frac{1}{2}}$(V)
Blank	-2.2	-1.55	-1.55	-1.5V
Anitmony & citric acid	-0.45	-1.02	-0.80	NW
Arsenic (111)	Three waves at -0.72, -0.9V, -1.23, middle wave bigger than other two	NW	NW	NW
Beryllium	NW	NW	NW	NW
Bismuth +0.5M hydrochloric acid	-0.14	-0.67	Three waves at -0.15, -0.44, -0.87	NW
Cadmium	-.068	-0.71	NW(PPtn)	-0.65
Cobalt (11)	-1.31	-1.18	NW(PPtn)	-0.94
Copper (11) *	-0.18	-0.45	NW(PPtn)	-0.28
Iron (11)	-1.38	NW	NW(PPtn)	-1.34

TABLE IV (contd)

Metal ion	Aqueous Phase in 0.1 M Li Cl $E_{\frac{1}{2}}$ (V)	Aqueous Phase & Pyridine in 0.1 M Li Cl $E_{\frac{1}{2}}$ (V)	Aqueous Phase of M-Py-SCN at pH 7.0 in 0.1M Li Cl $E_{\frac{1}{2}}$ (V)	Organic Phase after extraction $E_{\frac{1}{2}}$(V)
Iron (111)	Two waves at $E_{\frac{1}{2}} > 0.0$, -1.38	NW	NW (PPtn)	Two waves at $E_{\frac{1}{2}} > 0.0$, -1.34
Indium	-0.61V	NW	NW	NW
Lead	-0.49	NW(PPn)	NW(PPtn)	NW
Molybdenum (V1)	-0.34,-0.66	NW	NW	NW
Molybdenum (V)	-0.34,-0.66	NW	NW	NW
Manganese	-1.6V	NW	NW(PPtn)	-1.34
Niobium	NW	NW	NW	NW
Nickel	-1.1V	-0.94	NW(PPtn)	-0.72
*Palladium	$E_{\frac{1}{2}} > 0.0$	-0.38	NW	NW
Thallium (1)	-0.58	-0.54	-0.39	NW.
Tin (11)	-0.56	NW	NW	NW
Tin (1V)	-0.56	NW	NW	NW

TABLE IV (contd)

Metal ion	Aqueous Phase in 0.1 M LiCl $E_{\frac{1}{2}}$ (V)	Aqueous Phase & Pyridine in 0.1 M LiCl $E_{\frac{1}{2}}$ (V)	Aqueous Phase of M-Py-SCN at pH 7.0 in 0.1M LiCl $E_{\frac{1}{2}}$ (V)	Organic Phase after extraction $E_{\frac{1}{2}}$(V)
Titanium (111)	-0.93	NW	NW	NW
Uranium	-0.26,-1.02	-0.82,-1.12	-0.46,-0.9V	NW
Zinc	-1.1	-1.1	-1.0	-1.03
Zirconium	NW	NW	NW	NW

NW indicates No Wave due to metal ion observed.

(PPtn) indicates Precipitation observed.

* indicates grey coating observed on mercury pool.

The following experimental variables were then investigated using a solution 4×10^{-4} M in copper-pyridine-thiocyanate following solvent extraction into a 3:2 toluene/methanol medium containing 0.1 M lithium-chloride.

2. Effect of ionic strength

This effect was investigated using a solution of magnesium nitrate to vary the ionic strength of the aqueous phase. The solutions were prepared as above.

The results showed that an improvement in extraction efficiency and phase separation could be obtained with increasing concentration of magnesium nitrate. No further enhancement was given in either of these when the concentration was $\geqslant$ 2 M.

3. Electrode requirements

(a) Distance between electrodes

The effect on the limiting current and half-wave potential ($E_{\frac{1}{2}}$) was negligible provided the distance between the top of mercury pool and the tip of dropping mercury electrode was $\leqslant$ 0.5 M. Values below this produced erratic results. The distances investigated were (0.5, 1.0, 2.0, 3.0 cms. respectively)

(b) Drop time

The limiting current was found to increase slightly with increasing drop time.

(c) Mercury pressure

A linear relationship was obtained between the limiting current and the square root of the height of the mercury reservior which suggests that the limiting current is diffusion controlled. This was further verified by the fact that a direct proportionality was obtained between the wave-height and the concentration of metal ion.

(d) Reference electrodes

The mercury pool, calomel and silver/silver chloride reference electrodes were investigated. Although all gave similar results, it was considered that from an analytical view point, the internal mercury pool was the least troublesome in all respects and was consequently selected for further investigations.

4. Reversibility of Reduction Waves

It can be shown [82] that the expression relating current to the potential of the dropping mercury electrode for a simple reversible polarographic step is

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \frac{id - i}{2}$$

where E is the potential of electrode expressed in volts (V), $E_{\frac{1}{2}}$ the potential at which $i = \frac{id}{2}$ or the half-wave potential of the step or wave, n the number of electrons transferred in the electrode reaction, i_d the diffusion current, i the current produced by the reduction of metal ion, R the gas constant, T the absolute temperature and F is the Faraday.

This equation shows that a plot of $\ln \frac{i}{id - i}$ against E for a reversible polarographic step should give a straight line, of slope $n \left(\frac{F}{RT}\right)$, crossing the abscissa $\left(\ln \frac{i}{i_d - i} = 0\right)$ at $E = E_{\frac{1}{2}}$. It is important to realise, however, that this plot may also be approximately a straight line when the electrode reaction is irreversible, and its straightness is therefore no criterion of the reversibility of the electrode reaction. However, the slope of the log plot against the potential of the electrode will differ from the theoretical value if the reduction is irreversible.

The same expression holds for the reduction to the metallic state of the complex metal ion in solution[83]. Such a reduction may be represented by the equation

$$MX_a^{(n-ab)} + ne + Hg \rightleftharpoons M(Hg) + aX^{-b}$$

where X^{-b} is the complexing agent and M(Hg) is the amalgam formed on the surface of the dropping electrode. This, of course, assumes that the metal ion is soluble in mercury. The above reaction may be regarded as the sum of two reactions:

$$MX_a^{(n-ab)} \rightleftharpoons M^{n+} + aX^{-b} \qquad (1)$$

and

$$M^{n+} + ne + Hg \rightleftharpoons M\,(Hg) \qquad (2)$$

where M^{n+} is the 'simple' or hydrated ion of the metal.

If the polarographic step is irreversible with the complex metal ions in solution then, as before, the slope of log plot against potential will differ from the theoretical value. Another useful criterion of reversibility of an electrode reaction is the temperature effect on the half-wave potential. If irreversible, then the half-wave potential ($E\frac{1}{2}$) is usually shifted to a more positive value with increasing temperature because of a now easier reduction.

Figures 2 and 3 show the plot of $\log_{10} \frac{i}{id - i}$ against E for the cadmium and copper (11) as their pyridine-thiocyanate complexes in the organic phase. The slope of the log plot $(n \frac{F}{RT})$ gave a value for cadmium of 1.88 (i.e. approximately 2) and for copper of 1.02 (i.e. approximately 1) which suggests a reversible behaviour of the electrode reactions.

The plot of $\log_{10} \frac{i}{id - i}$ against E was also obtained for iron, manganese (11), and zinc which gave reversible behaviour for these reductions with $n = 2$ (Figures 4, 5 and 6 respectively).

When cobalt was extracted as pyridine-thiocyanate a reversible behavior for cobalt (11) was observed (Fig. 7). However, in case of nickel a irreversible wave was obtained (Fig. 8).

This was further verified by examining, the above solutions containing cobalt (11) and nickel, with increasing temperature. The results showed that with nickel the half-wave potential ($E\frac{1}{2}$) of the wave became more positive with temperature and the slope of the wave also became more steep. This suggests irreversible behavior of the electrode reaction. In case of cobalt (11) reduction, no variation in half-wave potential ($E\frac{1}{2}$) and slope of the curve was obtained with temperature. This suggests the reversible behaviour of the electrode reaction.

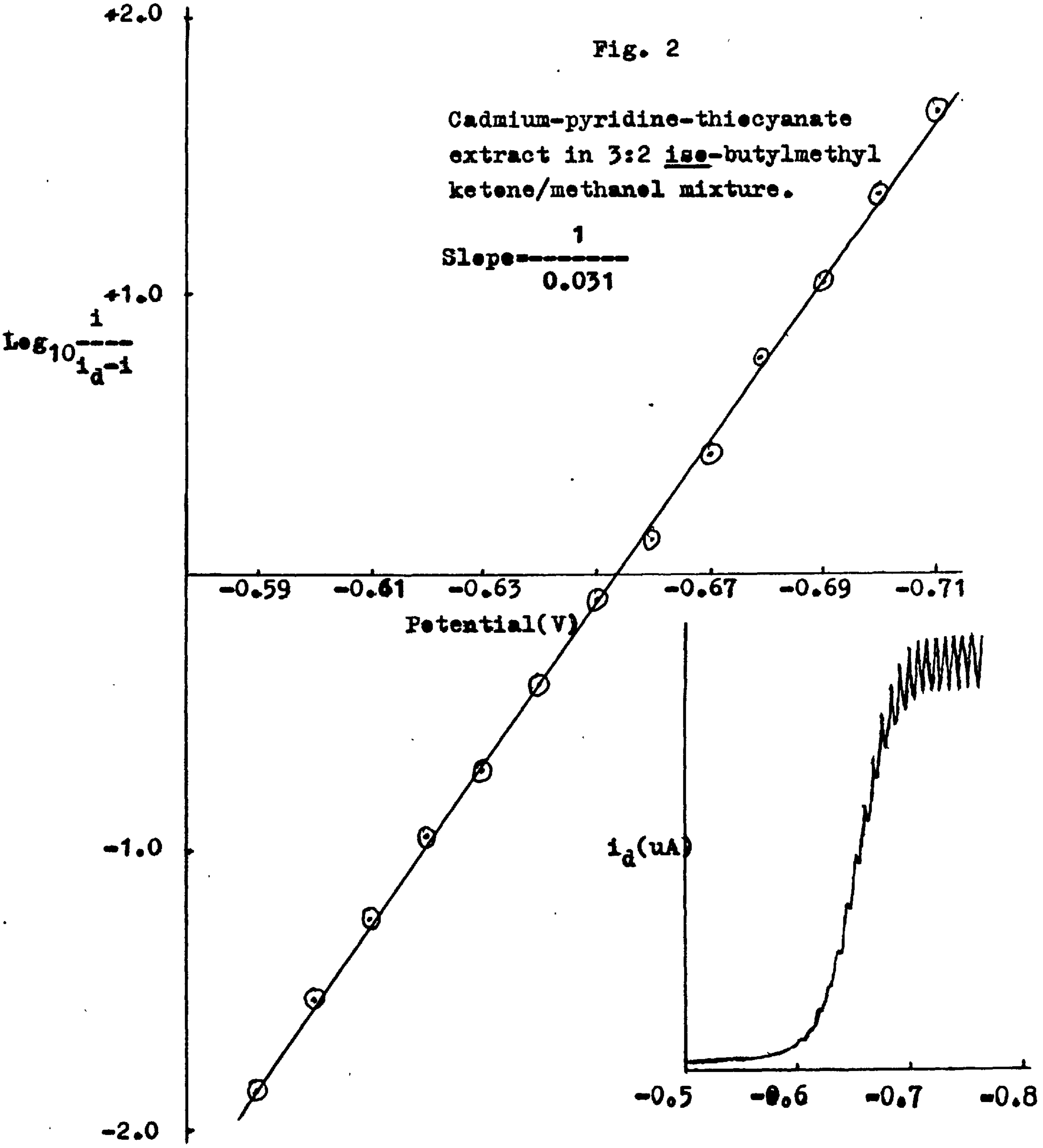


Fig. 2

Cadmium-pyridine-thiocyanate extract in 3:2 *iso*-butylmethyl ketone/methanol mixture.

$\text{Slope} = \frac{1}{0.031}$

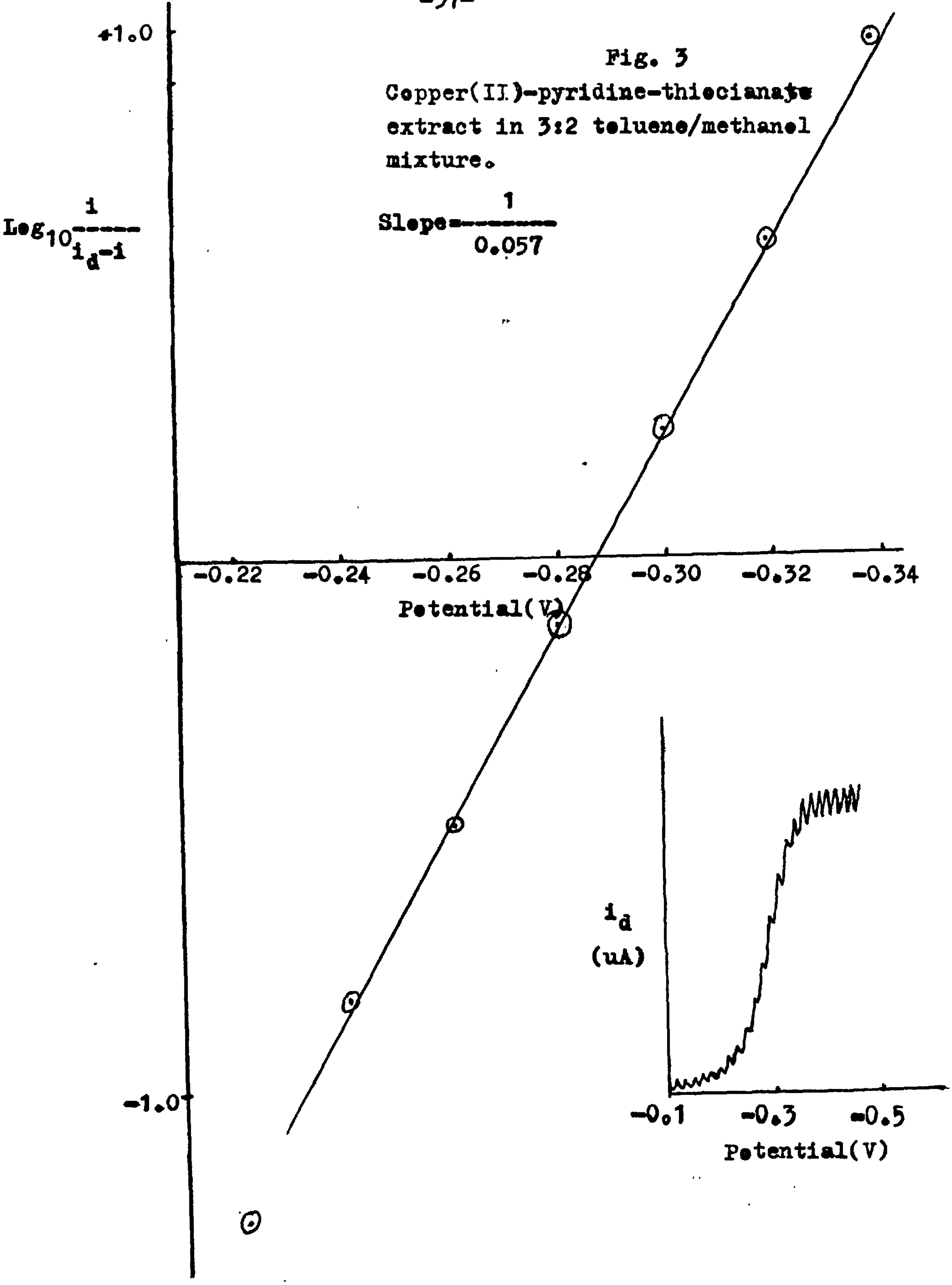


Fig. 3

Copper(II)-pyridine-thiocianate extract in 3:2 toluene/methanol mixture.

$\text{Slope} = \frac{1}{0.057}$

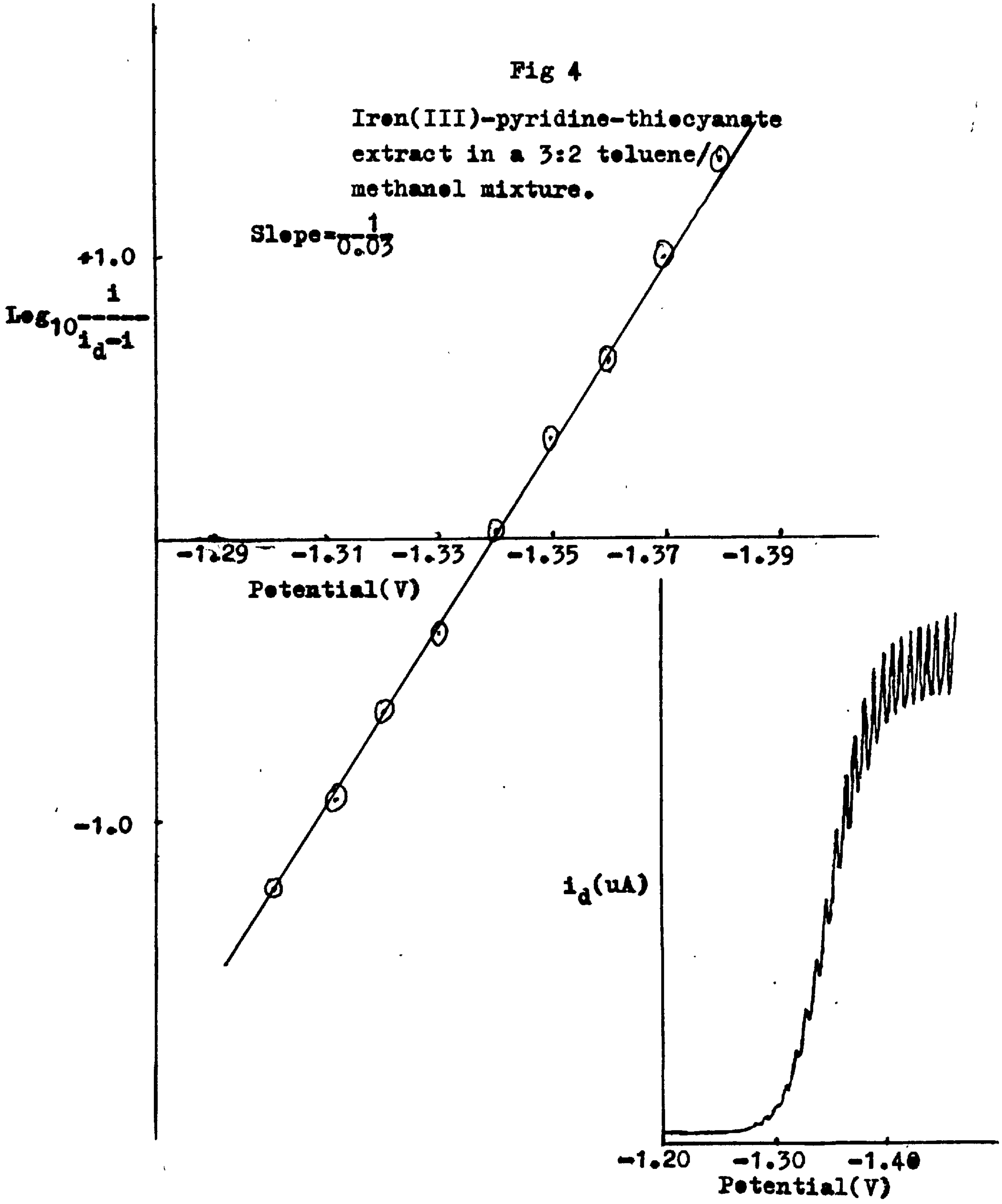


Fig 4

Iron(III)-pyridine-thiocyanate extract in a 3:2 toluene/methanol mixture.

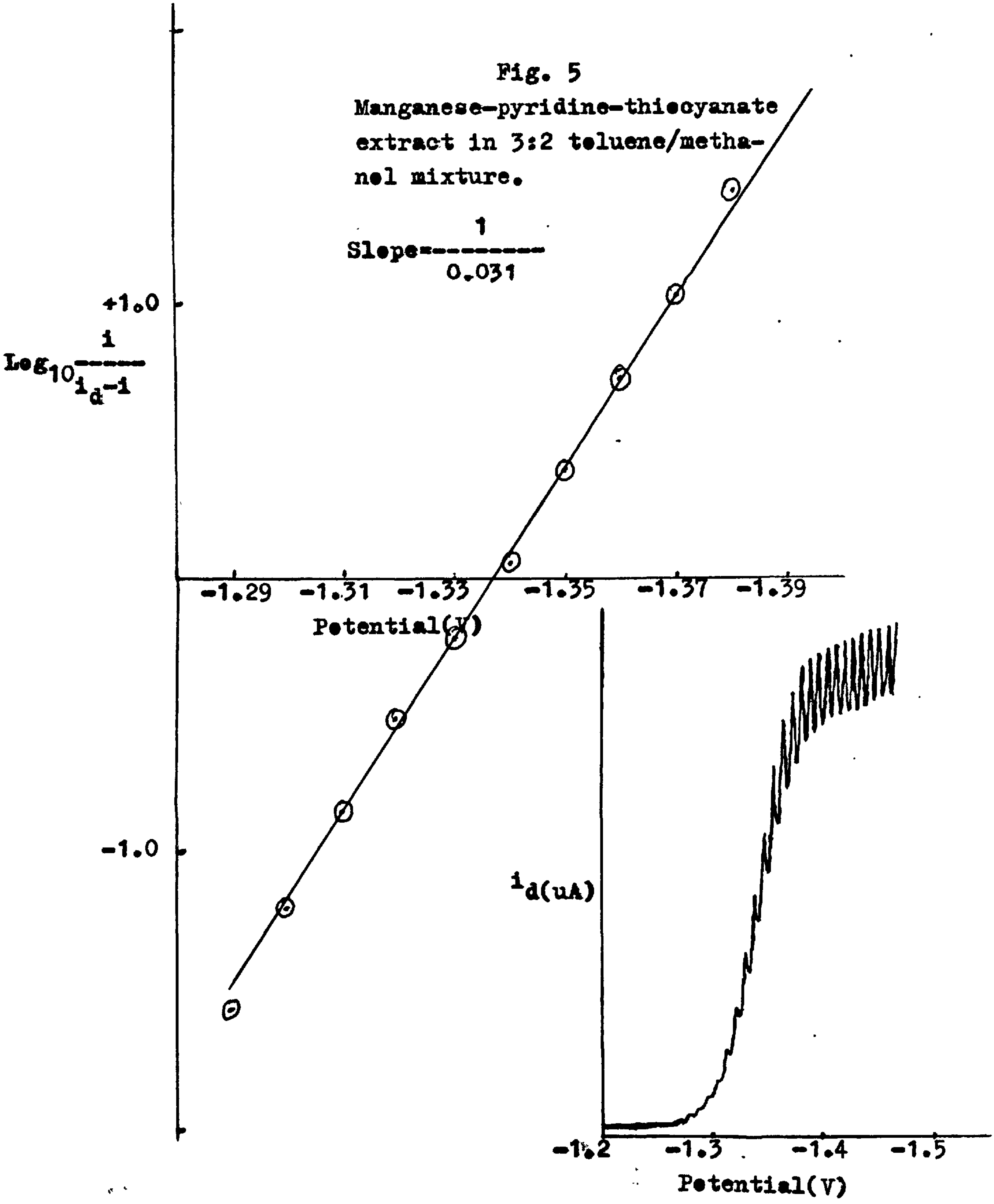


Fig. 5
Manganese-pyridine-thiocyanate extract in 3:2 toluene/methanol mixture.

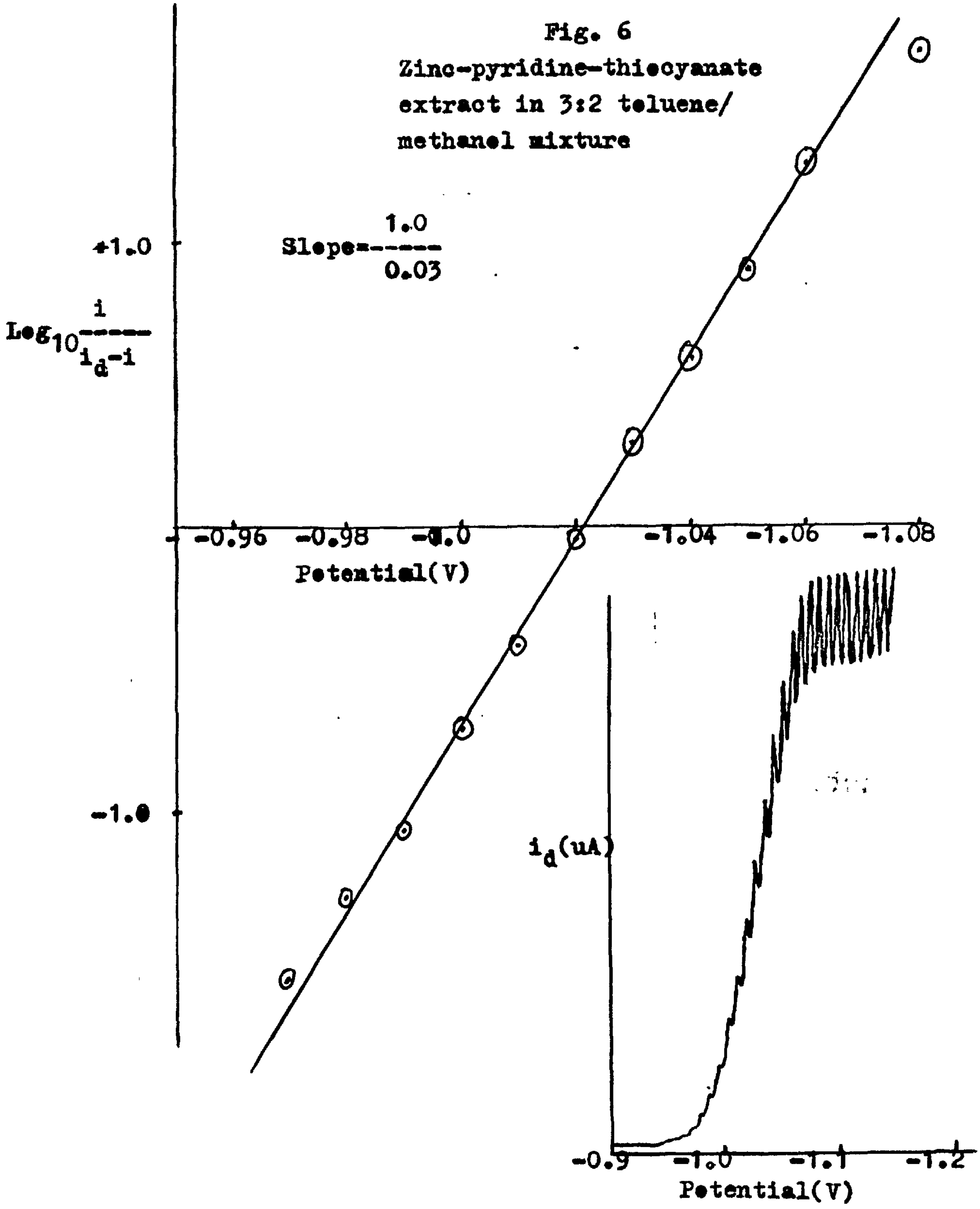


Fig. 6
Zinc-pyridine-thiocyanate
extract in 3:2 toluene/
methanol mixture

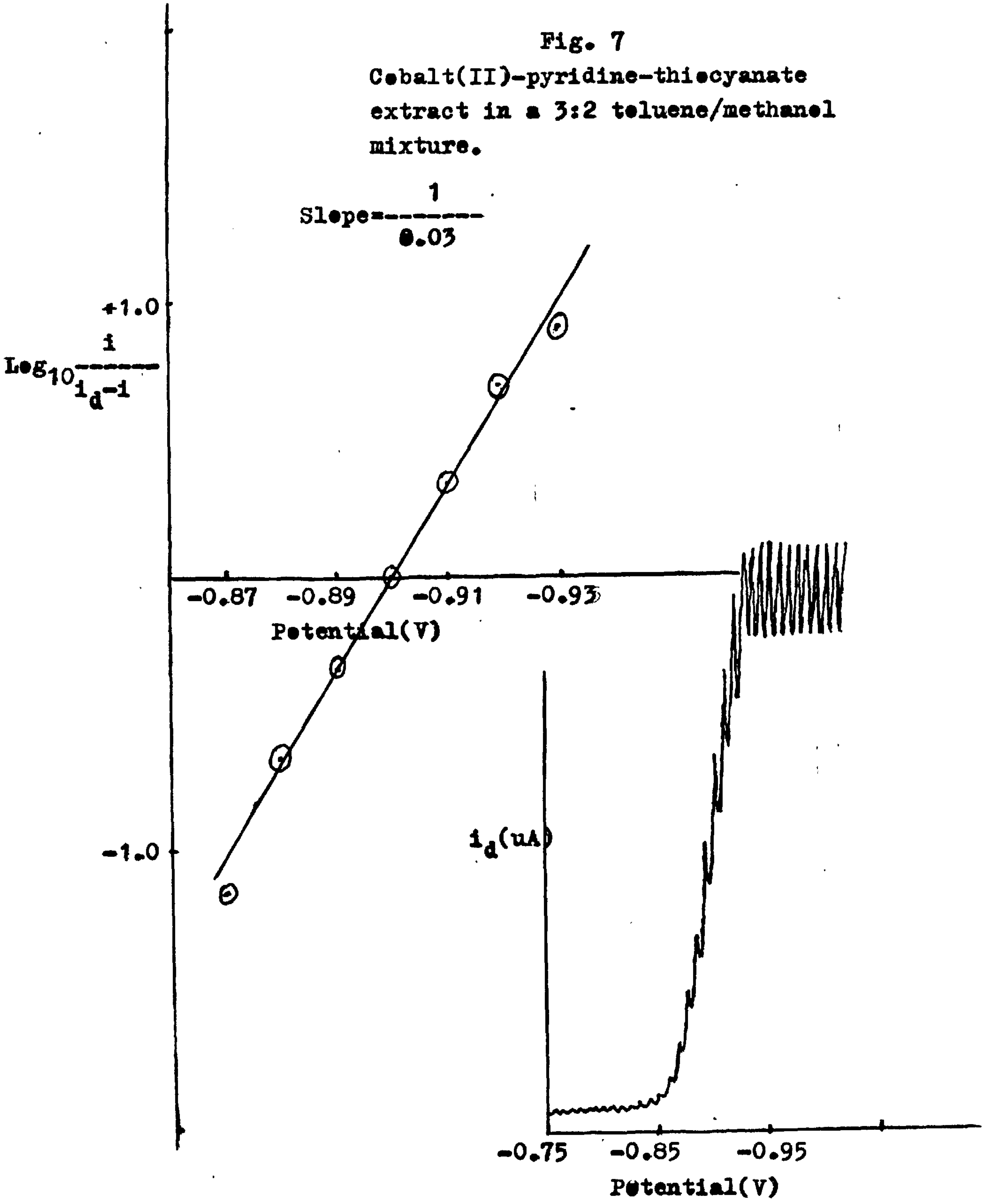


Fig. 7
Cobalt(II)-pyridine-thiocyanate extract in a 3:2 toluene/methanol mixture.

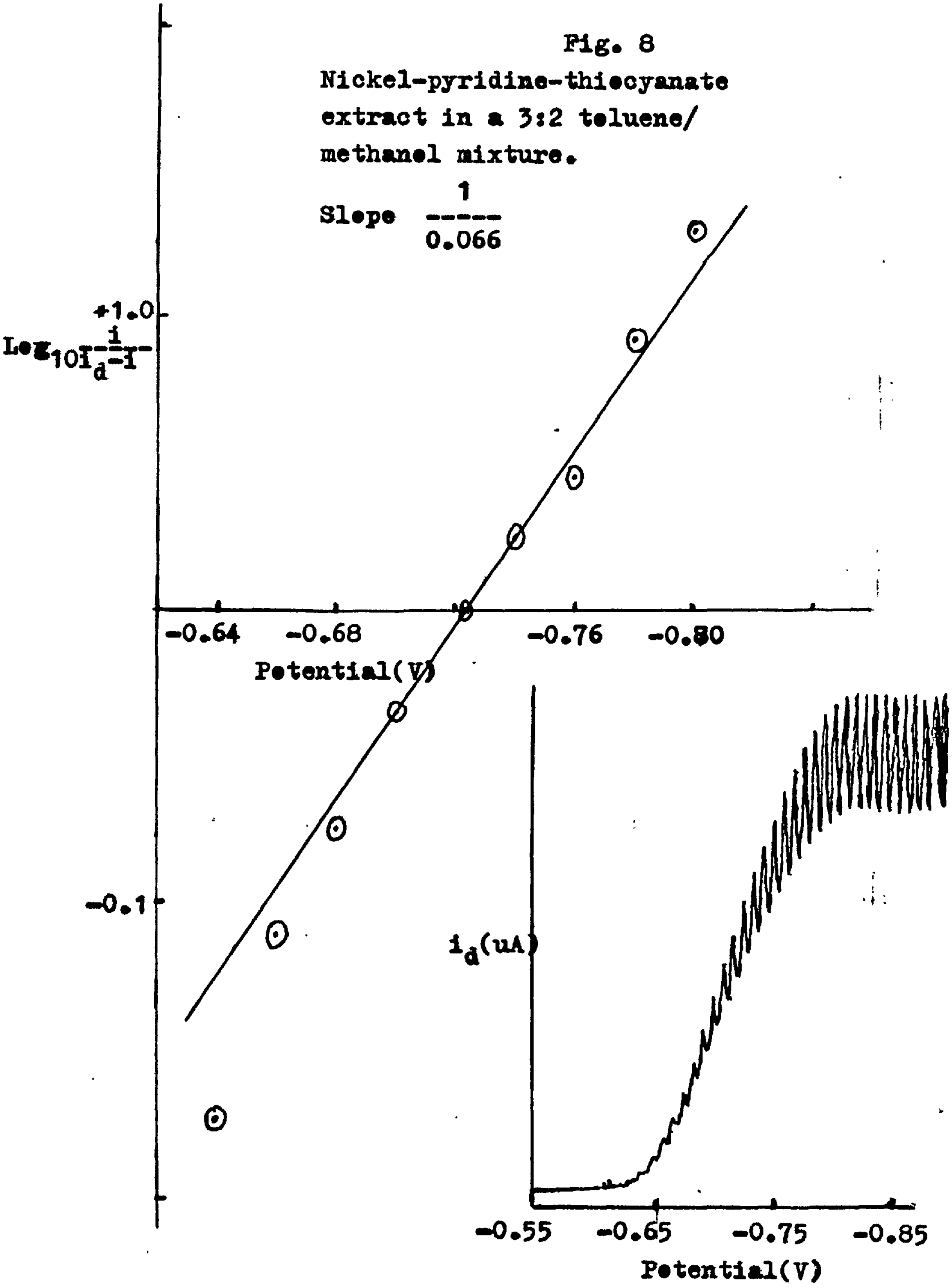


Fig. 8

Nickel-pyridine-thiocyanate extract in a 3:2 toluene/methanol mixture.

Slope $\frac{1}{0.066}$

(B) Determination of some metals as their pyridine-thiocyanate complexes

1. Determination of Copper

(i) Preparation of calibration curve

A calibration was prepared by taking a series of copper (11) solutions (from 2 x 10^{-5} M to 10^{-4} M) through the recommended method given under "Effect of pH" (page 47) of this chapter. A 5 ml. aliquot of the solution was transferred to the electrolysis cell and after deoxyenation the solution was polarographed. In this instance a sensitivity of 2 u A /full scale was used.

The plot of the wave-height against the concentration of copper was a straight line ~~and~~ passing through the origin from 2 - 6 ppm.

(ii) Extraction from larger volumes

The efficiency of extraction from 50, 100, 250 and 500 ml. of aqueous solution into 15 ml. of toluene was investigated. The aqueous phase contained 1 ml. of 10^{-2}M cupric chloride solution as well as the other reagents described above.

Exactly similar results were obtained as those using 25 ml. of aqueous solution. Thus, the overall sensitivity can be increased by using the extraction system as a means of concentration.

2. Determination of other metals

The effect of the different experimental variables on the pyridine-thiocyanate complexes of other metals for example cadmium, cobalt (11), iron, manganese (11), nickel and zinc were found to be essentially the same that obtained with copper. Therefore, the same general procedure was followed for their determinations. Table V summarises the polarographic information regarding the determination of these metal ions.

TABLE V

cation	Half-wave Potentials ($E\frac{1}{2}$) (V)	Optimum concentration range in ug/ml in organic extract	Detection limit in ug/ml in organic extract
cadmium	-0.65	2.5 to 11.2	1.0
cobalt (11)	-0.94	1.2 to 5.9	0.5
copper (11)	-0.28	1.3 to 6.3	0.6
iron (11)	-1.34	1.1 to 5.6	0.5
manganese (11)	-1.34	1.0 to 5.9	0.5
nickel	-0.72	1.2 to 5.9	0.5
zinc	-1.03	1.3 to 6.5	0.6

3. Sequential Determinations

In order that polarography may be used for the simultaneous determination of two or more constituents, it is essential that the appropriate reduction waves be both well-defined and well-resolved.

From our observations, the reduction waves of the metal ions cadmium, cobalt (11), copper (11), manganese (11), nickel and zinc occurred at different potentials and the possibility therefore exists ~~for~~ of a sequential determination of these elements.

In the first instance an equimolar mixture of these ions at the concentration level of 5×10^{-5} M was polarographed as the simple aquo-complexes in aqueous solution. Then pyridine-thiocyanate complexes were examined following solvent extraction in toluene. The results showed (Fig. 9a) that in aqueous solution nickel and zinc gave coincident waves. However, in toluene following solvent extraction both waves were clearly defined (Fig. 9b). However, one disadvantage is that the wave due to nickel is close to that of cadmium.

Therefore, an equimolar mixture of the five cations cadmium, cobalt (11), copper, manganese (11) and nickel were sequentially determined. Figure 10 shows the polarograms obtained by analysing such a mixture following solvent extraction as their pyridine-thiocyanate complexes into toluene.

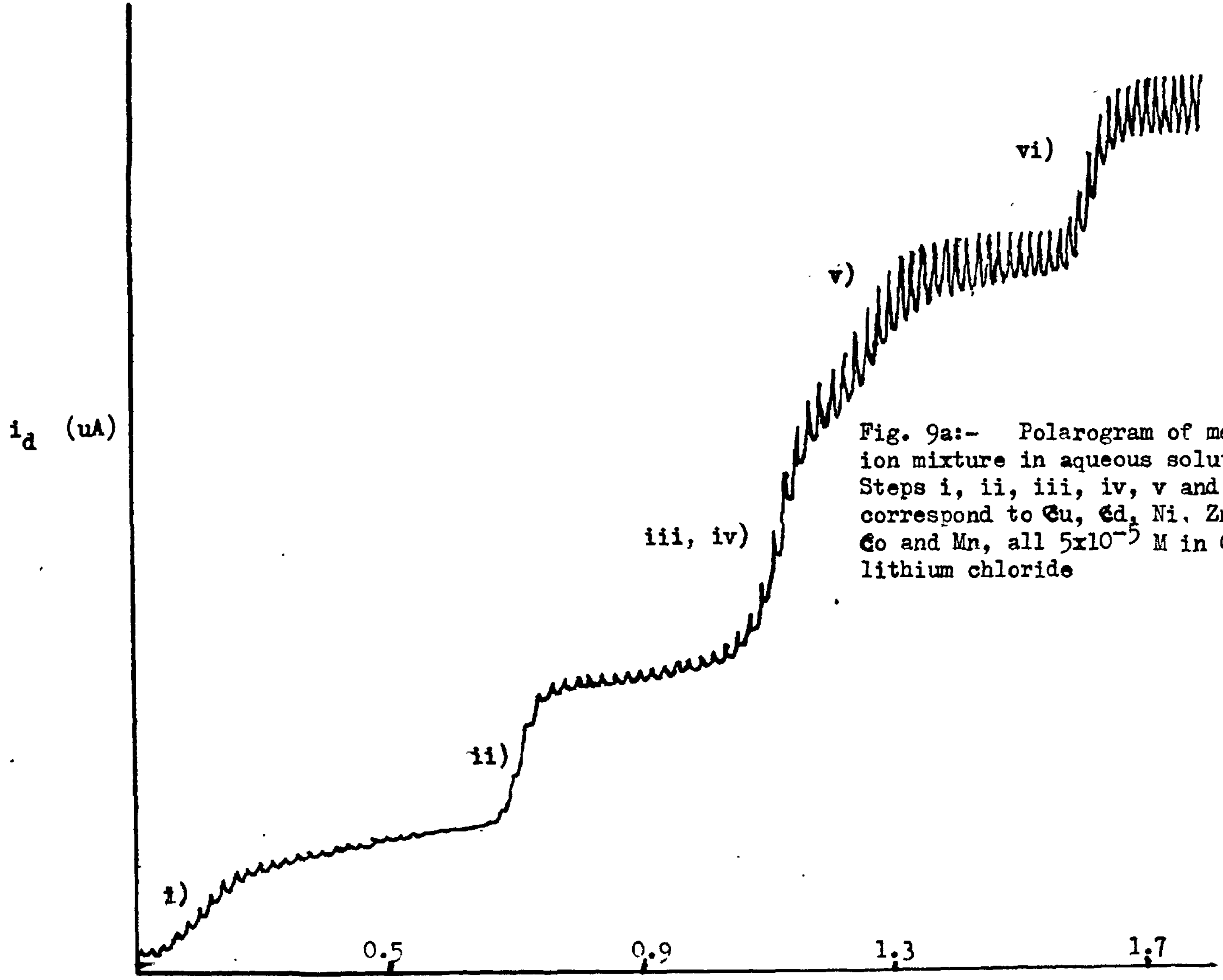


Fig. 9a:- Polarogram of metal ion mixture in aqueous solution. Steps i, ii, iii, iv, v and vi correspond to Cu, Cd, Ni, Zn, Co and Mn, all $5x10^{-5}$ M in 0.1 M lithium chloride

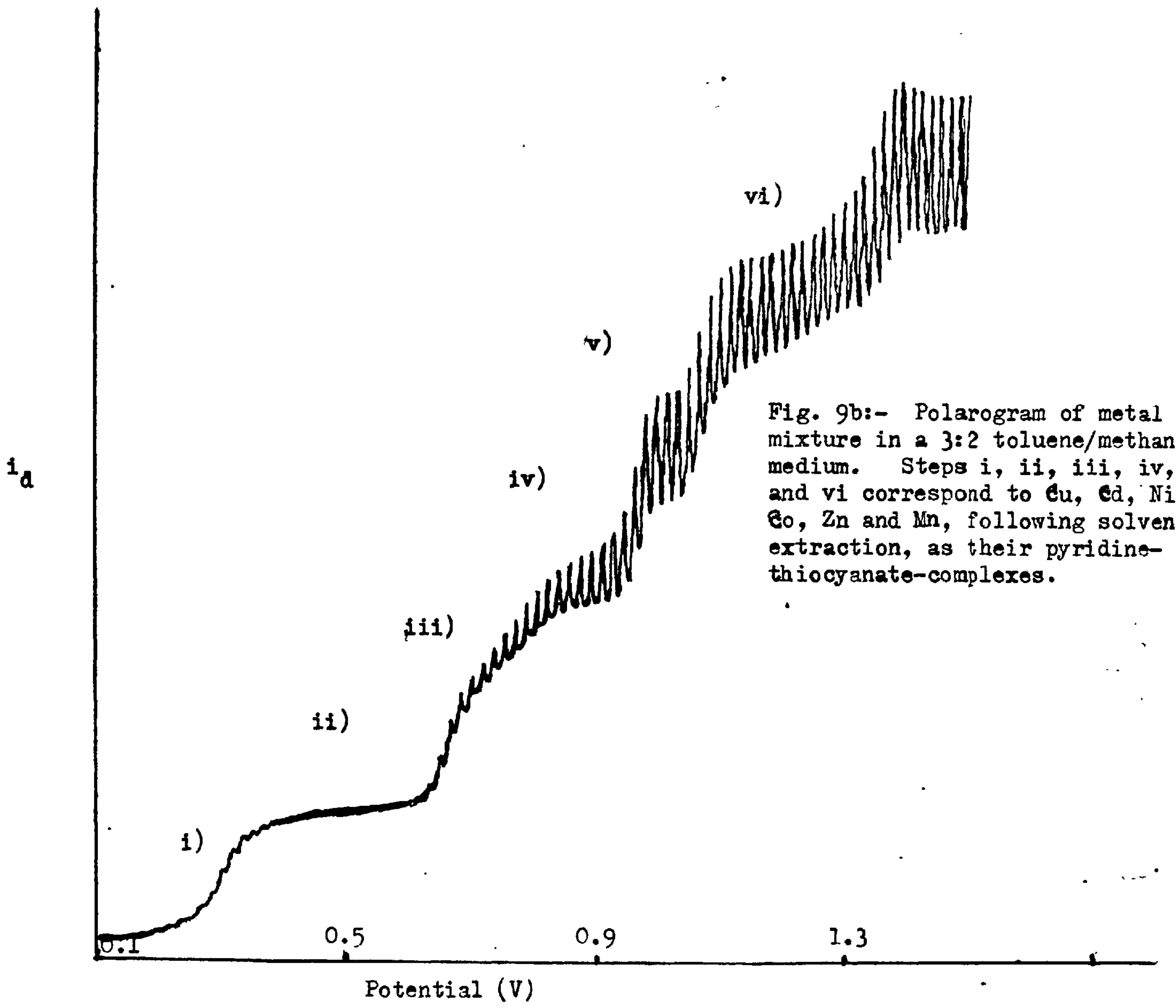


Fig. 9b:- Polarogram of metal ion mixture in a 3:2 toluene/methanol medium. Steps i, ii, iii, iv, v and vi correspond to Cu, Cd, Ni, Co, Zn and Mn, following solvent extraction, as their pyridine-thiocyanate-complexes.

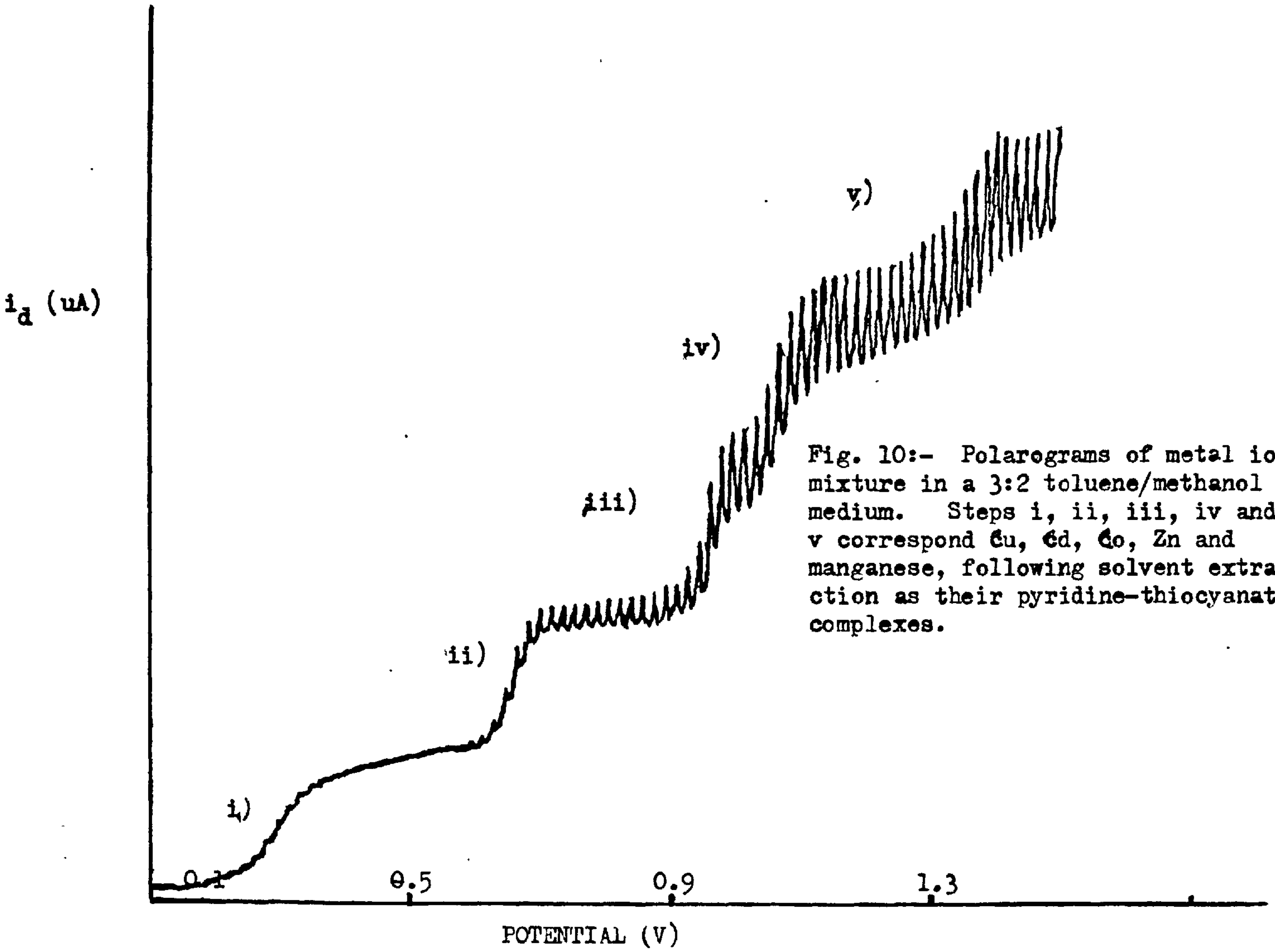


Fig. 10:- Polarograms of metal ion mixture in a 3:2 toluene/methanol medium. Steps i, ii, iii, iv and v correspond Cu, Cd, Co, Zn and manganese, following solvent extraction as their pyridine-thiocyanate-complexes.

Discussion

It can be said that none of the disadvantages associated with aqueous polarography, e.g. time consuming choice of supporting electrolyte, sensitivity limitations, insolubility of certain species, elimination of major constituents, effect of pH variation, etc. constitutes a problem by applying polarography directly to an organic phase following solvent extraction. In addition, the technique, which has received as yet little attention, offers a new advantage such as an effective extension of the normal potential range. This occurs because the half-wave potentials of the metal-aquo complexes can be shifted towards more positive or more negative potentials. This can be effected either by ion-pair or complex formation. Also, although not considered in this thesis, some theoretical studies, such as the determination of stability constants or the reacting ratios of complexes normally insoluble in aqueous solution, may become possible.

In subsequent chapters the results obtained, using potentially more useful extraction systems, and their application to some technical samples, are reported.

CHAPTER II

Metal - Thiocyanates

Introduction

The use of alkalithiocyanates as reagents for the colorimetric estimation of a number of metals has been known for some time. Iron has been analysed as its thiocyanate complex and can be extracted as a stable red complex in the presence of excess thiocyanate into oxygen containing solvents[84]. Extractable yellow complexes which can also be used for colorimetric purposes are formed by bismuth, niobium and uranium. In the presence of reducing agents and thiocyanate, molybdenum and tungsten can also be extracted.

More recently the thiocyanate complexes have been used more as a means of chemical separation. For example, several of the rare earth elements have been separated by a method based on the different solubilities of their thiocyanates in butanol[85]. Conversely, a separation of thorium from the rare earths is attained by extracting aqueous solutions of these substances containing ammonium thiocyanate with 1-pentanol[86]. One of the most effective separations using thiocyanate is the extraction of scandium with diethyl ether[87]. Another interesting application is the separation of hafnium from zirconium utilising differences in their extractabilities in diethyl ether[88, 89].

An extensive study of the distribution of many metal-thiocyanate complexes in diethyl ether at various ammonium thiocyanate concentrations has been made by Bock[90].

The work in this chapter is concerned with the polarographic study of the above system. The metal-thiocyanate complexes were selected as an example of one of the more useful ion association systems used in analytical chemistry and, in addition, they were the next logical step in the line of investigation already described.

Experimental

Apparatus

Polarograph

The polarograph used was an Elliot Polarograph Model 200 with a dropping mercury electrode. Unless otherwise stated the operating conditions were as follows:
rate of potential increase 0.25 v/100 sec, drop time 3.4 sec, height of mercury reservoir 60 cm, mercury flow-rate 2.2636 mg/sec, no damping or counter current. An internal mercury pool was used and the de-aeration was achieved by bubbling nitrogen through a 5 ml. sample for 2 minutes. A mercury seal was used instead of the more usual water seal to prevent re-absorption of oxygen. pH meter E.I.L. Vibron (Model 39A).

Reagents

All chemicals used were of analytical grade unless otherwise stated. The general purpose reagent grade is indicated by G.P.R.

Ammonia	Sp. gr. 0.88
Ammonium Molybdate	
Ammonium thiocyanate	Aqueous saturated solution
Ascorbic acid	G.P.R.
Citric acid	
Hydrochloric acid	Sp. gr. 1.18
Lithium chloride (dried)	G.P.R.
Lithium hydroxide	

Magnesium nitrate hexahydrated	
Perchloric acid	Sp. gr. 1.54
Sodium perchlorate	G.P.R.
Sulphuric acid	Sp. gr. 1.84
Tetra ethyl ammonium chloride	G.P.R.

Solvents:

Amylacetate, benzene, iso butylmethyl ketone, carbon tetrachloride, chloroform, diethyl ether, methanol, toluene and xylene.

Stock solutions

5 M Hydrochloric acid

Dilute 215.5 ml of concentrated hydrochloric acid to 500 ml with distilled water.

1×10^{-2} M metal ion solutions

Prepare 100 ml. of metal ion solutions by dissolving suitable amounts of the salts in distilled water.

0.5 M Lithium chloride solution

Dissolve 5.3 g of anhydrous lithium chloride in methanol and dilute to 250 ml with methanol.

1×10^{-3} M Molybdenum solution

Dissolve 0.1766 g of ammonium molybdate $(NH_4)_6 Mo_7 O_{24}.4H_2O$ in distilled water and dilute to 1 litre.

1. Preliminary Polarographic Investigation

The solvent extraction procedure followed was as described by Morrison and Freiser[84]. The aqueous phase (25 ml) was made 10^{-3} M in metal ions, ca. 0.5 M in hydrochloric acid and _ca_. 2 M in ammonium thiocyanate (obtained by the dilution of 2.5 ml. of a saturated aqueous solution). Extraction was carried out with 15 ml. of diethyl ether and the resulting organic phase, after the addition of 5 ml. of a 0.5 M lithium chloride solution in methanol, was diluted to 25 ml. with methanol. This solution was degassed with oxygen-free nitrogen and polarographed using an instrument sensitivity of 10 uA/full scale deflection. The efficiency of the extraction was followed by examining the resulting aqueous phase.

Table (VI) shows the half-wave potentials (V) of the reduction waves in the organic phase (column 5) together with those obtained in an aqueous phase before and after complex formation (columns 2 and 3 respectively). All the metal ions known to extract under these conditions were examined.

TABLE V1

Metal ion	Aqueous phase in 0.1 M Li Cl and 0.5 M H Cl	Aqueous phase after complex formation	Aqueous phase after extraction	Organic phase after extraction
Blank	-1.35v(CHW)*	-0.90v(CHW)*	-0.90(CHW)*	-1.0(CHW)*
Antimony (111)	-0.18	> 0.0	>0.0	NW
Arsenic (111)	-0.5,-0.74	-0.42,-0.70	-0.42,-0.7	NW
Beryllium	NW	NW	NW	NW
Bismuth	-0.14	-0.04	-0.04	NW
Cobalt (11)	-1.28	NW	NW	NW
Copper (1)	-0.25	-0.38	-0.38	NW
Copper (11)	-0.24	>0.0,-0.42	>0.0,-0.42	NW
Iron (11)	NW	NW	NW	NW
Iron(111)	>0.0	>0.0	NW	>0.0
Gallium	NW	-0.80	NW	NW
Indium	-0.64	-0.68	NW	NW
Molybdenum (V)	Ca.-0.28, -0.51,-0.82	>0.0	NW	-0.09
Molybdenum (V1)	Ca.-0.24, -0.75	>0.0	NW	-0.1

TABLE V1 (cont.)

Metal ion	Aqueous phase in 0.1 M Li Cl and 0.5 M H Cl	Aqueous phase after complex formation	Aqueous phase after extraction	Organic phase after extraction
Nickel	-0.98	NW	NW	NW
Palladium	>0.0	>0.0	>0.0	NW
Scandium	NW	NW	NW	NW
Tin (11)	-0.52	-0.5	NW	NW
Tin (1V)	-0.18,-0.54	-0.36	NW	NW
Titatnium (1V)	-0.86	-0.16	-0.16	NW
Tungsten (V1)	NW	NW	NW	NW
Uranium (V1)	-0.25	>0.0	>0.0	NW
Vanadium (V)	>0.0,-1.03	>0.0,-0.46	>0.0,-0.46	NW
Zinc	-1.02	NW	NW	NW

(CHW) indicates catalytic hydrogen wave

NW indicates no wave obtained due to metal ion

Most of the metal ions examined and their thiocyanate complexes give polarographic waves in acidic aqueous solution. However, in the organic phase only those due to iron (111), molybdenum (V) and molybdenum (VI), are produced. The thiocyanate complexes of gallium, indium, tin (1V) and uranium (V1) are not reduced in the organic phase, although they give waves in aqueous solution and are certainly extracted to some extent (ca. 70%, 70%, 99% and 40% respectively)[84]. As a consequence, the direct application of polarography to the organic phase gives a greater degree of selectivity. It can be seen from Table (V1) that the reduction waves for some metal-thiocyanate complexes in aqueous solution (column 3) occur at more positive potentials than those for the corresponding aquo- or chloro- complexes (column 2), e.g. arsenic (111), antimony, bismuth, gallium, molybdenum (V), molybdenum (V1), tin (1V), titanium (1V), uranium (V1) and vanadium (V). This effect can be used to advantage with an element such as gallium which does not give a reduction wave in the acidic aqueous solution. It can also be used to obtain a separation of the reduction waves for mixtures of metal ions, e.g. antimony (111) and bismuth, arsenic (111) and molybdenum (V) or molybdenum (V1), etc. In addition, the three molybdenum reduction waves in acidic aqueous solution are ill-defined and the individual wave-heights are very small. As a result, they are of no use either for theoretical or analytical purposes. However, the extracted thiocyanate complex gives a well defined wave with a wave-height approximately equal to the sum of the three waves in aqueous solution.

The available potential range under these conditions was ca. 0.0 to 0.9 V Vs mercury pool and was controlled by the anodic dissolution of mercury and the catalytic reduction of hydrogen.

The addition of ascorbic acid to the aqueous phase reduces iron (111) to iron (11) and was found to render the combination of techniques specific for molybdenum (V).

2. Optimisation of conditions for molybdenum (V) - thiocyanate complex reduction wave

The following experimental variables and their effect on 4 x 10^{-4} M molybdenum (V)-thiocyanate reduction wave were examined.

(a) Organic Solvents

An aqueous solution of the molybdenum (V)-thiocyanate complex was equilibrated, as above, with number of organic solvents viz. amyl acetate, benzene, iso butylmethyl ketone, carbon tetrachloride, chloroform, diethyl ether, toluene and xylene. Only amyl acetate, iso butylmethyl ketone and diethyl ether extracted the complex and gave polarographic reduction waves.

Iso butylmethyl ketone also extracted 65% copper (1) and copper (11) which gave rise to a wave with a half-wave potential ($E\frac{1}{2}$) at -0.3V vs mercury pool.

All efforts to prevent the extraction of copper and its reduction by the addition of complexing agents were unsuccessful. The different complexing agents used included acetylacetone, dimethylglyoxime, dithizone, EDTA, 8-hydroxyquinoline, 1, 10-phenanthroline, sodium diethyldi-thiocarbamate, tri-benzylamine, thioglycollic acid and thiourea.

During these investigations, it was noticed that with lower concentrations of thiocyanate the copper (1) thiocyanate precipitated but the molybdenum-thiocyanate was still extracted. An attempt was, therefore, made to prevent the copper from being extracted by precipitation of its thiocyanate. On extraction, however, this precipitate collected at the interface of two phases and made the phase separation difficult. Filtration of the extract resulted in a slight loss of molybdenum.

This interference could only be completely eliminated by first extracting the copper as its pyridine-thiocyanate complex in toluene at pH 7.0. Under these conditions molybdenum is not extracted. This, of course, adds an additional step and the method becomes rather time consuming.

However, amylacetate was found not to extract copper, but it did extract tin (11) quantitatively. In the presence of molybdenum an additional wave with a half-wave potential ($E\frac{1}{2}$) at -0.45V<u>vs</u> mercury pool was given and the molybdenum (V) wave possessed a very large maximum which could not be removed. It was not possible to prevent the extraction of tin (11), whilst at the same time allowing the extraction of molybdenum (V). In the absence of molybdenum, no wave for tin (11), was observed in the organic phase, although from an examination of the aqueous phase it had been extracted quantitatively. The height of the tin (11) wave and the molybdenum maximum both increased with increasing concentrations of tin.

Both solvents extracted iron (111) quantitatively, but not iron (11), and thus diethylether was selected for further studies because of its greater selectivity.

(b) Hydrochloric acid concentration

The concentration was varied between 5 M and 0.001 M and its effect on the extraction and half-wave potential of the molybdenum (V)-thiocyanate complex was evaluated. Table V11 shows the results obtained.

TABLE VII

Molarity of hydrochloric acid in aqueous phase	Half-wave Potential (V)	Diffusion current (u Amu)
0.001	-	-
0.01	-0.19	0.4
0.05	-0.17	2.0
0.1	-0.16	1.95
0.25	-0.145	1.5
0.5	-0.12	0.7
1.0	> 0.0	-
2.5	> 0.0	-
5.0	> 0.0	-

The polarographic wave moved towards more positive potentials with increasing acid concentrations until above 1 M, the wave was indistinguishable from that due to the anodic dissolution of mercury. At concentrations $\lesssim$ 0.01 M, the efficiency of the extraction decreased to 20% or less. An acid concentration of ca.0.1 M was, therefore, selected as being the most suitable.

(c) Thiocyanate concentration

The reduction wave characteristics were found to be independent of the thiocyanate concentration provided it was between 1-3 M. Low concentrations, $<$ ca. 0.05 M, gave incomplete extraction and high concentrations, $>$ ca. 4 M, moved the wave to more positive potentials so that it became difficult to distinguish from the anodic wave due to the dissolution of mercury.

(d) Supporting electrolytes

A number of supporting electrolytes normally soluble in methanol were investigated. A suitable amount of the supporting electrolyte (to give an overal concentration of 0.1 M) was dissolved in the diethyl ether/methanol medium containing the molybdenum (V)-thiocyanate complex. The results obtained are shown in Table V11l. These suggest that lithiumchloride is one of the most suitable supporting electrolyte.

TABLE V111

Supporting electrolyte (0.1 M)	Observations
Citric acid	Wave possessed maximum *ca.* 5 times wave-height
Lithium chloride	Normal wave
Lithium hydroxide	Precipitation
Magnesium nitrate	Wave possessed maximum *ca.* 2 times the wave-height
Sodium perchlorate	Wave possessed maximum *ca.* 5 times the wave-height
Tetraethyl ammonium chloride	$E_{\frac{1}{2}} > 0.0$

Although lithium chloride is the most suitable supporting electrolyte, its concentration is important and should be controlled between certain limits. Table 1X shows that if the concentration is less than 0.05 a large maximum is observed and, if greater than 0.15 the wave moves to more positive potentials and eventually at the concentration of 0.25 M it merges with the anodic wave due to the dissolution of mercury.

TABLE IX

Concentration of Lithium chloride(M)	Half-wave Potential (V)	Limiting current (uA)	Observations
0.0	NM	-	Wave possessed maximum *ca.* 15 times the wave-height
0.0004	NM	-	Wave possessed maximum *ca.* 10 times the wave-height
0.001	NM	-	Wave possessed maximum *ca.* 5 times the wave-height
0.05	-0.16	2.0	Normal wave
0.10	-0.16	1.95	Normal wave
0.15	-0.16	1.95	Normal wave
0.25	-0.12	0.08	Wave moved to more positive potentials
0.5	0.0	-	Wave merged with the anodic wave due to dissolution of mercury

NM indicates wave not measurable

(e) Oxygen removal

Polarograms were obtained after bubbling oxygen-free nitrogen through the diethyl ether/methanol medium for 0, 2, 5 and 10 minutes. The flow rate in these experiments was made as fast as possible without splashing. From the above experimental observations two minutes were found sufficient to deoxyginate a 5 ml. sample. There was an appreciable loss of the solvent with longer periods of bubbling but this was eliminated by attaching a semi-micro condenser on the outlet arm of the polarographic cell.

(f) Electrode requirements

(i) Distance between electrodes

Polarograms were independent of the distance between the dropping mercury electrode and mercury pool reference anode. This indicates the medium is sufficiently conductive and that the ohmic drop in the bulk of the solution is negligible.

(ii) Effect of mercury pressure

This was studied by varying the height of mercury reservoir. A linear relationship was obtained between the diffusion current and the square root of the height of the mercury reservior.

(iii) Reference electrodes

The internal mercury pool anode and the ordinary saturated calomel electrode fitted with an agar bridge, held in place by a sintered glass disc, gave satisfactory results. In the case of an external reference electrode, using the same medium as the electrolysis cell, elongated waves were observed. This could be due to the high resistance of such an arrangement.

(g) Reversibility of the reduction wave

A plot of $\log_{10} \frac{i}{i_d - i}$ against E (Fig. 11) was made for the 4×10^{-4} M molybdenum thiocyanate complex following solvent extraction into diethyl ether. The slope of the log plot $(n. \frac{F}{RT})$ gave a value for n of 1.5 and crossed the abscissa $\left(\log_{10} \frac{i}{i_d - i} = 0\right)$ at a potential of -0.165 $(E\frac{1}{2})$. It is worthwhile noting that the plot of $\log_{10} \frac{i}{i_d - i}$ is approximately a straight line, but since the slope is not equal to the theoretical value the process is assumed to be irreversible. Linearity is, therefore, no criterion of the reversibility of the electrode reaction.

From the above value of n, it was thought that the irreversible nature of the molybdenum (V)-thiocyanate complex might be due to the high resistance of the solution. Additional experiment was, therefore, performed in order to obtain the actual resistance of the solution. Table X shows the results obtained using "Philips PR 9500" conductivity bridge. The two different types of cell employed included ordinary conductivity cell with two identical platinum electrodes separated at unit length and polarographic cell with platinum indicator electrode and mercury pool as electrode system.

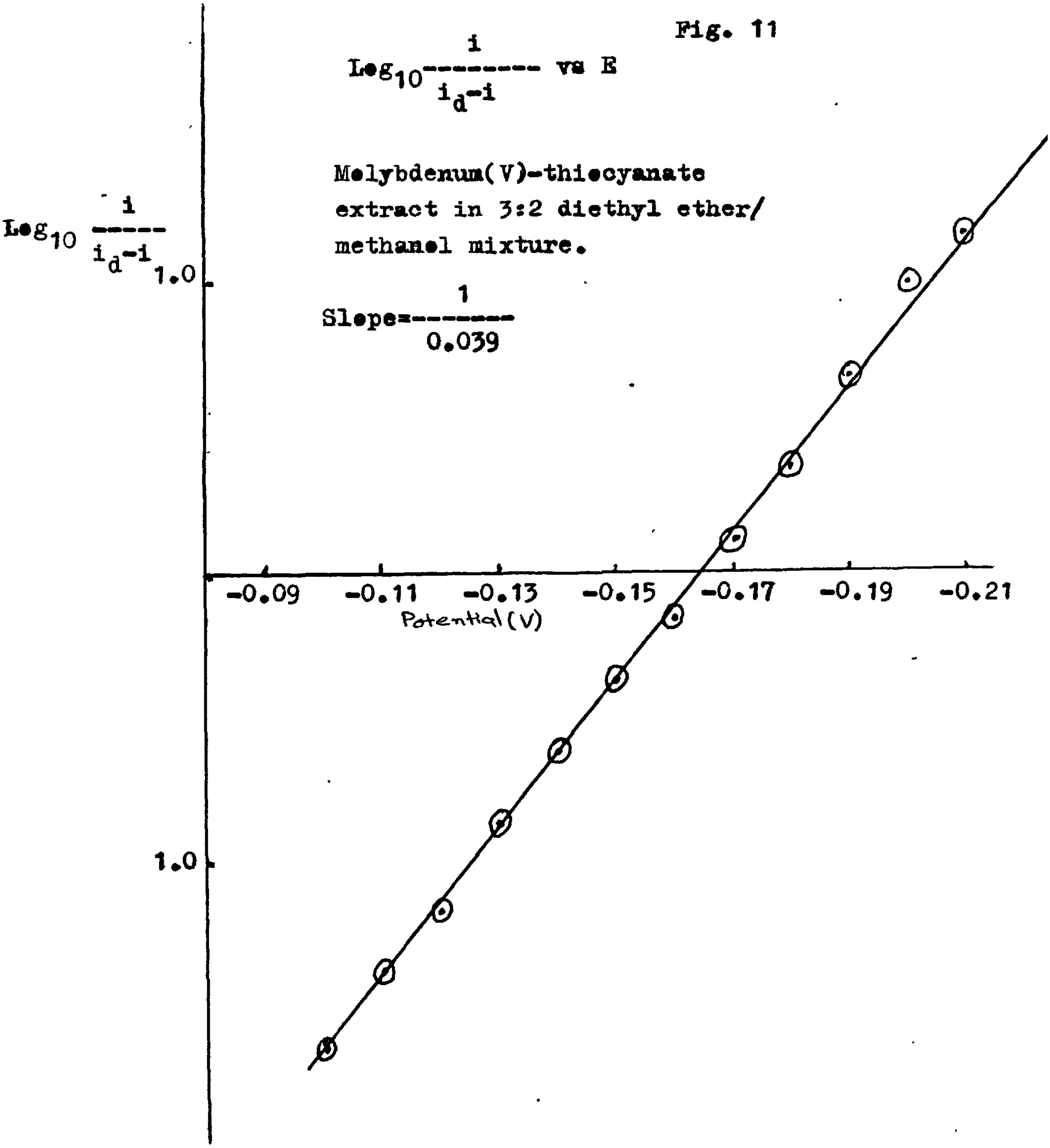


Fig. 11

$\mathrm{Log}_{10}\frac{i}{i_d-i}$ vs E

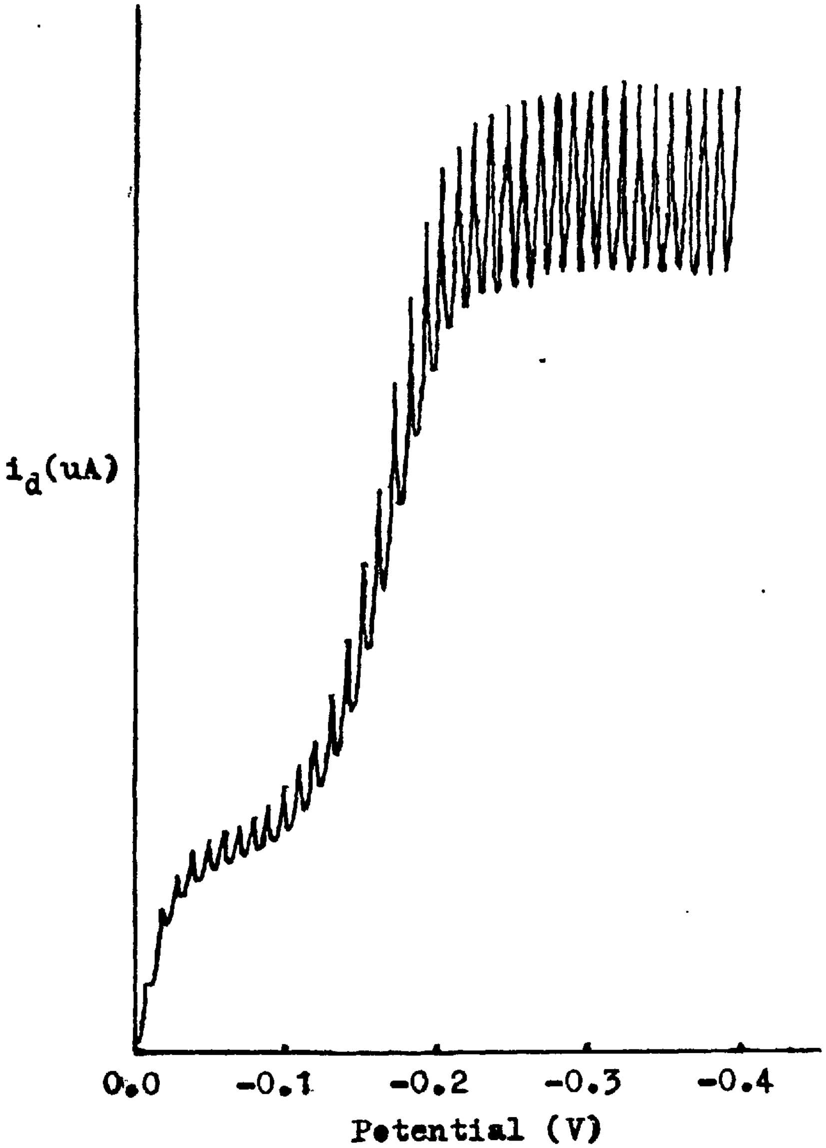
Molybdenum(V)-thiocyanate extract in 3:2 diethyl ether/methanol mixture.

$\mathrm{Slope}=\frac{1}{0.039}$

TABLE X

Medium	Resistance using ordinary conductivity cell with two platinum electrodes (Ohms)	Resistance using mercury pool/ platinum indicator electrode (Ohms)
1 M potassium chloride in water	0.08×10^2	0.075×10^2
0.1 M potassium chloride in water	0.095×10^3	0.09×10^3
0.1 M lithium chloride in water	0.11×10^3	0.10×10^3
0.1 M lithium chloride in 3:2 diethyl ether/methanol medium	0.76×10^3	0.74×10^3
4×10^{-4} M molybdenum(V)-thiocyanate complex in 3:2 diethyl ether/methanol	0.49×10^3	0.445×10^3

Figure 12 shows the polarogram obtained by extracting 4×10^{-4} M molybdenum-thiocyanate complex into diethyl ether using the above optimum conditions. In this instance a sensitivity of 5 uA/full scale deflection was used.



Molybdenum reduction wave. 4×10^{-4}M molybdenum(V)-thiocyanate extract in 3:2 diethylether/methanol mixture.

3. Preparation of calibration curve

Procedure

Add 2.5 - 15 ml. of 10^{-3} M molybdenum solution to 100 ml. separating funnels followed by 2.5 ml. of 1 M hydrochloric acid solution, 1-2 g. of ascorbic acid and 2.5 ml. of saturated ammonium thiocyanate solution. Dilute to *ca.* 25 ml. with distilled water and extract with 15 ml. of diethyl ether. Transfer the organic phase to a 25 ml. volumetric flask, add 5 ml. of 0.5 M lithium chloride in methanol and make up to volume with methanol. Deoxygenate an alliquot (5 ml.) of this solution with a fast stream of oxygen-free nitrogen for 2 minutes and polarograph it from zero to 0.5 V *vs* mercury pool using an instrumental sensitivity 5 uA/full-scale deflection. Finally measure the height of the wave at the half-wave potential ($E\frac{1}{2}$).

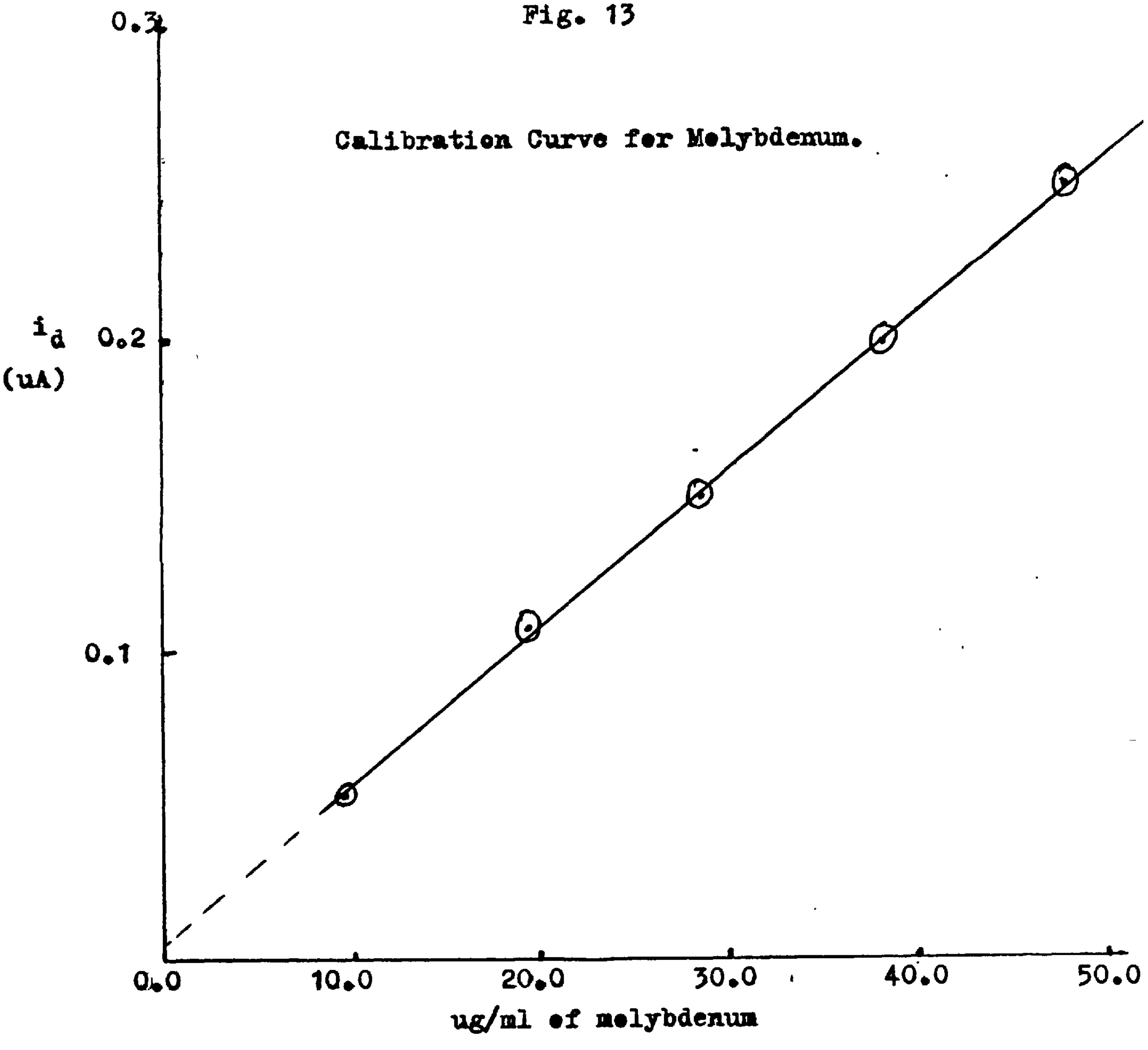
A graph of wave-height against concentration of molybdenum is a straight line from 10-60 ppm. 10 ppm is the lowest limit of the measurement with this instance but the plot can be extended above 60 PPm using larger volumes of reagents (Fig. 13).

4. Interferences

The effect of metal ions wholly or partially extracted, from acid solutions in diethyl-ether, was determined. The tests were carried out with a 10-fold molar excess of these ions on a solution 4 x 10^{-4} M in molybdenum (V) taken through the recommended extraction procedure.

Antimony, arsenic (111), beryllium, bismuth, cadmium, chromium, cobalt (11), copper (1), iron (11), gallium, indium, nickel, palladium, scandium, tin (11), titanium (111),

Fig. 13


Calibration Curve for Molybdenum.
0.3
0.2
0.1
i_d (uA)
0.0
10.0
20.0
30.0
40.0
50.0
ug/ml of molybdenum

tungsten (V), uranium (V1), vanadium (V) and zinc were examined. The height and the position of the reduction wave due to molybdenum (V)-thiocyanate complex did not alter by any of the above ions.

The aqueous phase was also made 0.1 M in perchloric acid, nitric and sulphuric acid. Again no interference was noted.

The ion that might cause major difficulties in the polarographic measurement of the molybdenum wave can be classified as; those which give rise to polarographic wave over the same potential range as the molybdenum (V)-thiocyanate complex, those, in large excesses, which are reduced at more positive potentials and those which produce catalytic waves.

The level of the interferences was limited to a 10 fold excess over molybdenum because it was considered to be unnecessary to use larger excesses merely to observe a reduction wave. With a given medium and electrode parameters, the heights of the reduction waves expected from various metal ions would be of the same order. Certainly a metal ion concentration of 4×10^{-3} M (i.e. 10 x molybdenum concentration) would be detected if it were to be reduced in the above region of applied voltage. Furthermore a 10 fold excess was examined because it was proposed to analyse mild and alloy steels by the above method and the content of other ions, except iron, was only 2-3 times that of molybdenum.

5. Extraction from larger volumes

Extractions were also carried out from 50, 100, 250 and 500 ml. of the aqueous phase (presaturated with diethyl ether) containing the amounts of molybdenum as used in the calibration curve. An exactly similar calibration was obtained and the overall sensitivity was increased to 0.5 to 3.0 ppm.

6. Precision of the method

The precision of the method was investigated by determining the percentage standard deviation from the multiple analyses of a series of organic phases, each 4×10^{-4} M in molybdenum (V)-thiocyanate complex and 0.1 M in lithium chloride in 3:2 diethylether/methanol medium. The results obtained are shown in Table Xl.

TABLE X1

Sample	Diffusion current (i_d)	Deviation from mean (D)	$(\text{Deviation})^2$
1	2.025	+ 0.059	0.003
2	2.000	+ 0.034	0.001
3	1.925	- 0.041	0.002
4	1.900	- 0.066	0.004
5	1.025	- 0.41	0.002
6	1.975	+ 0.009	0.000
7	2.000	+ 0.034	0.001
8	1.950	- 0.016	0.000
9	2.000	+ 0.034	0.001
10	1.975	+ 0.009	0.000
11	1.950	- 0.016	0.000
Total	21.625		0.014
Average	9.166		

Standard deviation $\pm \sqrt{0.0014} = \pm\ 0.031$

$\therefore$ Percentage standard deviation = 1.5

7. Determination of molybdenum in mild and alloy steels

In view of the great selectivity which has been obtained by the combination of solvent extraction and polarography in this instance, it was decided to test the method for the analysis of molybdenum in mild and alloy steels. The determination of molybdenum has been carried out in such complex mixtures by other workers, but the methods involved have been time consuming because of the difficulty in selecting a suitable supporting electrolyte. As a consequence, the methods have appeared unattractive in comparison with other techniques.

The general procedure adopted in this instance was as described under "Preparation of calibration curve", except for the initial dissolution of the steel which was achieved as follows:

Dissolve a suitable weight of the steel containing not less than 250 ug of molybdenum (<u>ca</u>.0.1 - 1 g) in 10 ml. of concentrated hydrochloric acid in a 100 ml. beaker, warming to assist solution. Evaporate the solution almost to dryness (avoid baking) and redissolve the residue in 10 ml. of 5% ($^{v}/_{v}$) hydrochloric acid. If a large amount of tungsten is present, add sufficient citric acid solution to obtain complete solution. Add 1-2 g of ascorbic acid and 10 ml. of aqueous saturated ammonium thiocyanate solution. Adjust the pH of solution to 1.0 with ammonia solution under a pH meter. Transfer this solution to a 250 ml. separating funnel with the aid of distilled water and dilute to <u>ca</u>. 40 ml. Finally, extract and proceed as under "Preparation of calibration curve". The amount of molybdenum is determined by comparision with a calibration curve (Fig. 13).

The calibration curve was checked by taking 1 g of electrolytic iron with standard molybdenum aliquots through the procedure. An exactly similar calibration to that obtained above was given.

The results of the analysis of some British Chemical Standards certificated mild and alloy steels are shown in Table X11.

TABLE X11

Sample No.	Type of steel	Found %	Certificated value %	Spread in certificate %
273	mild steel	0.045 0.041 0.040	0.04_5	0.041-0.046
275	mild steel	0.100 0.101	0.09_5	0.092-0.100
320	mild steel	0.208 0.217	0.22	0.21-0.22
321	mild steel	0.069 0.068 0.065	0.068	0.064-0.072
323	mild steel	0.105 0.104 0.111	0.100	0.095-0.105
325	mild steel	0.167 0.167	0.16	0.15-0.16
219/2	alloy steel	0.421 0.439	0.43	0.40-0.45
241/1	alloy steel	0.511 0.516	0.52	0.51-0.52

DISCUSSION

This polarographic method of analysis for molybdenum in steels has many advantages over those previously described. For instance, the method used by Haight[91], although sensitive depends on the use of a catalytic wave due to perchlorate and the measurements are taken from a non-linear calibration curve. In addition the careful control of experimental conditions and the anions such as perchlorate and sulphate is essential. Further-more,the presence of other salts or acids in the solution decreases the wave-height and the presence of tungstic acid produces precipitates at the acidity employed, thereby making determinations difficult.

A method for molybdenum in nickel alloys devised by Wolfson[92] uses a citric-sulphuric acid supporting electrolyte, but is interfered with by large amounts of iron and copper.

Parry and Yakubic[93] described a method suitable for steels using a tartrate supporting electrolyte. However, only synthetic mixtures were examined and even then only after removal of iron and chromium.

The method evolved by Stackelberg et al[94] can only be used after chemical separation of molybdenum from all the other alloying elements.

Other potentially useful polarographic reduction waves for molybdenum involve the use of either a non-linear calibration curve[95], a catalytic wave[96] or the extensive removal of other elements[97, 98].

The most widely used method for the determination of molybdenum is spectrophotometrically[99] using the red color produced with thiocyanate ion. However, we have found that interference is given in certain instances, for example the high chromium content (5.03%) of the alloy steel B.S.C. No. 241/1 produces an intense green color under the recommended conditions and interferes in the spectrophotometric method.

Other ion-association systems have been investigated but were unsuccessful for one reason or another. These included metal - 1, 10-phenanthroline-thiocyanates, metal-iodides and metal-bromides. In the case of metal-1, 10-phenanthroline-thiocyanates the nature of extraction and reduction characteristics were nearly similar to those obtained using metal-pyridine-thiocyanates. The iodide and bromide systems gave very large anodic waves at about zero applied potential and, therefore, no further studies were made on those systems.

SECTION III

CHAPTER I

Metal-Acetylacetonates

Introduction

Acetylacetone is colorless liquid that boils at 135-137°C at 745 mm of mercury pressure and has a density of 0.976 at 25°. It is miscible with alcohols, benzene, chloroform, diethylether and other organic solvents and is soluble in water to the extent of 0.17 g/ml at 25°[100].

It forms well-defined chelates with over 60 metals, many of which are soluble in organic solvents. The solubility of acetylacetonate complexes in organic solvents is of a much higher order of magnitude than is usual for the majority of analytically useful chelates; their solubilities are of the order of grams per litre rather than milligrams per litre, so that macro as well as micro scale separations are feasible. The quantitative extraction of iron^{59} produced (in less than spectrographic limits) in neutron-irradiated cobalt to give carrier-free iron^{59} [100] may be cited as an example of the effectiveness of acetylacetone.

Extractions have been carried out with acetylacetone dissolved in such solvents as benzene, carbon tetrachloride, chloroform, as well as with the pure liquid acting both as extracting agent and solvent[101]. The use of EDTA as masking agent provides the basis for a selective extraction of berylium[102] and uranium (V1)[103].

J.P. Mekaveney and H. Freiser[104] have taken advantage of the slowness of the rate of the formation of chromium (111) chelate, at low pH values, in separating chromium (111) from such metals as copper (11), iron (111) and molybdenum (V1).

This particular extraction system was chosen for polarographic studies because of the wide range of metal ions are extracted by acetylacetone. Furthermore, the selection was made because of its higher solubility in the organic solvents as compared to the other chelate compounds. Another important reason is that acetylacetone is not reducible at a dropping mercury electrode until - 1.45 V which is a fairly large working range.

Experimental

Apparatus

Polarograph

Elliot Model 200 with dropping mercury electrode. Unless otherwise stated the operating conditions were as follows:

Rate of potential increase 0.5V/100 sec. drop time 4.1 sec, height of mercury reservior 70 cm., mercury flow rate 2.4213 mg/sec, no damping or counter current. All the measurements were made at the room temperature. An internal mercury pool anode was used and de-aeration was achieved by bubbling nitrogen (oxygen-free) through a 5 ml. sample for 5 minutes. A mercury seal was used instead of more usual water seal to prevent re-absorption of oxygen.

pH meter E.I.L. Vibron
Model 39A

Reagents

Unless otherwise stated all the solvents and salts used in this study were of analytical grade purity. G.P.R.

indicates general-purpose grade quality of the reagent.

Acetylacetone	G.P.R. sp. gr. 0.976
Ammonium ferric sulphate	
Hydrochloric acid	sp. gr. 1.18
Indium (metallic)	
Lithium chloride (dried)	
Palladium chloride	
Perchloric acid	sp. gr. 1.54 and 5 per cent $(^{v}/_{v})$ in distilled water
Sodium hydroxide	5 per cent $(^{w}/_{v})$ in distilled water
Sulphuric acid	Sp. gr. 1.84

Solvents

Amylacetate	
Benzene	
Iso-butylmethyl ketone	G.P.R.
Carbon-tetrachloride	
Chloroform	
Ethylacetate	
Methanol	
Toluene	

Stock solutions

1×10^{-1} M Acetylacetone solution

0.1 M solution of acetylacetone was prepared in the above solvents except in methanol.

1×10^{-2} M Indium solution

Dissolve 0.5741 g of metallic indium in 5 ml. of concentrated hydrochloric acid and dilute to 500 ml. with distilled water. Standardise this solution against a standard EDTA solution, at pH 8-10, using Eriochrome Black T as indicator

1×10^{-2} M Iron solution

Dissolve 0.9645 g. of ammonium ferric sulphate in distilled water and after adding 2 ml. of concentrated sulphuric acid, dilute to 100 ml. with distilled water.

5×10^{-1} M Lithium chloride

Dissolve 21.2 g of dried lithium chloride in methanol and dilute to 1 litre by the further addition of methanol.

1×10^{-2} Palladium solution

Dissolve 0.8805 g of palladium chloride in 10 ml. of concentrated hydrochloric acid and dilute to 500 ml. with distilled water. Standardise this solution by adding excess of EDTA and back titrating with zinc using Xylenol orange as indicator.

1 M Sodium perchlorate

Dissolve 70.2 g of sodium perchlorate in distilled water and dilute to 500 ml. with distilled water.

1×10^{-2} M Zinc solution

Dissolve 0.2876 g of zinc sulphate in distilled water and dilute to 100 ml.

1. Purification of acetylacetone

Acetylacetone was purified by following the procedure used by J.F. Steinbach and H. Freiser[105]. This was carried out by shaking 1 litre of acetylacetone with 100 ml. of dilute (1:10) ammonia solution, followed by two successive 100 ml. portions of distilled. Finally, the acetylacetone was fractionally distilled and the fraction given at 136° was collected.

2. Preliminary investigations of metal-acetylacetonates

In this study the extraction procedure was essentially that recommended by J. Stary[106] but with extraction into toluene instead of chloroform. Toluene was chosen as an extracting medium because of its similarity to chloroform and benzene which are normally used. The use of chloroform was not encouraged because it is too easily reduced at the dropping mercury electrode (-0.8 V) and benzene was not selected because of its toxic nature.

30 ml. of a 0.1 M acetylacetone solution in toluene was shaken with an equal volume of an aqueous phase containing appropriate metal ion (10^{-3} M) and a small quantity of acetylacetone (5×10^{-3} M) to prevent the precipitation of some metal ions as their hydroxides. The pH was adjusted under a pH meter by the addition of sodium hydroxide or perchloric acid. Potassium perchlorate was added to give a constant ionic strength of 0.1 M (except, of course, in experiments below pH of <u>ca</u>. 1). The aqueous and organic phases were not mutually presaturated before equilibration as the volume changes were negligible.

After the equilibrium had been reached, the two phases were separated. The extracted organic phase was transferred into a 50 ml. volumetric flask containing 10 ml. of 0.5 M lithium chloride and the solution was diluted to the mark by the further addition of methanol. A 5 ml. aliquot of this solution was then added to the electrolysis cell, containing ca.5 ml. of mercury to serve as the reference electrode and the solution was deoxygenated by bubbling nitrogen (oxygen-free) through the solution for 5 minutes. Finally, polarograms were recorded over as wide potential range as possible.

Table X111 shows the half-wave potentials of the reduction waves in the organic phase (column 5) together with those obtained in an aqueous phase before and after extraction (column 3 and 4).

TABLE X111

Metal ion	pH of aqueous phase before extraction	Aqueous phase after complex formation(A)	Aqueous phase (A) after extraction	Organic phase after extraction
Blank	4, 6, 8, 10	-1.3	-	-1.45
Aluminum	7.0	NW	-	NW
Antimony	1.0	-0.10(max)	-0.10(max)	NW
Arsenic	2.0	Two very close waves between -0.26 to -0.6V	Two very close waves between 0.26 to -0.6V	NW
Beryllium	6.0	NW	-	NW
Bismuth	2.0	>0.0	>0.0	NW
Cadmium	7.0	-0.59	-0.6	NW
Cerium (111)	9.0	NW	-	NW
Cerium (1V)	9.0	NW	-	NW
Chromium (111)	4.0	-1.14	-1.14	-1.34 (*ca.* 40% extraction)
Cobalt(11)	9.0	-1.2	-1.2	NW
Copper(11)	7.0	-0.30	-0.32	-0.46 (*ca.* 60% extraction)
Gallium	6.0	-1.24	NW	NW
Indium	9.0	-0.72	NW	0.92
Iron(111)	6.0	-0.28	NW	-0.48
Lead	7.0	pptn.	-	pptn. at interface

TABLE X111 (cont.)

Metal ion	pH of aqueous phase before extraction	Aqueous phase after complex formation(A)	Aqueous phase (A) after extraction	Organic phase after extraction
Manganese (11)	10.0	NW	-	NW
Palladium	6.0	-0.66	NW	-0.78
Scandium	7.0	NW	-	NW
Thallium (111) (H_2O_2 added to Tl(1) solution)	7.0	-	-	Wave due to H_2O_2
Tin(11)	7.0	-0.9	small wave at -0.78	NW (ca. 80% extraction)
Tin(1V)	7.0	-0.82 with very small prewave at -0.46	NW	NW
Titanium (111)	3.0	pptn.	-	pptn. at interface
Titanium (1V)	3.0	-0.52	-0.54	-0.8 (ca. 25% extraction)
Tungsten (V1)	3.0	NW	-	NW
Uranium (V1)	4.0	-0.33,-0.65	-0.32,-0.69	NW
Vanadium (V)	2.0	NW	-	NW
Zinc	9.0	-1.08	-1.08	NW
Zirconium	2.0	pptn.	-	pptn. at interface

NW denotes no wave obtained
pptn. denotes precipitation observed

Among 28 metal ions investigated only chromium, copper, indium, iron, palladium, and titanium (lV) gave polarographic waves in the organic phase following solvent extraction with the half-wave potentials of-1.34, -0.46, -0.88, -0.38, -0.68 and -0.9 V respectively. The extraction of chromium, copper and titanium (lV) was incomplete (ca. 40%, 60% and 25% respectively).

Most of the metal-acetylacetonates examined gave polarographic waves in aqueous phase. The acetylacetonate complexes of gallium, tin (ll) and tin (lV) are not reduced in the organic phase although they give waves in aqueous solution and are certainly extracted to some extent (ca. 100%, 80%, 80% respectively). In consequence, the direct application of polarography to the organic phase gives a greater degree of selectivity.

The available potential range, under these conditions, was ca. 0.0 to -1.45 V vs mercury pool and was governed by the dissolution of mercury on the one hand and by the reduction of acetylacetone on the other.

From the above experimental observations, the extractions for indium, iron, and palladium were quantitative and it was, therefore, decided to develop analytical methods for the above metal ions.

The following experimental variables and their effects on a solution of 4×10^{-4} M indium-acetyl acetonate reduction were examined.

(a) Effect of pH

A series of solutions covering the pH range of 2-10 were prepared; the aqueous phase (25 ml) contained 1 ml. of 10^{-2}M indium solution, 2.5 ml. of a 10^{-2} M solution of acetylacetone and 2.5 ml of 1 M sodium perchlorate solution. The pH was adjusted to the required volue with sodium hydroxide or perchloric acid as necessary. The solution was transferred to a separating funnel and extracted with a one 15 ml. portion of 0.1 M acetylacetone in toluene. After careful phase separation, the organic phase was transferred to a 25 ml. volumetric flask containing 5 ml. of 0.5 M lithium chloride solution and the volume was made to the mark with methanol. The results obtained showed that the half-wave potential ($E_{\frac{1}{2}}$) of the indium-acetylacetonate reduction wave was moved to more negative potentials, from -0.84 to -0.92, with increase in pH value. This suggest a more stable chelate at higher pH values. In addition complete extraction was obtained between pH 6 to 9 (Fig. 14).

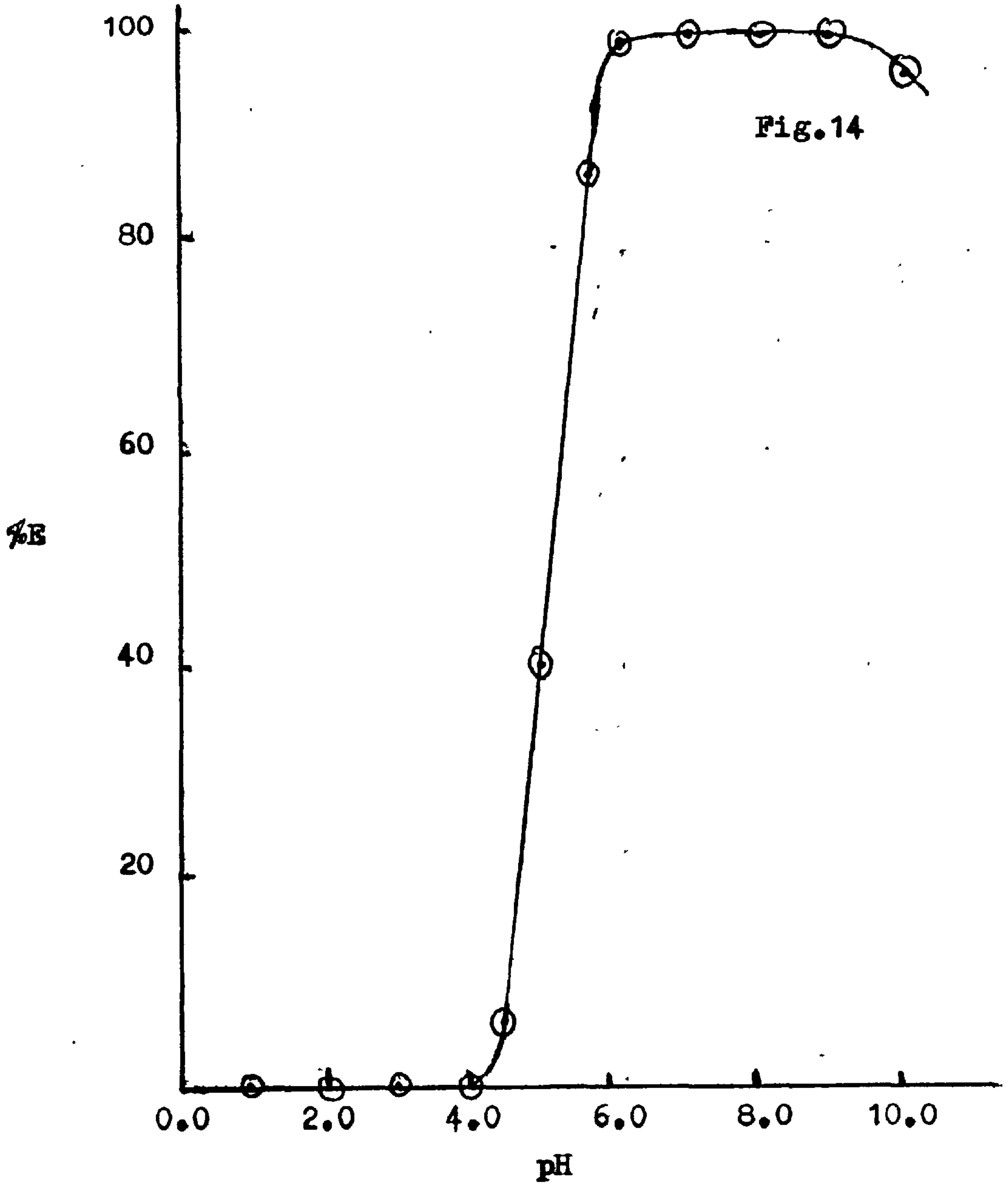


Fig. 14: Effect of pH on the extraction of indium by 0.1M acetylacetone in toluene.

(b) Effect of some masking agents

With a view to the possible use of masking agents to prevent any interference of metal ions, a study was made of the effect of ascorbic acid, citrate, oxalate, tartarate and cyanide on the extraction of indium acetylacetonate in toluene.

A series of solutions was prepared each 10^{-2} M in the above masking agent together with the other reagents as described above. Indium-acetlyacetonate complex was extracted at pH 9.0 and the organic phase, following solvent extraction, was examined polarographically.

The presence of ascorbic acid, citrate, oxalate, tartarate and cyanide had no effect on the efficiency of the extraction.

(c) Effect of solvents

In this instance the aqueous phase (25 ml) contained 1 ml of 10^{-2} M indium solution and 2.5 ml. of 10^{-2} M acetylacetone together with 2.5 ml. of sodium perchlorate. The above solution was adjusted to pH 9.0 and extracted with an equal volume of an organic solvent, viz. amylacetate, iso-butylmethyl ketone, chloroform and ethylacetate.

With c loroform, the wave due to the indium complex was masked by the reduction of the solvent. With amylacetate, iso-butylmethyl ketone and ethylacetate a maximum was observed which could not be removed by cetyltrimethyl ammonium bromide or methyl red. Thus, toluene was selected for further investigations.

(d) Effect of acetylacetone concentration

A series of aqueous solutions were prepared as described above and extracted with one 15 ml. portion of toluene containing concentrations of acetylacetone from 10^{-3} to 5×10^{-1}M.

The polarograms obtained showed that with more dilute solutions of acetylacetone (10^{-2}M), the extraction was slow, incomplete and in addition elongated waves were obtained. With increasing concentrations of acetylacetone the half-wave potentials ($E\frac{1}{2}$) were shifted to more negative potentials from -0.88V -0.94V. This suggests a more stable chelate formation with increase in acetylacetone concentration. Thus the concentration of 0.01 M of acetylacetone was chosen for further investigations.

(e) Supporting electrolyte

The effect of varying concentrations (0.0 to 0.3 M) of lithiumchloride as supporting electrolyte was studied on a solution 4×10^{-4} M in indium, following solvent extraction, as described above. TableXlV shows the effect of increasing lithiumchloride concentration on the shape and position of the reduction wave. In this instance a sensitivity of 5 uA/full-scale deflection was used. With increasing concentrations of the supporting electrolyte the slope of the curve was found to increase also. At a concentration of 0.1 M, the shape of the wave was quite normal and this concentration was, therefore, selected for further studies.

TABLE XIV

Concentration of Lithium chloride (M)	Half-wave potential (V)	Limiting current (uA)	Observations
0.0	-	-	N.W.
0.0004	-1.12	3.65	Very elongated wave
0.001	-1.06	2.85	Elongated wave
0.005	-1.02	2.65	Elongated wave
0.05	-0.95	2.40	Slightly elongated
0.1	-0.89	2.35	Normal wave
0.2	-0.90	2.25	Normal wave
0.3	-0.92	2.20	Normal wave

N.W. denotes no wave

(f) Electrode variables

The various electrode variables, viz., distance between the electrodes, drop time, mercury pressure and reference electrodes, were the same as found in the previous chapters.

4. Reversibilities of the electrode reactions for indium, iron and palladium

Another method, apart from the plot $\log_{10} \frac{i}{i_d - i}$ vs E, normally used to test the reversibility of the electrode reaction is by oscillographic polarography.

The term "oscilographic polarography" has been used in various senses. On one hand, it may be associated with techniques involving a programmed voltage sweep with polarization voltage impulses, which may be differenciated into a single sweep and multi-sweep methods. Usually, a current-voltage relation is utilized. On the other hand, the term has been applied to the technique where a dropping-mercury or streaming-mercury electrode is polarized by the application of a constant, sinewave, alternating current and the potential-time relationship is measured. This latter approach, when introduced by Heyrovsky and Forejf[111] in 1943, was termed "oscilographic polarography with alternating current".

In oscillographic polarography, the electrode is polarized by the passage of a constant alternating current and the potential changes of the electrodes are measured. If these changes were to be recorded as a functional of time, a curve for $F = f(t)$ is obtained. In practice, the evaluation is improved by the use of the first derrivative with respect to time, $dE/dt = f(E)$. This derivative function can be displaced in the shape of a curve on a cathode-ray oscilloscope. Such is the case for the commercially available Polaroscope. The elliptically shaped curve, thus obtained, runs from the positive potential governed by the oxidation of elemental mercury to the negative one governed by the reduction of the cation of the supporting electrolyte. The upper and lower parts of the curve correspond to the cathodic and anodic processes, respectively. On this oscillographic curve, incisions appear in the presence of substances in the cell solution that are reduced, oxidized or adsorbed on the mercury of the electrode. The position and the depth of these incision on the potential axis serves for qualitative and quantitative purposes, respectively. This depth is conveniently measured on the screan of the commercial instrument by a brightly lit horizontal axis (e.g. in Fig. 15), which may be moved by a potentiometer control.

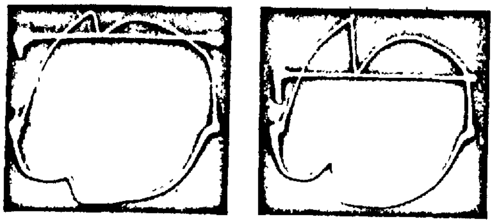


FIGURE 15 OSCILLOGRAMS FOR $dE/dt = f(E)$ WITH HORIZONTAL AXIS FOR MEASURING INCISION DEPTH SHOWN. *Left*, $3.3 \times 10^{-4} M$ lead(II) in $1M$ KOH, *right*, $6.5 \times 10^{-4} M$ lead(II) in $1M$ KOH.

Immediately after introducing oscillo-polarography, Heyrovsky examined by this method the reversibility of the electrode processes, which is important in the study of the character of electrode reaction.

During our investigations, for testing the reversibilities of indium, iron and palladium acetylacetonates, conclusive results were not obtained. This might be due to the fact that the term "oscillographic reversibility" does not have the same meaning as "polarographic reversibility". By the term "reversible" are denoted such processes as are found to be mobile when using the particular method. In the case of "polarographic reversibility", systems are denoted as mobile when the half-wave potentials of the oxidized and reduced forms coincide and the wave possess a characteristic shape. In the case of "oscillographic reversibility", potentials of the cathodic and anodic incisions have to coincide and the shape and approximately the depth of both incisions should be similar. The difference between the "reversibilities" lies in the time which is necessary for establishing the mobile equilibrium. In classical polarography, it is sufficient if the equilibrium is established during a time comparable with the drop time (about 2-3 seconds). In oscillographic polarography, the 'reversible' processes must reach equilibrium much more quickly, because one cycle lasts only 1/50 sec. "Polarographic reversibility" may also be observed in cases where the system behaves irreversibly in oscillographic polarography. In this case, equilibrium is not established in due time.

A plot of $\log_{10} \frac{i}{i_d - i}$ against E was made for 4×10^{-4}M indium, iron and palladium acetylacetonate complexes extracted into toluene (Figures 16, 17 and 18 respectively).

The slope of log plot $(n \frac{F}{RT})$ gave values for n of 0.905 for indium and 1.02 and 0.81 for iron and palladium. From the conductivity measurements of the above solution it was found that their conductance were between 300 to 400 ohms. Therefore, no i R drop corrections were made on the polarograms.

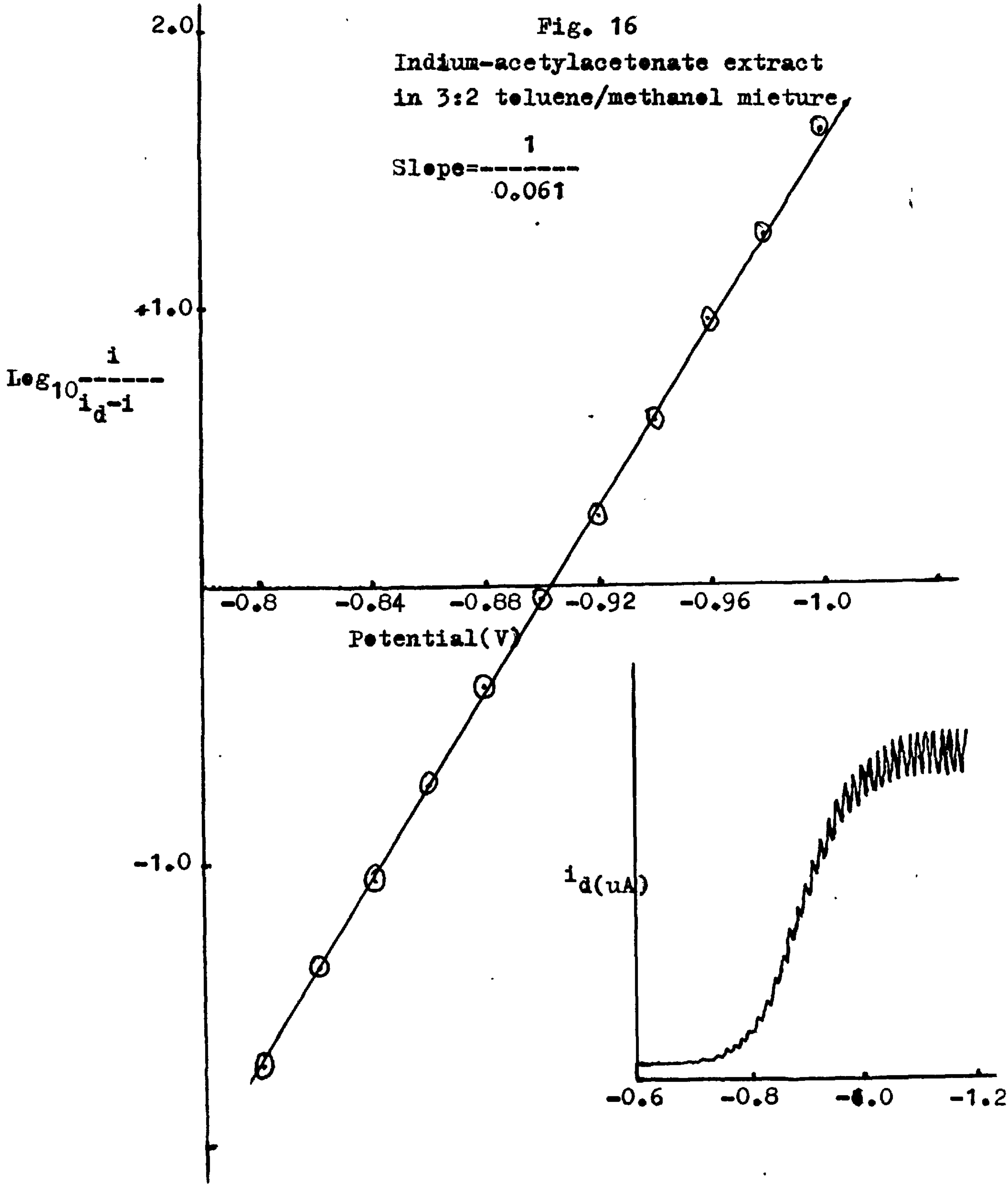


Fig. 16

Indium-acetylacetonate extract in 3:2 toluene/methanol mixture

$\text{Slope} = \dfrac{1}{0.061}$

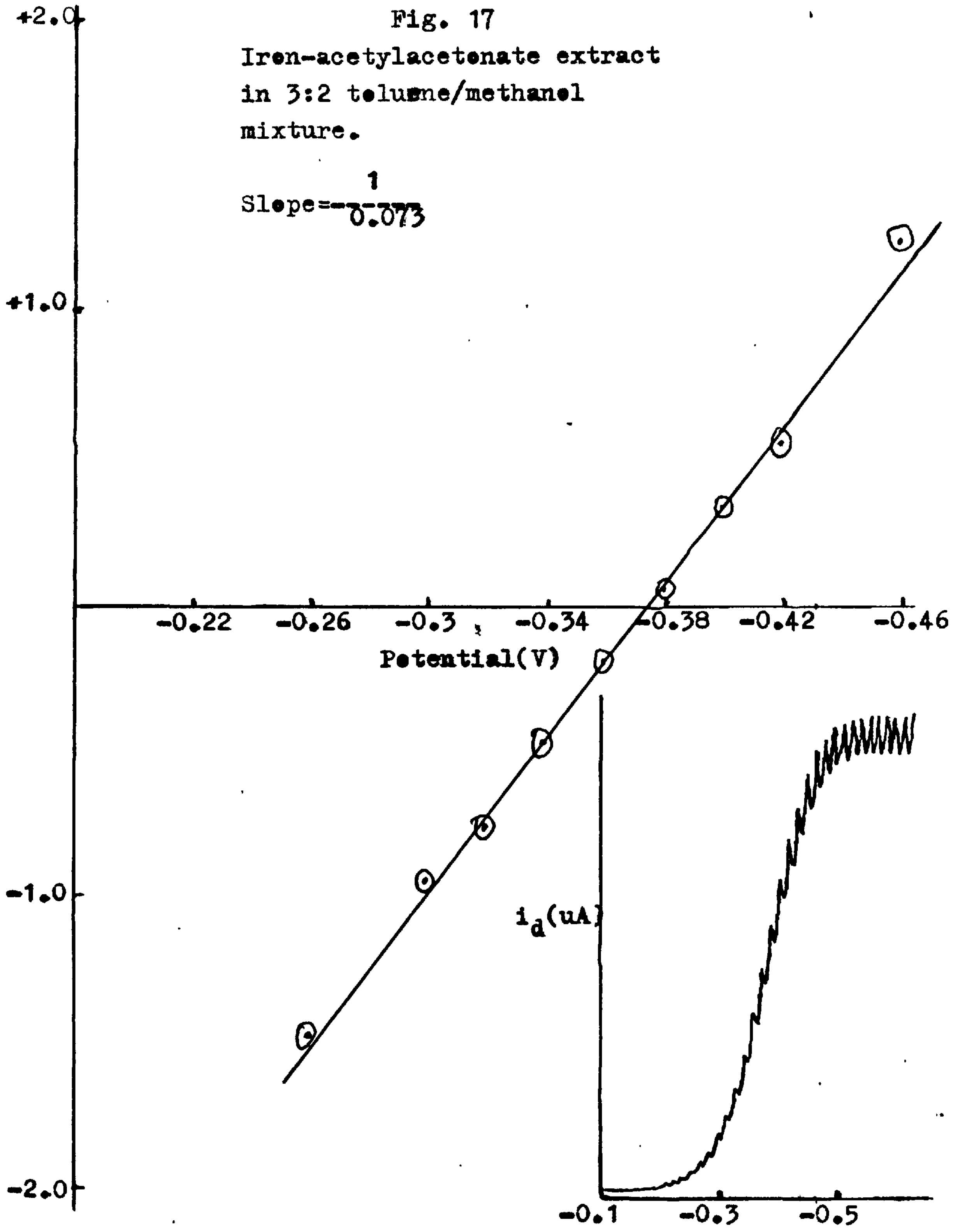


Fig. 17
Iron-acetylacetonate extract in 3:2 toluene/methanol mixture.

Slope = $\frac{1}{0.073}$

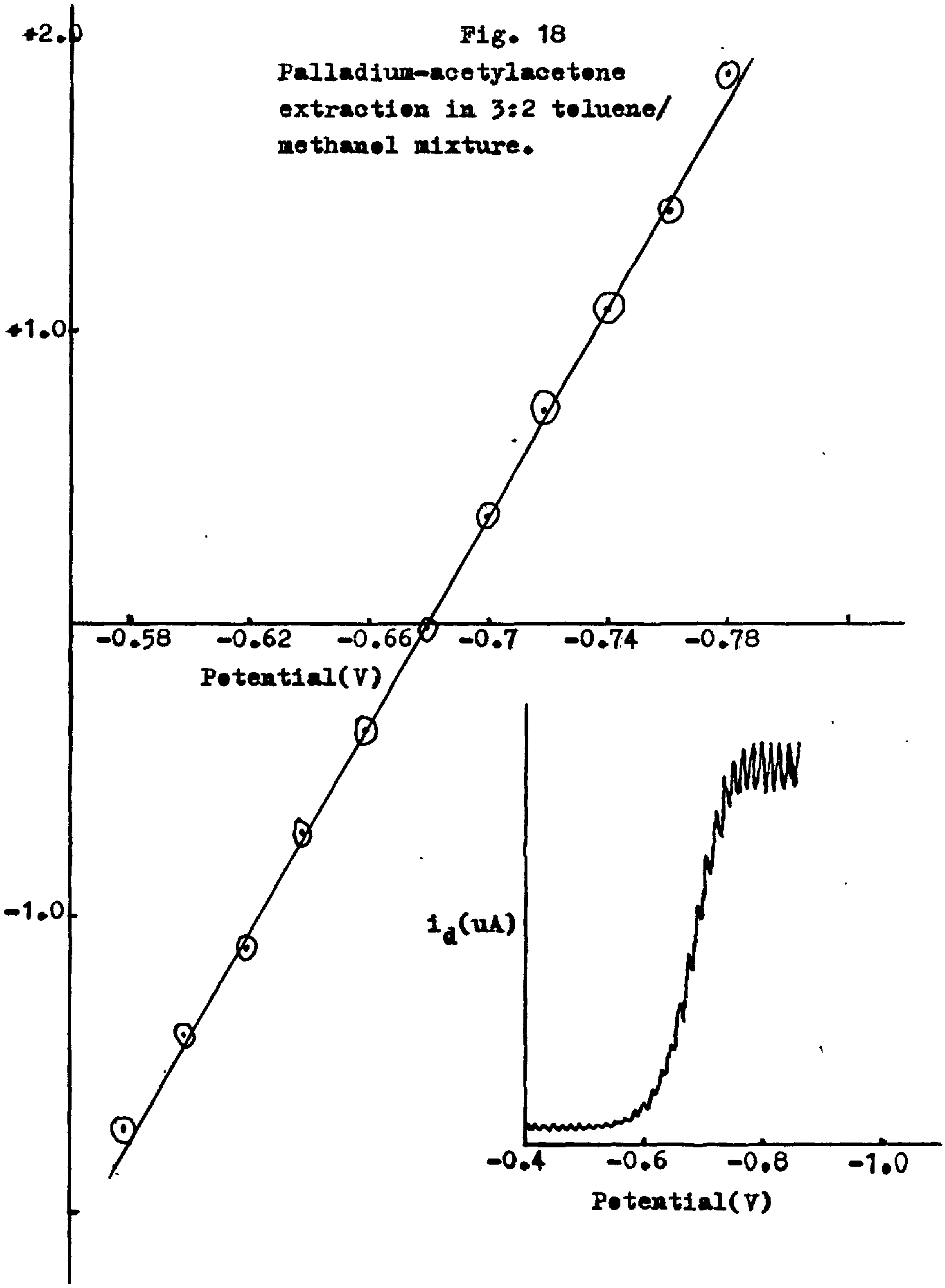


Fig. 18
Palladium-acetylacetone extraction in 3:2 toluene/methanol mixture.

5. Analytical Applications

(i) Determination of indium

(a) Preparation of calibration curve

Pipette out 1-5 ml. of a 5 x 10^{-4} M indium solution into 50 ml. beakers containing 2.5 ml. of a 10^{-2} M solution of acetylacetone, 2.5 ml. of a 1 M sodium perchlorate solution and dilute to ca. 25 ml. with distilled water. Adjust the pH of the aqueous solution to 9.0 under a pH meter and transfer the aqueous phase to a 100 ml. separating funnel. Extract with a 15 ml. aliquot of 0.01 M acetylacetone in toluene for about 1 minute. Then, transfer the organic phase to a 25 ml. volumetric flask containing 5 ml. of 0.5 M lithium chloride solution in methanol and dilute to the mark by the further addition of methanol. Transfer a 5 ml. aliquot of this solution to the polarographic cell and after deoxygenating the solution for 5 minutes obtain the polarogram using a sensitivity of 1 uA/full scale deflection. Measure the wave-height at the half-wave potential ($E\frac{1}{2}$) of the indium-acetylacetonate complex (-0.9V).

The graph of the wave-height against the indium concentration is a straight line from 2 to 10 PPm (Fig. 19). The detection limit was found to be 1 ppm.

The extractions have also been carried out from 500 ml. of aqueous phase containing the same amounts of indium as used in above calibration curve. Similar results were obtained and the overall sensitivity was increased to 0.1 to 0.5 ppm.

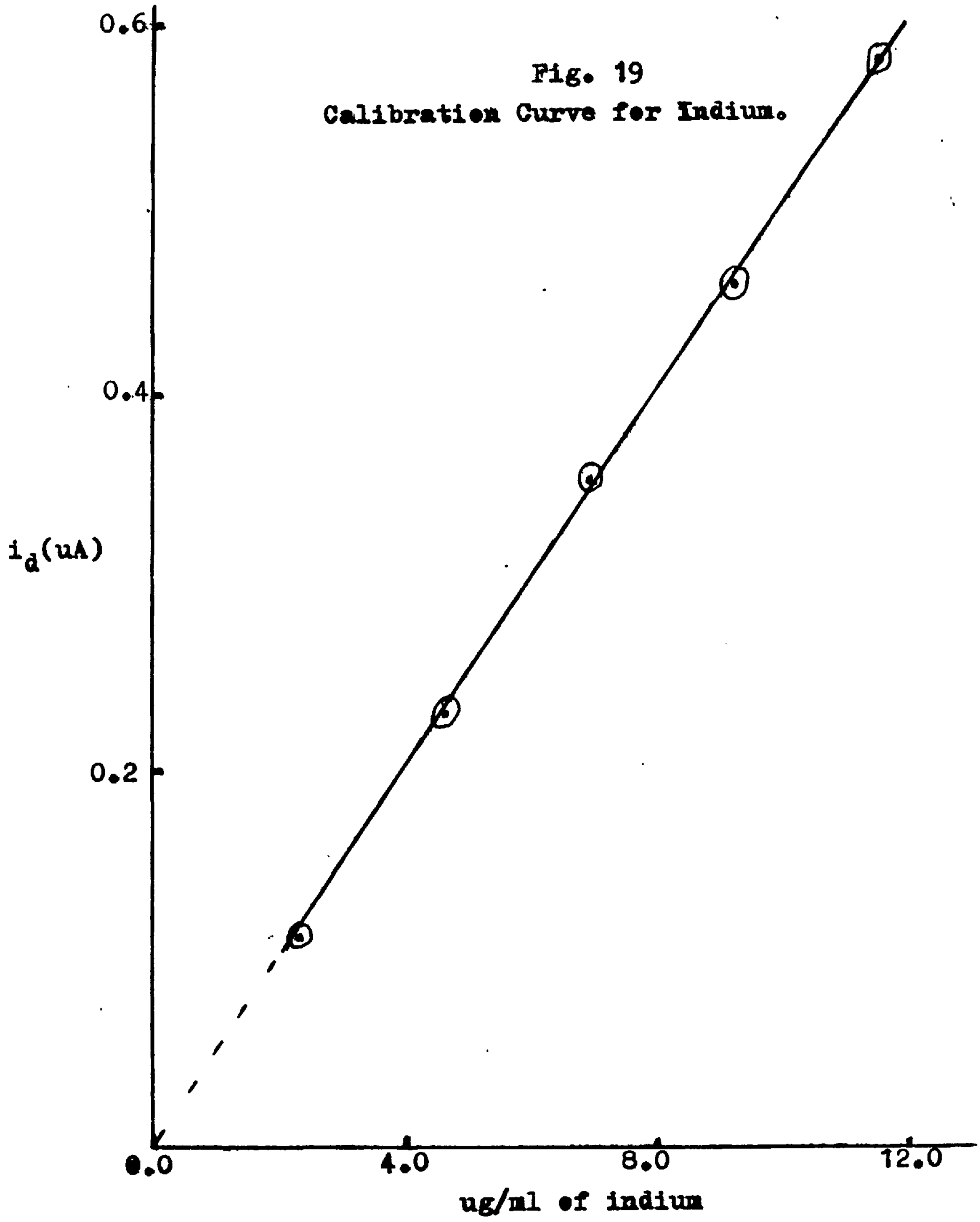


Fig. 19
Calibration Curve for Indium.

(b) Interferences

A number of cations which are wholly or partially extracted, as acetylacetonates by toluene, were investigated. The effect of these ions was examined by preparing a solution 5×10^{-5} M in indium-acetylacetonate and containing a 50 fold molar excess of these ions over indium. These solutions were then extracted according to the recommended procedure. The metal ions investigated included:

aluminium, beryllium, bismuth, cadmium, cerium (lll), cerium (lV), chromium (lll), cobalt (ll), copper (l), copper (ll), gallium, indium, iron (lll), manganese (ll), nickel, palladium, scandium, tin (ll), tin (lV), thallium (lll), titanium (lV), tungsten (Vl), uranium (Vl), vandium (V), zinc and zirconium.

Among 28 metal ions investigated only copper (l), copper (ll), iron (lll), and palladium interfered by giving waves with half-wave potentials (-0.46, -0.46, -0.38 and -0.68V respectively) more positive than the indium wave ($E\frac{1}{2}$ at -0.90V). It was noted that when thallium (l) was oxidised to thallium (lll) by hydrogenperoxide and extracted, as described, in toluene, a wave with a half-wave potential of -0.85V was obtained. This was first suspected as the reduction wave for the thallium (lll) chelate but it was later shown to be due to the presence of hydrogen peroxide.

In order to develop a selective procedure for indium attention was paid to the possibility of using selective masking agents (page 111) for these interfering metal ions viz. copper, iron and palladium.

Ascorbic acid did not successfully mask iron (111) at pH 9.0. This may be due to the reoxidation of iron (11) to iron (111) in alkaline solutions. This is suggested by the development of the red iron (111)-acetylacetonate chelate in these alkaline conditions.

Citrate, oxalate and tartarate were found to be completely ineffective. Cyanide was able to mask copper and palladium. However iron (111) was masked by the combination of ascorbic acid and cyanide when the solution was warmed.

(c) Precision of the method

The precision of the method was investigated by determining the percentage standard deviation from the multiple analyses of a series of solutions each 4 x 10^{-5} M in indium and extracted into toluene by the recommended procedure.

The results obtained are shown in Table XV from which it will be seen that at the limiting current of 0.23 uA there is a percentage standard deviation of 5.4.

TABLE XV

	Current (u A)	Mean	Deviation (D)	$(D)^2$
1.	0.235	-0.23375	+0.001	0.1562×10^{-5}
2.	0.230		-0.003	1.3062×10^{-5}
3.	0.240		-0.006	3.9122×10^{-5}
4.	0.240		-0.006	3.9122×10^{-5}
5.	0.225		+0.007	6.0062×10^{-5}
6.	0.245		+0.011	124.0312×10^{-5}
7.	0.230		-0.003	1.3062×10^{-5}
8.	0.225		-0.008	7.6562×10^{-5}
9.	0.2275		-0.006	3.844×10^{-5}
10.	0.240		-0.006	3.9122×10^{-5}

$$S.D. = \sqrt{\frac{D^2}{n - 1}} = \sqrt{\frac{0.00156}{10 - 1}} = \sqrt{0.000173}$$

$$= 0.0126$$

in Percentage standard deviation = 5.4

(d) Analysis of known indium samples in the presence of other metal ions

A standard indium solution containing varing amounts of the ions cadmium, copper (11), iron (111) and palladium at pH 9.0 was prepared. Aliquots of this solution were extracted with a 15 ml. portion of 0.01 M acetylacetone in toluene and the polarograms were obtained in a usual manner. The amounts thus extracted were calculated by comparing the wave-height with the calibration curve. The data for these analyses are shown in Table XV1. As can be seen the results obtained are quite satisfactory.

TABLE XVI

Run No.	Wave-height (u A)	Indium content found(ug/ml)	Indium content present(ug/ml)	Foreign ions present
	Part A $5x10^{-5}$M indium containing 25 fold excess of			cadmium, copper iron and palladium
1.	0.28	5.700	5.741	
2.	0.275	5.650	5.741	
3.	0.275	5.650	5.741	
	Part B $5x10^{-5}$M indium containing 50 fold excess of			cadmium, copper, iron and palladium
1.	0.29	5.85	5.741	
2.	0.28	5.700	5.741	
3.	0.2825	5.75	5.741	
	Part C $5x10^{-5}$M indium containing 100 fold excess of			cadmium, copper iron and palladium
1.	0.27	5.600	5.741	
2.	0.29	5.85	5.741	
3.	0.275	5.65	5.741	

(ii) Determination of iron

(a) Effect of pH

A series of solutions covering pH range of 2-10 were prepared, the aqueous phase (25 ml.) contained 1 ml. of 10^{-2} M iron (111) solution, 2.5 ml. of 1 M sodium perchlorate solution. The pH was adjusted to the required value with sodium hydroxide or perchloric acid as necessary. The solution was transferred to a separating funnel and extracted with a one 15 ml. portion of 0.1 M acetylacetone in toluene. After careful phase separation, the organic phase was transfer d to a 25 ml. volumetric flask containing 5 ml. of 0.5 M lithium chloride solution and the volume was made to the mark with methanol.

The results obtained show that the quantitative extraction occurred between pH 4 - 8. Before and after this range the extraction efficiency decreases (Fig. 20). Furthermore, it was notices that on increasing the pH the color of the iron-acetylacetonate chelate changes from red to yellow. The color of the chelate remained almost unchanged between pH 4 - 8. This might suggest the formation of different solute species at different pH values. A pH value of 8.0 was selected for subsequent studies, because of the ease of masking the other interferring metal ions such as copper and palladium, in alkaline medium.

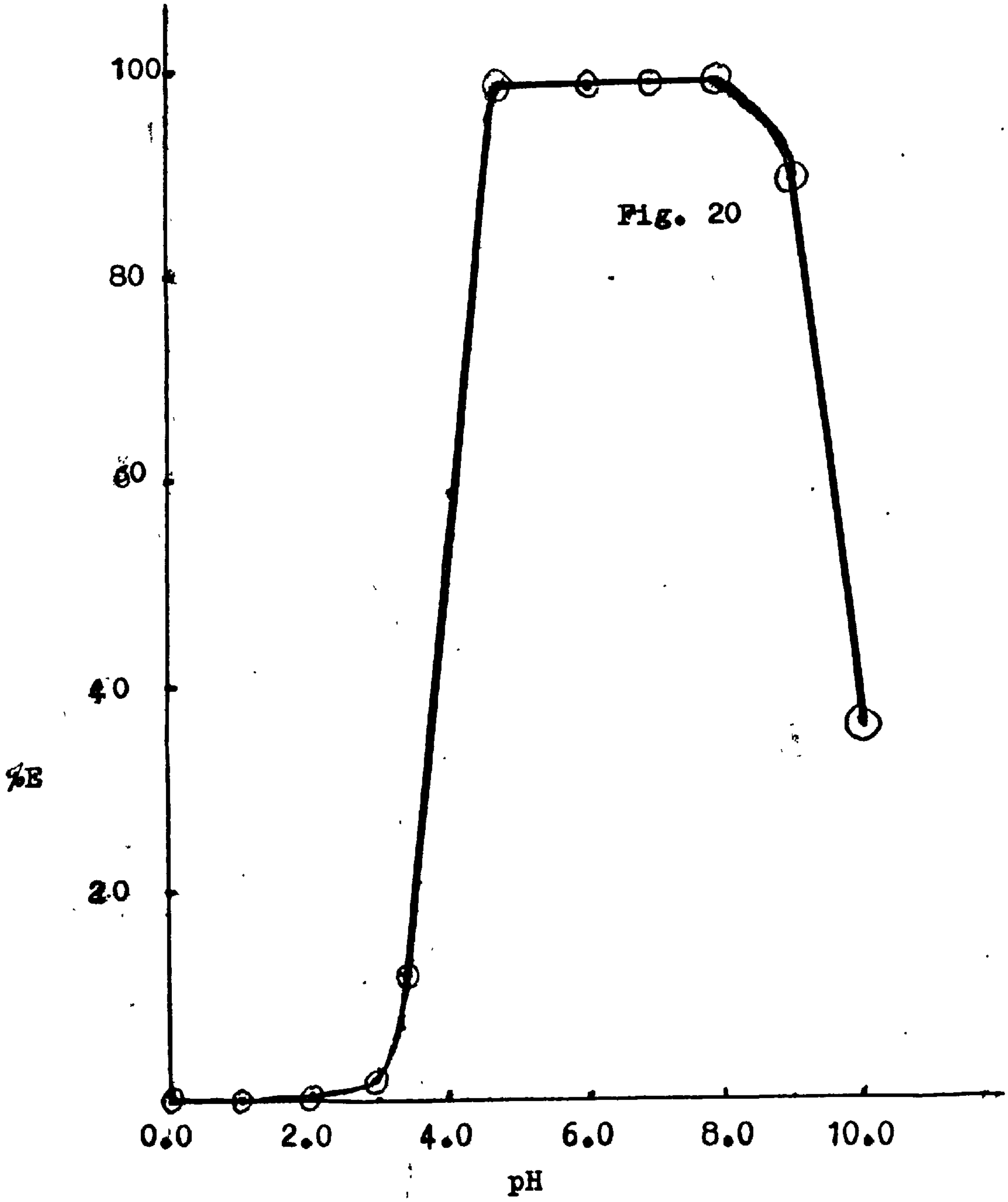


Fig. 20: Effect of pH on the extraction of iron(III)-acetylacetonate in toluene.

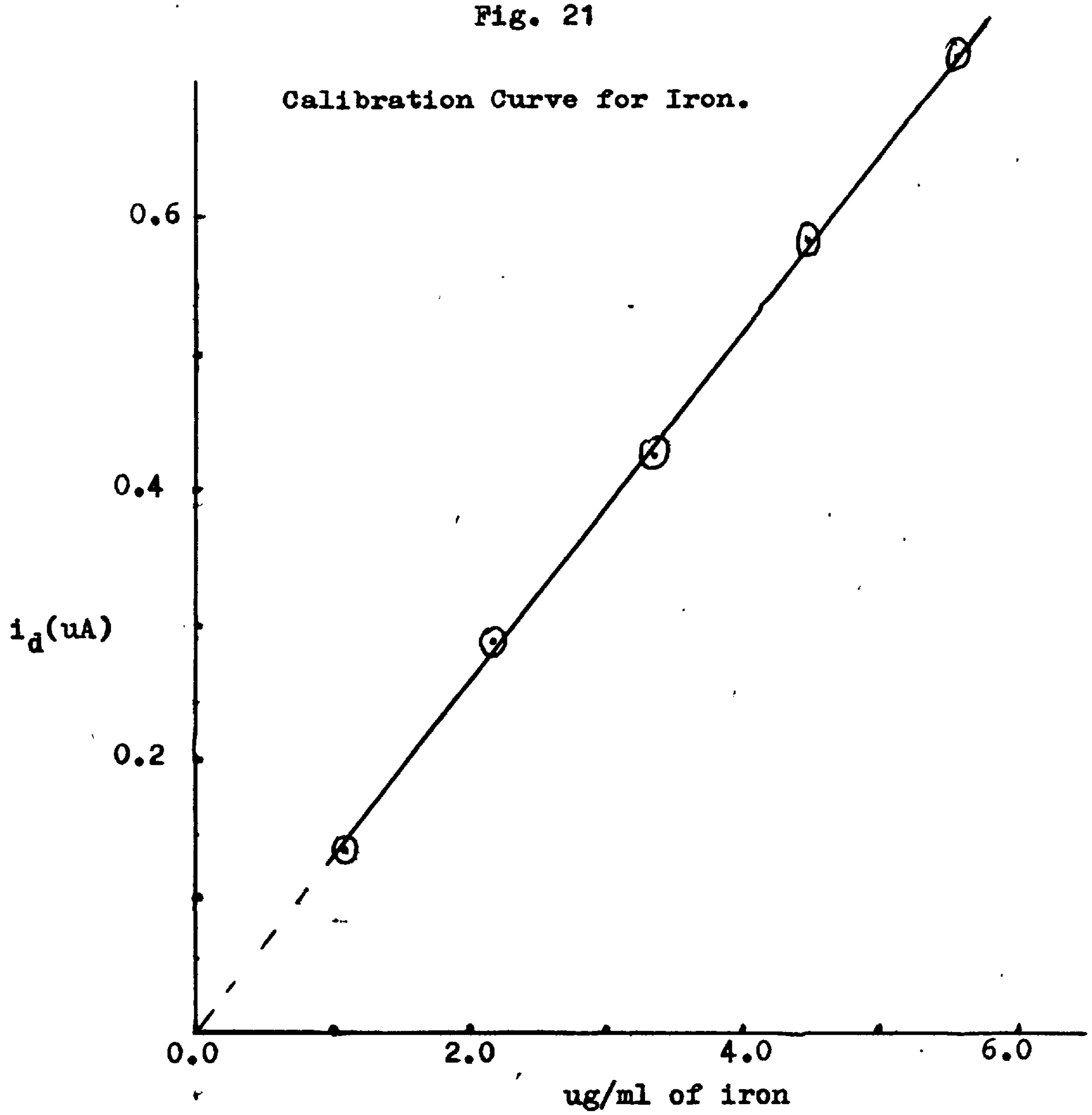
(b) Preparation of calibration curve

A calibration curve was prepared by taking a series of solutions through the recommended procedure as given under "Determination of indium" at pH 8.0. Polarograms were obtained and the wave-heights were measured at the half-wave potential of the reduction wave (-0.38V).

The calibration curve from 1 to 5 ppm (Fig. 21) was a straight line passing through the origin. The detection limit was 0.5 ppm.

Extractions were also carried out from 500 ml. of the aqueous phase containing the same amounts of iron as used in the above calibration curve and similar results were obtained. Thus the overall sensitivity was increased twenty fold to 0.05 to 0.25 ppm.

Fig. 21


Calibration Curve for Iron.
0.6
0.4
0.2
i_d(uA)
0.0
2.0
4.0
6.0
ug/ml of iron

(c) Interferences

The cations, already listed in the determination of indium, were investigated. Only copper (11) and palladium interfered by giving the waves with half-wave potentials (-0.46 and 0.68 V respectively) near to the reduction of the iron-acetylacetonate chelate. The interference of copper (11) and palladium was easily removed by adding cyanide (10^{-2} M) to the aqueous phase before extraction with toluene.

(d) Sequential determination of iron and indium

As the reduction waves for the iron and indium acetylacetonate complexes were well defined and well resolved, it was thought worthwhile to sequentially determine these metals. Fig. 22 shows the polarograms obtained with an equimolar mixture of these ions. It is worthy of note that the sequential determination, via direct c-v curves, is only applicable if the concentration of iron is below certain limits (i.e. not more than ca. 5 times the indium concentration). Otherwise the iron wave, at more positive potentials tend to mask the indium wave. This, of course, may be avoided using derivative polarography with its superior resolution.

Fig. 22

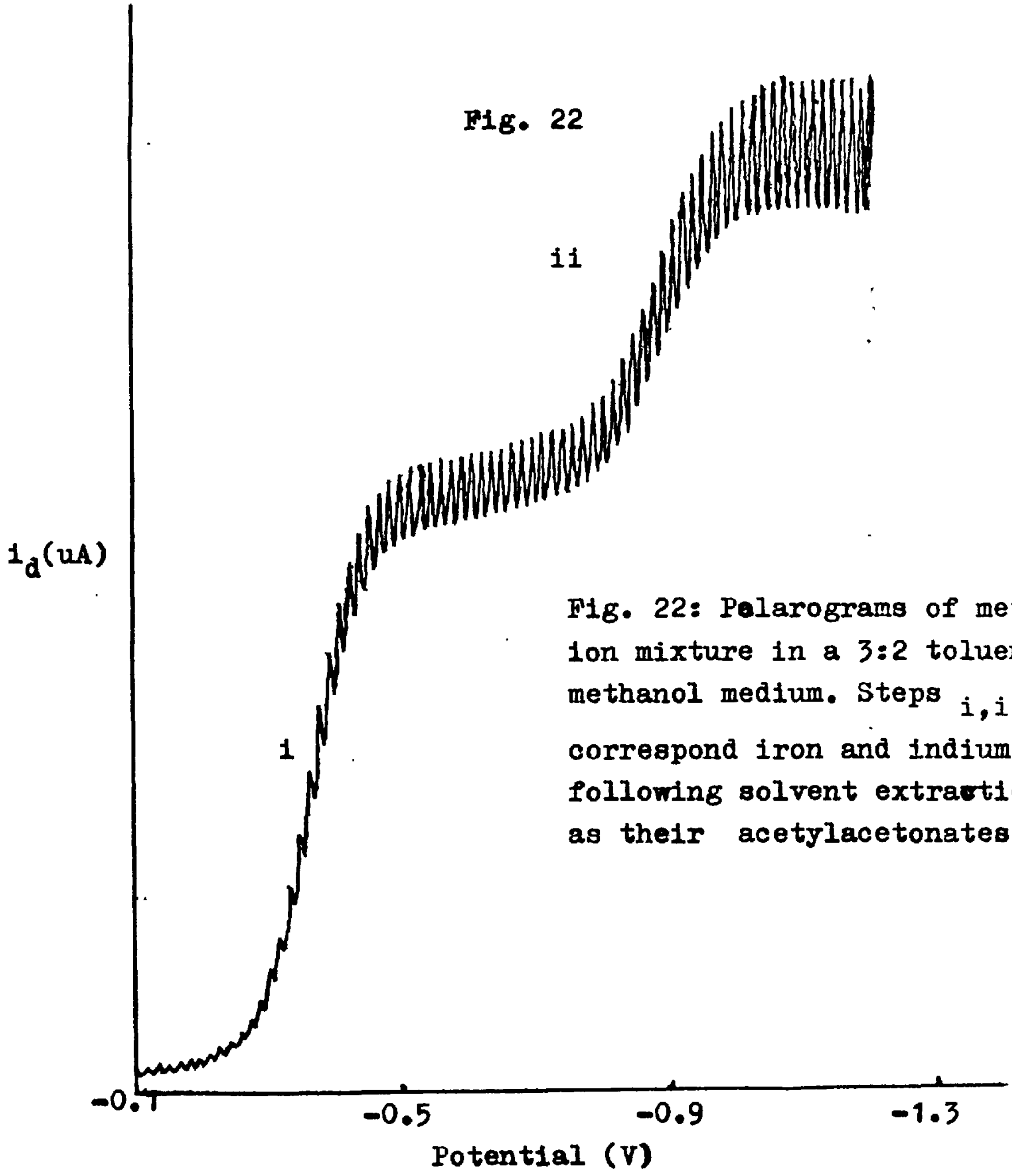


Fig. 22: Pelarograms of metal ion mixture in a 3:2 toluene/ methanol medium. Steps i,ii correspond iron and indium(10^{-4}M) following solvent extraction as their acetylacetonates.

(iii) Determination of Palladium

(a) Effect of pH

A series of solutions covering pH range of 2-10 were prepared, the aqueous phase (25 ml) contained 1 ml. of 10^{-2}M palladium solution, 2.5 ml. of 1 M sodium perchlorate solution. The pH was adjusted to the required value with sodium hydroxide or perchloric acid as necessary. The solution was transferred to a separating funnel and extracted with one 15 ml. portion of 0.1 M acetylacetone in toluene. After careful phase separation, the organic phase was transfered to a 25 ml. volumetric flask containing 5 ml. of 0.5 M lithium chloride solution and the volume was made to the mark with methanol.

The results showed that complete extraction was obtained over the whole pH range studied. However, unlike the indium wave, the wave due to palladium-acetylacetone moved to more negative potentials, from -0.70 to -0.78, as the pH of the aqueous phase decreased. This indicates the more stable complex in acidic solutions.

A pH value of 2.0 was selected for further studies, because at this pH the interference of copper and iron can be easily eliminated.

(b) Preparation of calibration curve

A calibration curve was prepared by taking a series of solutions through the recommended procedure as given under "determination of indium" at pH 2.0. Polarograms were obtained and the wave-heights were measured at the half-wave potential of the reduction wave (-0.68 v).

The calibration curve was the straight line passing through the origin from 2 to 10 ppm. The lowest detection limit using above particular instrument was 1 ppm. (Fig. 23)

Extractions were also carried out from 500 ml. of the aqueous phase containing the same amounts of palladium as used in the above calibration curve and similar results were obtained. Thus the overall sensitivity was increased twenty fold to 0.1 to 0.5 ppm.

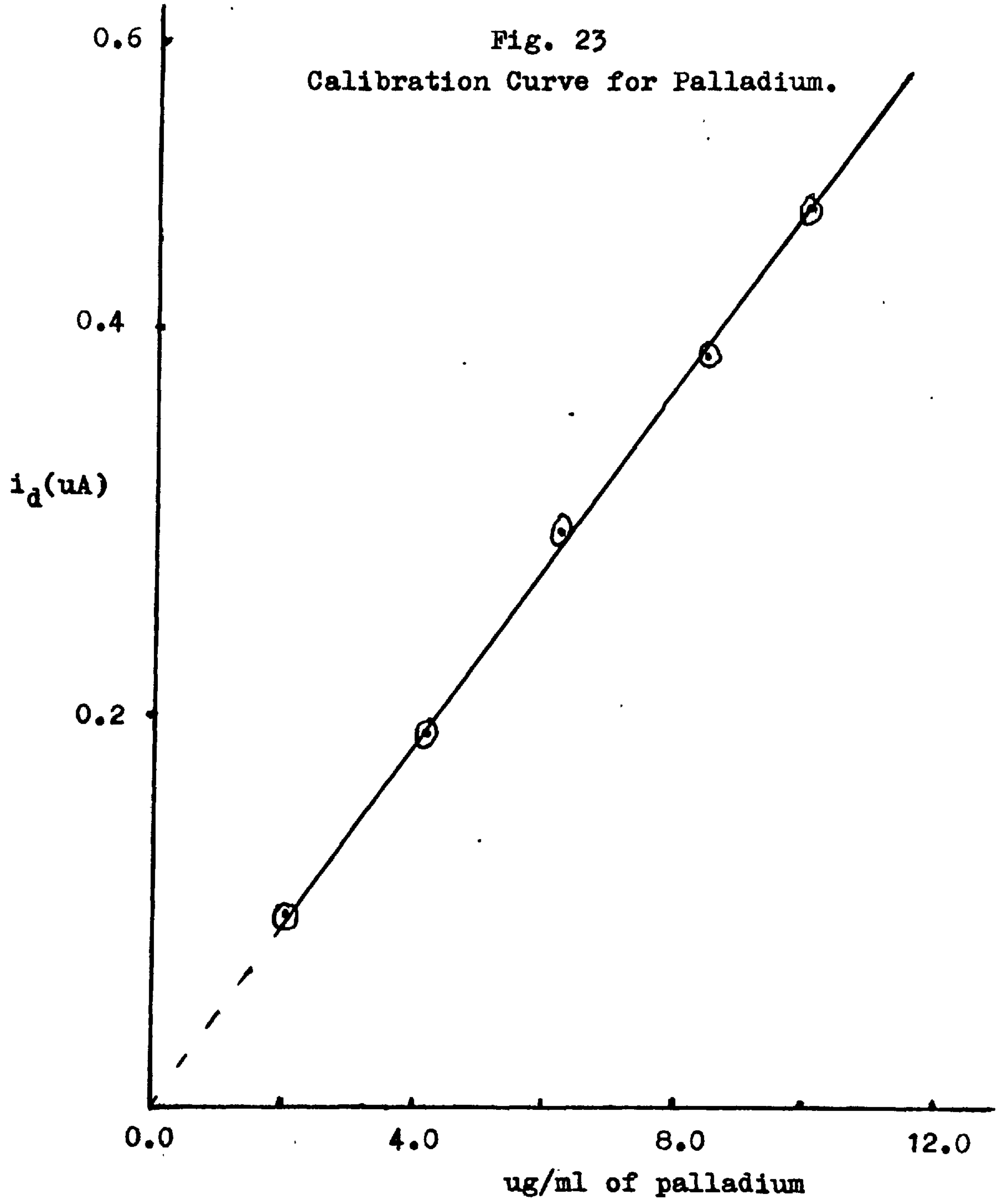
(c) Interferences

The effect of various metal ions was examined by preparing a solution 5×10^{-5} M in palladium-acetyl acetone and containing a 50 fold molar excess of these ions over palladium. These solutions were then extracted according to the recommended procedure. The metal ions investigated included:

bismuth, cadmium, chromium, cobalt, copper (1), copper (11), indium, iron (111), nickel, tin (11), tin (1V), tungsten (V1) uranium (V1) and zinc.

Copper and iron interfered with the palladium by giving waves at more positive potentials than the palladium wave (i.e. -0.46, -0.38 v respectively). However, it was noted that copper is not extracted from the aqueous solutions at pH values (≤ 2) and the interference of copper was, therefore, easily eliminated by extracting the palladium-acetyl acetonate chelate at pH 2.0. Both ascorbic acid and EDTA were examined as masking agents for iron. EDTA was found to be of no use as it also masked the extraction of palladium. However, ascorbic acid proved to be successful provided its concentration was kept between certain limits. At higher concentrations of ascorbic acid ($< 10^{-2}$ M), palladium ions are reduced to palladium metal, hence giving low recoveries.

Fig. 23
Calibration Curve for Palladium.



Discussion

The polarographic study of metal acetylacetonates, extracted into an organic phase, has evolved a very selective method for the determination of indium.

Normally, in the polarographic determination of indium, the polarographic measurement is preceded by the lengthy processes involving the concentration of indium and the separation of interfering impurities. Frequently cadmium occurs with indium and is reduced under the same conditions with a half-wave potential($E\frac{1}{2}$) very close to that of indium. Other ions which interfere include those ions that are reduced at more positive potentials than indium and are present in an appreciable (ca. 10 fold) excess.

A method developed by Rozlianskaya[107] deals with the determination of small quantities of indium in sulphide ores. The method involves the separation of indium from cadmium, copper, lead, tin, and with Trilon B. Indium is separated quantitatively by precipitation from 1-2% alkaline solution of Trilon B. Cadmium, copper (11), lead, tin and zinc form complexes in solution. Large quantities of indium can be estimated by gramimetric analysis as indium oxide (In_2O_3) and small quantities (0.08 - 0.05 mg) by polarography.

Wolfgang Zimmer[108] developed a method for the rapid polarographic determination of indium for operational control of the hydro- matallurgical products of zinc. After the quantitative separation from interfering metals such as cadmium, copper, iron, lead and zinc, sufficiently accurate analytical results for the determination of small quantities of indium in the presence of large quantities of the above metals were obtained. Lead is separated, as sulphate, after fuming the aqua-regia solution with sulphuric acid. Cadmium, copper and zinc are separated by repeated reprecipitations with ammonia in the presence of ammonium chloride and iron is removed by a double extraction in 6.1 - 6.4 hydrochloric acid solution with diethyl ether. The remaining solution is then polarographically examined.

Milner[83] has used the step obtained from a hydrochloric acid/sodium formate/hydrazine hydrochloride base solution for the determination of microgram amounts of indium in beryllium compounds. Indium is extracted from beryllium compounds such as berylliumoxide or beryllium sulphate, as its oxinate into chloroform. After evaporating of the chloroform extract, the organic material is destroyed with sulphuric and nitric acids and evaporated to dryness. The salt is then dissolved in a small quantity of hydrochloric acid and, after diluting with distilled water, the aqueous phase is shaken with diethyl ether to remove any other impurities. The aqueous phase is finally analysed polarographically for the determination of indium.

The proposed method for the determination of indium can be used to analyse traces of indium in cadmium, because cadmium is not extracted under the experimental conditions employed. During our investigations, even a 100 fold excess of cadmium did not alter the wave-height of the extracted indium acetylacetonate reduction wave. Although the proposed method has not been applied to actual samples, it should undoubtable to be superior to those methods in which the prior separation of interfering metal ions, by lengthy processes is essential.

The nature of the reduction of palladium at the dropping mercury electrode has been investigated by a number of authors.

Willis[83] observed that +2 palladium (probably Pd $(CN)_4$) in 1 M potassium thiocyanate is reduced reversibly to the metal. The half-wave potential (-1.77V vs. S.C.E.) is so close to the final current rise that the diffusion current plateau is not developed fully.

The tetraamino-palladous ion Pd $(NH_3)_4$ produces a well-formed reduction wave from a supporting electrolyte containing 1 M each of ammonia and ammoniumchloride and 0.005% methyl red as a maximum suppressor[83]. The reduction does not proceed reversibly and the half-wave potential ($E\frac{1}{2}$) shifts from -0.72V vs. S.C.E. with 0.2 mM palladium to -0.8V with 5 mM.

The pyridine complex of +2 palladium (probably Pd $(Py)_4^{++}$) undergoes reversible reduction to the metal and the diffusion current is directly proportional to concentration[110].

Stankoviansky[109] has investigated the polarographic behaviour of gold, palladium, platinum, and silver in ethylene diamine/citrate solutions. The half-wave potentials ($E\frac{1}{2}$) of gold and platinum were essentially different from that of palladium, however, palladium was not actually determined. The half-wave potential ($E\frac{1}{2}$) values vs. S.C.E. in 0.5 M potassium iodide solution were gold -0.065, palladium -0.39 and platinum (1V) + 0.072.

R. Portillo[110] noted the irreversible reduction wave of palladium at the dropping mercury electrode using two supporting electrolytes (one of 0.042 M lithium sulphite and other, which can be used with palladium solutions at pH 1, 0.83 mM potassium dihydrogen phosphate). Furthermore, it was noted that no interference due to copper and iron was observed, but cadmium, chromium, nickel and silver interfered.

It has been noted in a literature survey, that no method has been cited, so far, for the determination of palladium by ordinary d.c. polarography in ores, alloys and other platinum metals. The method, described above may prove quite satisfactory in the analysis of ores, alloys, other platinum metals, etc. in which the other interfering elements were easily removed.

CHAPTER II

Metal-oxinates

Introduction

8-hydroxyquinoline (oxine) is a white crystalline compound, insoluble in water but freely soluble in alcohol, chloroform, benzene and aqueous solutions of mineral acids. The reagent is somewhat sensitive to light; hence the solutions should be stored in brown bottles.

Oxine is known to react with more than forty metal ions[113]. Oxine, having both a basic nitrogen and a phenolic hydroxyl group, is an amphoteric substance in aqueous medium and thus because of its amphoteric nature, it is incompletely extracted below pH 5 and above pH 9.0.

Oxine extraction has been studied in detail for almost twenty metal ions and the relevant data is summarised by Morrison and Freiser[84]. The applicability of this reagent has been greatly extended by the use of masking agents. Thus, interference from elements such as Fe, Cu, Mo and nickel may be removed by the use of cyanide, either by forming the cyanide complex prior to extraction[114, 115] or by washing the chloroform layer with aqueous cyanide solution[116]. A systematic study of the application of EDTA as a masking agent in oxine extractions has been carried out by Taylor[117].

This system was investigated in order to obtain the necessary information regarding the polarographic reducibility of metal-oxinates following solvent extraction.

Experimental

Apparatus

Polarograph

Elliot model 200 with dropping mercury electrode.

Unless otherwise stated the operating conditions were as follows:

rate of potential increase 0.5 V/100 sec., drop time 3.25 sec., height of mercury reservior 70 cm., mercury flow rate 2.3291 mg/sec., no damping or counter current. All the measurements were made at the room temperature. An internal mercury pool anode was used and deaeration was achieved by bubbling nitrogen (oxygen-free) through a 5 ml sample for 5 minutes. A mercury seal was used instead of more usual water seal to prevent any reabsorption of oxygen.

pH meter	E.I.L. Vibron, Model 39A

Reagents:

Unless otherwise stated all the solvents and salts used in this study were of analytical grade purity. G.P.R. indicates general-purpose reagent grade quality of the reagent.

8 hydroxyquinoline	
Lithium chloride (dried)	G.P.R.
Perchloric acid	Sp gravity 1.54 and 5 per cent ($v/_v$) in distilled water
Sodium hydroxide	5 per cent ($w/_v$) in distilled water

Solvents

Iso-butylmethyl ketone
Chloroform
Ethylacetate
Methanol

Stock solutions

1×10^{-1} M 8 hydroxyquinoline solution in water

Dissolve 1.1452 g. of oxine into distilled water containing 5 ml. of glacial acetic acid and dilute to 100 ml. by further addition of distilled water.

1×10^{-1} M 8 hydroxyquinoline solution in organic solvents

Prepare 0.1 M solution of 8 hydroxyquinoline in the above solvents except in methanol, by dissolving suitable amounts of oxine in the above solvents.

5×10^{-1} M lithiumchloride solution

Dissolve 5.3 g. of dried lithium chloride in methanol and dilute to 250 ml. by the further addition of methanol.

1×10^{-3} M solutions of metal ions

Prepare 100 ml. stock solutions of metal ions by dissolving suitable amounts of salts in distilled water.

Preliminary investigation of the solvent extraction of metal-oxinates

In this study the extraction procedure was the same as that recommended by Stary but the extraction was carried out into both *iso*-butylmethyl ketone and ethylacetate instead of chloroform. The change of the solvent was necessary because chloroform is readily reduced at the dropping mercury electrode (*ca.* -0.7v) and therefore limits the working potential range.

30 ml. of a 0.1 M oxine solution, in the organic solvent, was shaken with an equal volume of an aqueous solution containing appropriate metal ion (2×10^{-4} M) together with a small

quantity of oxine solution (10^{-3} M) to prevent any precipitation of certain metal ions as their hydroxides. The ionic strength was adjusted to 0.1 M by the addition of 1 M potassium perchlorate (except to pH values 1). The pH of the aqueous phase was adjusted under pH-meter by the addition of sodium hydroxide or perchloric acid. After the equilibration, the two phases were separated. The extracted organic phase was transfered into a 50 ml. volumetric flask containing 10 ml. of 0.5 M lithium chloride and the solution was diluted to volume with methanol. A 5 ml. aliquot of this solution was then added to the electrolysis cell, containing ca. 5 ml. of mercury to serve as the reference electrode and the solution was deoxygenated by bubbling nitrogen (oxygen-free) through the solution for 5 minutes. Finally, polarograms were recorded over as wide a potential range as possible.

Table XV11 shows the results obtained by analysing such solutions before and after extraction. In column 3 results are reported by analysing the aqueous phase before extraction; in columns 4, 5 and 6 the results obtained after extraction (with iso-butylmethyl ketone, chloroform and ethylacetate respectively) are recorded.

The results showed that in aqueous solutions most metal ions form insoluble chelates which cannot, therefore, be analysed polarographically. However, on extraction into organic solvents they form soluble species which are polarographically active and waves are obtained for the metal ions which are reduced between the potential range of 0.0 to -1.0V.

In case of chloroform the available potential range was from 0.0 to -0.6V; the limit on the positive side being the

TABLE XVII

Metal ion	pH of aqueous phase before extraction	Aqueous phase after complex formation	Iso-butyl methyl ketone phase after extraction	Chloroform phase after extraction	Ethylacetate phase after extraction
Blank	4,6,8,10	-1.0	-1.0	-0.7	-1.1
Beryllium	8.0	NW	NW	NW	NW
Bismuth	6.0, 9.0	pptn	pptn at interface	-0.38(max)	pptn. at interface
Cadmium	7.0	pptn	-0.52	wave masked by the reduction of solvent itself	-0.56
Cerium	10.0	NW	NW	NW	NW
Cobalt(11)	8.0	NW	-0.78	NW	-0.8
Copper	4, 8	pptn	-0.25(max)	-0.23(max)	-0.28(max)
Gallium	8.4	NW	NW	NW	NW
Iron(111)	4	pptn	-0.18	-0.2(max)	-0.2
Indium	9.0	pptn	NW	NW	NW
Lead	8.0	-0.32	-0.25(max)	-0.26(max)	-0.28(max)
Molybdenum (V1)	2.0	pptn.	>0.0,-0.68	>0.0,-0.54	>0.0,-0.60
Nickel	5.0	NW	-0.68	NW	-0.65
Palladium	8.0	pptn	-0.23(max)	-0.2(max)	0.26
Tin (11)	3.0	-0.4	NW	NW	NW
Tin (1V)	3.0	prewave -0.16,-0.4	NW	NW	NW
Titanium(1V)	4.0,8.0	pptn	NW	NW	-0.96
Uranium(V1)	7.0	pptn	-0.42	-0.46	-0.48
Vanadium(V)	4.0	NW	NW	NW	NW
Zinc	4.5	pptn	NW	NW	NW
Zirconium	2.0	NW	NW	NW	NW

oxidation of mercury and on the negative side by the reduction of the solvent itself. Of the various metal chelates extracted into chloroform only reduction waves due to following metal ions were observed: bismuth, copper, iron (111), lead, molybdenum, palladium and uranium.

The reduction of other cations was masked by the reduction of solvent itself

When either *iso*-butylmethyl ketone or ethylacetate was used as extractant, the available potential range was extended to -1.1V (reduction of oxine). With both of these solvents reduction waves were obtained for following cations : cadmium, cobalt, nickel and titanium.

in addition to those previously observed using chloroform. Furthermore, whereas in aqueous phase no waves were observed for cobalt and nickel, after extraction into both iso-butylmethyl ketone and ethylacetate well-defined waves were observed at -0.8V and 0.65 V respectively. No waves were observed for tin (1V) or tin (11), although extraction did take place to some extent (*ca*. 40%). The waves possessed maxima and they were easily eliminated by methylene blue.

Discussion

Three important factors emerge from this study of metal chelates.

i) The fact that insoluble metal oxinates can be extracted as soluble species into organic solvents opens up the possibilities for analysis of such insoluble compounds which otherwise were not possible to analyse polarographically.

ii) Furthermore the polarographic examination, following solvent extraction, into organic solvents increases the selectivity of the method by the fact that not all of the species are extractable necessarily give polarographic wave in organic solvent. For example, tin (11) and tin (1V) give a well-defined reduction wave at -0.4V, but on extraction into organic solvents the waves are not observed. This offers a suitable method, in some cases, for the removal of the interference of tin.

iii) The suitability of the method for the analysis of metal ions which form strong aquo-complexes is illustrated by the behaviour of cobalt and nickel.

In aqueous medium cobalt and nickel both form strong aquo-complexes with the results that the polarographic half-wave potentials ($E\frac{1}{2}$) are shifted to very negative potentials. On extraction into the organic solvent containing oxine, the water of co-ordination is replaced by oxine molecules and also by analysing these organic phases the activity of water is also decreased to negligible value. Thus these metal ions tend to reduce to more positive potentials. Thus similar considerations can be applied to other metho ions which form strong aquo-complexes.

We can envisage the extension of this system for developing analytical methods for metal ions such as bismuth, uranium and lead.

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