Solvent extraction of platinum group metals.

THOMAS, A. F.

SOLVENT EXTRACTION

OF

PLATINUM GROUP METALS

A. F. THOMAS A.P. (SHEFFIELD)

Department of Metallurgy

Sheffield Polytechnic

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PREFACE

The following work is a report on the results of research sponsored by Sheffield Smelting Company Ltd. into evaluation of new techniques for hydro-metallurgical processing of platinum group metals undertaken between October 1970 and December 1973. This work has been submitted as a thesis for candidature of The Council for National Academic Awards for the degree of Doctor of Philosophy.

During the course of this work visits have been made to many leading authorities, both commercial and academic, with a view to gaining a broad understanding of a "state of the art" in the processes of interest. Similarly during the period of this work the following symposia and courses have been attended.

Dec. 1970	Bradford University. "Comparison of Solvent Extraction and Ion Exchange Processes and Equipment (S.C.I.).
Dec. 1971	Liverpool Polytechnic "The Future Role of Nuclear Chemistry" (S.C.I.).
Jan.-March 1972	Sheffield Polytechnic. Course of Lectures on Solvent Extraction and Ion Exchange and Statistical Methods. (M.Sc. Course in "Instrumental Methods of Analysis")
May 1972	Antwerp. "Solvent Extraction in Metallurgical Processes (Technologisch Institut K. VIV).
Sept. 1972	Brunel University, London. "New Methods of Metal Extraction" (S.C.I.)
Nov. 1972	Bradford University. "Advanced SolventExtraction Technology" (I.C.E.)
May. 1973	Birmingham University. Research seminar on "Solvent extraction Processes. (S.C.I.)

To the best of my knowledge the work described is original except where reference is made to previous work.

No part of this work has previously been submitted for a higher degree at any other College or University.

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SYNOPSIS

A survey has been made of previous work on the application of solvent extraction and gaseous reduction processes to refining of platinum group metals. Amine extraction processes have been investigated by chemical shake-up tests and distribution ratios determined with all classes of amines and quaternary ammonium compound for rhodium, iridium, palladium, platinum, ruthenium, osmium and gold using radio tracer techniques. Proposed schemes for separation of platinum metals from base metals using primary amine and separation of Pt/Pd from Ir/Rh using tertiary amine were examined using commercially useful reagents, and specific processes defined. A continuous counter-current testing rig using mixer-settler contactors was built and the performance of the extraction processes determined. Extraction and separation by these processes was successful but continuous re-extraction of platinum metals from the solvent suggested certain limitations in progressing to full pilot-scale operation. It is suggested that gaseous-reduction of the metal from the organic phase in situ could be employed.

GLOSSARY

In the field of solvent extraction there is as yet no complete agreement between workers on the precise meaning of the terms commonly employed in both theory and practice. Whilst this objective is presently being pursued by the "Solvent Extraction and Ion Exchange Group" of the Society of Chemical Industry, for the purpose of this report the terms used should be understood to have the following meaning:

1 Solvent Extraction: Liquid-Liquid Extraction

The transfer of one or more solutes between immiscible liquid phases.

2 Solvent

The liquid phase which contains the extracting agent.

3 Extraction

The transfer of a solute from an aqueous feed solution to a solvent.

4 Stripping

The transfer of a solute from the solvent to an aqueous phase.

5 Scrubbing.

The selective removal of contaminating solutes from the solvent.

6 Distribution Ratio.

The ratio of the concentration of a solute in the organic phase to the concentration in the aqueous phase at equilibrium.

7 Separation Factor.

The ratio of the distribution ratios of two solutes to be separated.

8 Extraction Factor

The distribution ratio multiplied by the phase ratio used.

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1 Introduction

The extractive metallurgy of the platinum group metals from both primary and secondary sources has traditionally employed a wet chemical process technology. However, the separations are seldom clear cut and each precipitate requires purification in order to eliminate other unwanted members of the platinum family. Likewise a certain amount of each element escapes precipitation and is carried along in the mother liquor to reappear in a subsequent separation [1]. In addition the cementation processes incorporated in the process involve the production of large quantities of untreatable effluent in the form of concentrated solutions of base metal salts.

It has been remarked by Beamish [2] that "it is scarcely any exaggeration to suggest that no field of analytical research offers a more potentially useful scope for investigations both fundamental and practical than the chemistry pertinent to the analysis of platinum metals." The field of extractive metallurgy he declares " . . . has been strangely neglected by the analytical researcher, whose method of approach would surely contribute to the efficiency of methods of industrial extraction and refining."

Research was thus initiated in order to investigate alternative processing techniques by application of recent advances in analysis and extractive metallurgy to the refining of the platinum group metals.

1.1. Chemistry of Platinum Group Metals

In understanding the extraction and refining of the platinum metals great consideration must be given to the intrinsic peculiarities in the chemistry of these elements. Firstly, by definition the platinum metals are noble metals (here gold is included as it so often co-exists in the raw material), and are thus resistant to attack by acids, bases, oxygen and chlorine [1, 6]. In this respect gold, platinum and palladium are less resistant than iridium, rhodium, ruthenium and osmium to attack by mineral acids (i.e. aqua regia) and chlorine, while gold and platinum are more resistant than Iridium, rhodium, ruthenium, osmium and palladium to the action of oxygen on the hot metal.

Secondly all the platinum metals show polyvalency in solution, two or more valency states frequently occurring simultaneously and in equilibrium with each other. Ruthenium and osmium are the most marked in this respect, ruthenium possessing important compounds in the valency states of 0, 2, 3, 4, 6, 7 and 8 and osmium important compounds in the valency states of 0, 2, 3, 4, 6 and 8. The most important valency states of palladium and platinium are 2- and 4- although platinum can exist as chloride and oxide in the 3- and 6- states respectively. The situation is less problematic with rhodium and indium as the former exists effectively only in the 3- state and the latter only has important compounds in the 3- and 4- states although of equal significance. In the case of gold only the 1- and 3-valent states are of any concern.

Thirdly all platinium metals in solution have a strong tendency to form complexes (chiefly anionic) in the presence of suitable ligands [7].

1 **Ruthenium** The complexes of ruthenium are among the least satisfactorily characterised of any of the complexes of the platinum metals. The possible variation in oxidation states from Ru (I) to Ru(VIII) and the very

considerable tendency for ruthenium to form polynuclear complexes make the elucidation of the chemical reactions of ruthenium difficult. A number of mono-nuclear complexes of Ru(II), Ru(III), Ru(IV) and Ru(VI) are known and in these the ruthenium is generally 6- co-ordinate and presumably octahedral. A very considerable number of species appear to be present even in some solutions of relatively simple composition.

2 Osmium The complexes of osmium are very similar to those of ruthenium although there are features of the chemistry of each element which are lacking in that of the other. Complexes of Os(II), Os(III), Os(IV) and Os(VI) are known but the most important are those of Os(IV). These include the complex acids and halides where the co-ordination is six and the complex is octahedral.

3 Rhodium The chemistry of the co-ordination compounds of rhodium is primarily that of Rh(III) although some Rh(I) and Rh(II) complexes are known. The usual co-ordination number is six for Rh(III) but lower co-ordination numbers are found in some halogen complexes. Although practically no information is available on bond strengths of co-ordinate bonds involving rhodium, these complexes are generally considered to be very stable materials from both the thermo-dynamic and kinetic point of view. The substitution reactions are known to be rather slow so that the evidence for kinetic stability is more convincing.

4 Iridium The co-ordination chemistry of iridium shows more variety than that of rhodium because both the 3 and 4 valency states are reasonably stable and are found in numerous complexes. However, the complexes of Ir(III) are essentially the same as those of Rh(III) involving octahedral co-ordination.

5 Palladium The palladium complexes are mostly those of Pd(II) although some of Pd(IV) are known. In general the complexes of palladium (II) are

four-co-ordinate and may be assumed to be square-planar. In addition to the complexes of type $PdCl_4^{2-}$ there are also numerous square-planar complexes with bridging groups and it seems quite probable that the complex Pd(III) species which have been assigned a co-ordination number of three are of this type.

6 Platinum. The co-ordination chemistry of platinum is unusual in that in many respects, perhaps most impressively so in the kinetic stability of the bonds formed with many common ligands. But as with palladium, the chemistry is concerned primarily with the 2 and 4 valency states and similarly, simple ions of platinum are not known in aqueous solution. The platinum (II) complexes are less stable than platinum (IV) and are usually 4- coordinate and square-planar, with commond ligands such as ammine and halides. The Pt(IV) complexes are usually quite stable with respect to ligand exchange and reduction to Pt(II), and are always present as octahedral complexes.

7 Gold Like the heaviest elements in the platinum group gold shows very little tendency to form simple aquated cations. Gold exists in solution in either the Au(I) or Au(III) state, the aurous complexes being usually 2- coordinate (e.g. $Au(CN)_2^-$) whereas the auric complexes are always tetracovalent as in chloroauric acid, $HAuCl_4$.

1.2. Current Extraction Practice and its Disadvantages

There are three major sources of platinum metals available to refiners:

1 from concentrates produced from platinum bearing ores (chiefly South African ores)

2 from the anode slimes resulting from the electrolytic refining of nickel and silver

3 from scrap platinum metals.

Essentially, materials for all three sources undergo the same separation and refining procedures based on preferential leaching, precipitation of complexes and finally reduction by ignition or cementation [1, 3, 4].

Firstly the concentrate is treated with aqua regia which dissolves most of the platinum, palladium and gold while ruthenium iridium, osmium and rhodium remain unattacked. The gold is recovered by treating the solution with ferrous sulphate precipitating it as a brown metallic sponge which may be later purified electrolytically. Platinum is next precipitated from the solution as ammonium chloroplatinate (IV) by the addition of ammonium chloride. This precipitate is then further purified after redissolution in aqua regia and reduced by ignition. Palladium is at last removed from solution as dichlorodiammine palladium (II). Excess ammonia is first added followed by hydrochloric acid and the yellow salt precipitates out. Ignition of the precipitate yields the pure metal. However, this separation is not quantitative and the minor amounts of platinum and palladium in the filtrate are recovered by reduction with metallic zinc.

The insoluble residue from the aqua regia extraction is smelted with litharge and fluxes and the resulting lead alloy is then dissolved in nitric acid which removes most of the accompanying palladium, platinum and silver. The insoluble residue in this treatment is a concentrate of ruthenium, osmium, rhodium and iridium and this group of metals is known as the by-metals. Their subsequent treatment constitutes the difficult part of platinum metal refining. One method is to fuse the residue with sodium bisulphate and leach with water. Rhodium is thus dissolved and is purified by precipitation as ammonium nitrorhodite and reduced to the metal by ignition. The residue from the leaching operation is then fused with sodium peroxide and further leaching yields a solution of ruthenium and osmium and a residue of iridium and platinum. The latter pair are separated by a process of dissolution in aqua regia and repeated crystallisation of iridium as ammonium chloriridate (IV), the platinum remaining in the solution as ammonium hexachloroplatinate (IV) being recirculated and returned to the platinum recovery section. Ruthenium and osmium are separated by the preferential reduction to ruthenium oxychloride of the ruthenium tetroxide by hydrochloric acid and the osmium tetroxide is distilled off. Alternatively, and more commonly, they may be separated by repeated distillation of the tetroxides, the ruthenium tetroxide being trapped in hydrochloric acid solution and thus successively removed from the osmium tetroxide. The pure metals may then be obtained by the precipitation of the ammonium chlorocomplexes and ignition under hydrogen.

The drawbacks to the types of procedures outlined above are:

1 Lack of selectivity and therefore necessity to repeat purification steps to obtain pure metal from solutions.

2 Lack of quantitative recovery in separation procedures.

3 Production of concentrated effluent solutions of iron and zinc salts in the precipitation of gold and palladium [5].

4 Subsequent electrolytic refining of gold [5].

5 Production of toxic waste gases during the ignition reductions.

6 Vapourisation of ruthenium and osmium during oxidising fusions.

7 Inflexibility of the processes towards recirculation of reagents and towards continuous operation.

2 Alternative Refining Techniques

2.1. The Solvent Extraction Technique

Solvent extraction (i.e. liquid-liquid extraction) is a technique in which a molecular or ionic species is selectively transferred from one environment to another by enabling it to distribute itself between two immiscible liquids according to its thermodynamic needs. In the context of this work it should be understood that since extraction and refining of platinum metals involve species in aqueons solutions, solvent extraction here implies the use of an aqueons-organic solvent system.

Solvent extraction is probably the most efficient method for separating chemically similar elements which is suitable for operation on a commercial scale [8]. Its high selectivity and the use of relatively cheap reagents can make it an economically viable proposition for the extraction of metals of the value of copper and above [9, 10]. The process is one of partition although situations in which there is quantitative separation and stripping back from the organic phase are rare. But by using several stages of extraction and recovery in a counter-current system remarkably complete separations can be achieved.

Since a metal in aqueous solution frequently exists in a range of species and the proportions of these and their proportions change when pH is altered or reagents are added which cause the formation of complexes or ion association compounds, extraction by a particular solvent may vary and may be possible under some conditions and not under others. The solvent extracts only ions with which it has affinity: it does not extract all species in solution which contain a particular metal. The fundamental consideration when dealing with solvent extraction (particularly in the case of platinum metal) is the kind of ions and neutral complexes present in equilibrium in the aqueous solution.

At thermodynamic equilibrium of the species between the two liquid phases the activity of the metal in each phase must, by definition be the same. But since solvent extraction implies differential solubility between the two phase there must be interaction between the solvent and the metal species thus lowering the activity coefficient of the metal in the organic phase but raising its concentration relative to that in the aqueous phase. Solvent extraction processes are classified on the basis of the types of interaction which occur

(a) Solvation In this type of solvent extraction process there is an exchange between the water molecules solvating the metal species in the aqueous phase and the solvent molecules, thus conferring hydrophobic properties upon it and leading to its rejection from the aqueous phase. The metal species is thus in the same form in both phases. The solvents are usually simple e.g. ethers, ketones or esters and the metal species are neutral.

(b) Ion Association (Ion-Exchange) This refers to the formation of an ion-association complex which is soluble in the organic phase by interaction between an ionic metal species in the aqueous solution and the ionic solvent. This may be an organic acid such as alkyl phosphoric acid or naphthenic acid, or, an amine such as tri-n-octylamine. Clearly the acids will extract positively charged ions from water (cation-exchange) and the amines, negatively charged ions (an ion-exchange) since they behave in acid solutions as trisubstituted ammonium ions R_3NH^+ where R is the alkyl group. Under certain conditions ether may also be included in the ion association type of process since it becomes protonated in acid solutions and can thus form a weak, so called, oxonium salt with an anion e.g. $(FeCl_4^-)$.

(c) Chelation If the organic solvent can form stable complexes with a metal ion it will extract it from solution into an organic diluent.

The reagents which behave in this way (chelates) are usually too expensive to be used except in special cases such as treatment of nuclear fuels, for analytical purposes, or recently for copper extraction using substituted oximes (LIX reagents) specifically developed for this purpose.

2.1.1. Chemistry of Solvent Extraction

2.1.1.1. Partition Coefficient

According to the simple distribution law of Nernst (1891), at equilibrium,

$$\frac{(M)_o}{(M)_w} = \text{constant} = Kp \qquad (1)$$

where $(M)_o$ is the concentration of the metal ion in the organic liquid $(M)_w$ the concentration in the aqueous liquid and Kp is the partition coefficient. However this implies that the two solutions obey Henry's or Raoult's law, which is rarely the case. A more rigorous definition of the partition coefficient may be derived from the chemical potentials of the species in the two phases μ_o and μ_w.

The chemical potential of the metal ion in the organic phase is given by

$$\mu_o = \mu_o^o + RT\ln a_o \qquad (2)$$

and the chemical potential of the metal ion in the aqueous phase is given by

$$\mu_w = \mu_w^o + RT\ln a_w$$

At equilibrium,

$$\mu_o = \mu_w$$

therefore $\mu_o^o + RT\ln a_o = \mu_w^o + RT\ln a_w$

hence
$$\ln \frac{a_D}{a_W} = \frac{\mu_o^o - \mu_W^o}{RT}$$

but at a given temperature $\mu_o^o - \mu_W^o$ is constant for a given metal ion in the two solvents.

Therefore,
$$\ln \frac{a_D}{a_W} = K$$

therefore
$$\frac{a_o}{a_W} = Kp \qquad (3)$$

Thus the partition coefficient relates activities so that in general activity coefficients have to be known in order to determine partition coefficients.

2.1.1.2. Distribution Ratio

Of much greater significance, because of the lack of data concerning activity coefficients, is the overall or stoichiometric distribution of the metal ions between the two phases. It is thus necessary to introduce a more practical quantity to describe the extraction called the "distribution ratio" (D). This is a stoichiometric ratio including all species of the same component in the respective phases.

$$D = \frac{\text{Total Concentration in Organic Phase}}{\text{Total Concentration in Aqueous Phase}}$$

If conditions were ideal as in the case where species are not involved in any reactions in either phase then D would reduce to Kp the partition coefficient [11].

2.1.1.3. Types of Aqueous Equilibria Determining Extractability

If the aqueous solution contains two or more different species of the metal ion, both or all being extractable by the solvent, they will distribute themselves between solvent and water in accordance with their respective partition coefficients. However, the species may be in equilibrium with one another in the aqueous solution and also with other species not extracted by the solvent. Thus the amount of each kind of extracted ion or molecule in the organic liquid is determined not only by the partition coefficients but also by the equilibria in the aqueous solution.

Equilibria concerned with the aqueous member of the liquid pair are extremely important, varied and may serve as the limiting factor in determinining solvent extraction properties of a given inorganic species [12]. Some of the types of equilibria appearing are illustrated in equations (4) to (9). It is to be understood that these are not mutually exclusive: several generally exist in parallel.

$$AB + H_2O \rightleftharpoons ABnH_2O \qquad (4)$$

$$AB + H_2O \rightleftharpoons A^+ + B^- \qquad (5)$$

$$AB + H_2O \rightleftharpoons (AnH_2O)^+ + B^- \qquad (6)$$

$$AB + H_2O \rightleftharpoons AOH + H^+ + B^- \qquad (7)$$

$$AB + H_2O \rightleftharpoons AOH + HB \qquad (8)$$

$$AB + H_2O \rightleftharpoons A^+ + OH^- + HB \qquad (9)$$

where AB = some inorganic compound.

Equilibrium (4) may represent either a specific or non-specific solvation of AB. Equilibria (5) and (6) are typical of inorganic salts in water and lead to ionisation. These are the equilibria which are most involved in making water the natural solvent for inorganic substances. Equilibria (7), (8) and (9) illustrate hydrolytic reactions which are possible and which occur to varying degrees in specific cases. After such initial reactions the products may undergo further complicating equilibria such as

$$AB + B^- \rightleftharpoons AB^-_2 \qquad (10)$$

which is a situation typical in aqueous solutions of platinum metals.

In most practical cases one has an aqueous solution containing A^+ and B^- from which one desires to extract A as AB or $A(B_1B^1)$ or B as AB or $(A_1A^1)B$. Equations (4) to (9) may then be interpreted as suggestions of equilibria which may have to be considered in generating the extractable form of the desired species.

2.1.1.4. Processes of Extraction

Although details of the specific nature of the interactions obviously must differ from one metal to another a helpful organisation pattern may be adopted based on three essential aspects common to every metal extraction process [11].

Formation of an Unchanged Complex

This step involves the above mentioned types of reactions of the metal ion in the aqueous phase leading to the formation of an extractable species. Complex formation may be accomplished by chelation, simple coordination or by ion association.

The case of coordination may be described by

$$M^{n+} + nR^- \rightleftharpoons MR_n \qquad (11)$$

where M^{n+} is an n-valent metal ion and R^- is an anion of a suitable chelating or coordinating agent.

In ion association the metal may be incorporated by coordination in either the cation (12) and (13) or the anion (14) and (15) of the extractable ion pair.

$$M^{n+} + bC \rightleftharpoons MC_b^{n+} \qquad (12)$$

$$MC^{n+} + nB^- \rightleftharpoons (MC_{b}^{n+}.\ nB^-) \qquad (13)$$

$$M^{n+} + (n + a)B \rightleftharpoons MB_{n+a}^{a-} \qquad (14)$$

$$MB_{n+a}^{a-} + aD^+ \rightleftharpoons (aD^+.MB_{n+a}^{a-}) \qquad (15)$$

where C is a neutral mono or polydentate ligand, E^- is an anion appropriate either for pairing with the cation as called for in (13) or for coordination with the metal as shown in equation (14) and D^+ is a suitable cation required to form the ion-pair.

Distribution of the Extractable Complex

This is by far the simplest of the three stages from the mathematical point of view. At this stage it is required that the complex formed should become preferentially dissolved in the organic phase. However, it should be appreciated that it would be wrong here, uncritically to equate solubility ratio with the partition coefficient. One of the two major reasons for this, as has already been mentiond, is the fact that the partition coefficient depends on activities and these change with concentration. Only when saturation levels are achieved in both solvents is this equality valid. But by far the more important factor is the effect of the presence of the second solvent on the solubility of the solute in the first solvent. This may lead to the solvation of the solute by the second phase forming a new species which may have solubility characteristics totally different from those of the original solute.

Interactions of the Complex in the Organic Phase

Reactions involving the extractable complex in the organic phase e.g. polymerisation or dissociation of the complex, interaction with other compounds such as the reagent in the organic phase are included in this stage. In the case of polymerisation there is a tendency for the activity of the extractable species in the organic phase to be reduced and the overall extraction equilibrium is shifted in favour of higher distribution ratios. It should follow that the extent of most ion association extractions will depend on the concentration of the metal involved, as is found to be the case in practice.

2.1.2. Commercial Applications of Solvent Extraction

Following some classical experiments performed in the 19th century the use of a wide variety of solvents for extraction of a large number of metals was developed for use in analytical chemistry [13, 14, 15]. However, solvent extraction techniques were not applied on a commercial scale until about 1942 when nuclear fuels began to be required of high purity and in large amounts. Later, this technique was applied to the separation and purification of materials with special nuclear properties for use in power reactors. Examples of this are the separation of tantalum and inobium, zinconium and hafnium, vanadium and uranium. Similarly liquid - liquid extraction techniques were used in the separation of fission products and the rare earth metals. At the same time consideration was being given to the possibility of separation and refining of commoner metals by this means [16, 17]. Fortunately a liquid - liquid extraction technique had been applied since early days in the refining of petroleum and purification of organic materials. There was therefore a large amount of literature on the equipment and chemical engineering aspects and this was readily adaptable to metallurgical applications.

Some separations of industrial importance are:

Nuclear fuels: The most extensive development of the liquid-liquid extraction technique has been in the processing of uranium ores from the early technique of extracting uranium nitrate with ether, the procedures evolved incorporate phosphate esters and amines in a wide range of specific processes for treating widely differing uranium ores. Reagents used in the recovery of uranium include alkyl phosphoric acids such as (2-ethyl hexyl)phosphoric acid, tributyl phosphate as well as various secondary and tertiary amines [18, 19, 20, 21, 22].

Vanadium which is often associated with uranium from leach liquors may also be recovered and separated by pH adjustments in the phosphoric acid process after the removal of uranium [9].

Copper Nickel and Cobalt: Nickel and cobalt are chemically similar and co-occur frequently in nature. Since their separation is difficult by conventional means attention has been drawn to solvent extraction methods. Separation of cobalt and nickel can be effected by using tertiary amines and quaternary ammonium compounds [95]. One significant difference is that cobalt forms a ($CoCl_4^{2-}$) complex whereas nickel does not form corresponding complex ions. Thus cobalt may be preferentially removed from hydrochloric acid solutions.

Possible solvent extraction techniques for copper recovery have received considerable attention from the directions, first the separations of copper from co-occurring metals (i.e. Ni, Co, Zn) and secondly as a selective concentration method for low grade one solutions arising from dump and bacterial leaching. In the first case carboxylic acids (e.g. naphthenic acid) have been applied successfully by careful control of pH in order to maintain selectivity. In the second case, the LIX reagents developed by General Mills have been applied, particularly the more recent types which have high selectivity for copper over iron. Plants have been commissioned in the U.S.A. which incorporate this purification process in the production of cathode copper actually on the dump leach mine site [23].

Tantalum and Niobium: The demand for these materials was created by the advent of nuclear power reactors due to their high corrosion resistance and suitability as fuel cladding in fast reactors. Solvent extraction plants for the separation of these co-occurring metals make use of methyl isobutyl ketone (MIBK), and methyl cyclohexanone and tributyl phosphate which give higher selectivities [17, 24, 25].

Zirconium and Hafnium: These two co-occurring metals were also required in the nuclear power field, zirconium as fuel cladding and hafnium as control rod material. Thus their widely differing nuclear properties required complete mutual separation. Zirconium is extracted preferentially to hafnium by tributyl phosphate and tri-iso-octylamine from nitric acid solutions although methyl-iso-butyl ketone processes now also operate commercially.

2.2. Gaseous Reduction

One of the major disadvantages in the traditional refining methods in the precious metals industry is product impurity inherent in the precipitation methods employed and the associated effluent disposal problems. But this situation is not unique to the platinium metal processors. Hydrometallurgical techniques, in which the final step of recovering the metal of value has been by cementation (Au, Ag, Cu) or by electrolysis (Cu, Zn, Ni, Cd, etc.) have been widely used for many years. The possibility of using such reducing gases as sulphur doxide, carbon monoxide, or hydrogen under pressure to effect the final precipitation of the metals directly from their solutions was an obvious and attractive alternative and investigations along these lines go back over 60 years. A comprehensive review of the history and development of these researches is given by Evans [82].

2.2.1. Chemistry of Gaseous Reduction

2.2.1.1. Thermodynamic Treatment

Reduction of divalent metal ions such as copper, nickel, cobalt, lead and cadmium by hydrogen may be written as:

$$M^{2+} + H_2 \rightleftharpoons M^0 + 2H^+ \qquad (16)$$

with an equilibrium constant K (neglecting activity coefficients)

$$K = \frac{[H^+]^2}{[M^{2+}]\,P_H} \qquad (17)$$

where brackets denote molar concentrations and P_H the pressure in atmospheres.

The degree to which this reaction occurs is given by the familiar thermodynamic equation for the free energy ΔG(joules) or more conveniently the potential E (volts)

$$\Delta G = -23,060nE = -RT \ln K \qquad (18)$$

Reductions of copper, nickel, and cobalt solutions with hydrogen attain commercially attractive rates only at temperatures higher than 70°C. Extrapolation of thermodynamic data is certain to be speculative but actual data at elevated temperatures are not available. It is therefore convenient first to calculate E for room temperature conditions then to attempt to approximate E for elevated temperatures and finally to discuss briefly the effect of variation in experimental conditions. Fig. 1 plots the variation in E at 25°C for concentrations of the metal ions between 10^{-3} M and 1.0 M and also the hydrogen potential at various pH values and at 1, 100 and 1000 atomospheres (fugacity of H_2 at 25°C and 100 atmospheres = 106.1 atmospheres). Of course the metal potential is affected by pH only indirectly since the metal concentration is a function of pH due to complex formation and hydrolysis. For reduction to proceed the hydrogen potential must be more negative than the metal potential. It appears possible to reduce metals up to cadmium, perhaps including iron but hardly zinc. Cadmium turned out to be the least noble metal to be precipitated in pure form at an economical rate.

It will be noted that a 100 fold increase in pressure is comparable to an increase in only one pH unit.

Calculating the reduction equilibria in aqueous solution for elevated temperatures is difficult in view of the uncertainty in estimating the effect of temperature on the entropies of solutes, ions, or undissociated molecules. Since there are ions on both sides of the equation temperature changes in entropies can be assumed roughly to cancel out. This is admittedly not a very good approximation but it appears as good as any in the absence of experimental data. Equation (19) has been used to calculate reduction equilibria using room temperature data.

$$\Delta G_T = \Delta G_{298^oK} - \Delta S_{298^oK}\,(T - 298) \qquad (19)$$

It is based on the assumption that the reaction entropy at temperature T, ΔS_T is equal to the reaction entropy at 25°C, ΔS_{298^oK} [83].

2.2.1.2. Effect of Complex Formation

When considering how the formation of complexes of the metal influences the potential of the metal ion-metal electrode it is usual to deal with the case in which a large excess of the complexing agent or ligand, L, is present. For simplicity in writing equations it is assumed here that, L, is uncharged [10]. The reaction which forms the complex is then:

$$M^{2+} + nL \rightleftharpoons ML_n^{\;2+} \qquad (20)$$

and the overall equilibrium constant β_n is given by

$$\beta_n = \frac{[ML_n^{\;2+}]}{[M^{2+}]\;[L]^n} \qquad (21)$$

n being the maximum co-ordination number of the metal ion with the particular ligand considered.

In order to calculate the electrode potential it is assumed that only the uncomplexed metal ion M^{2+} is reduced to metal, and the effect of complex formation is to reduce the activity of the simple ion. Then the value of (M^{2+}) obtained from equation (21) is substituted in the Nernst equation. This is done as follows. Since the complex is stable and for simplicity all activity coefficients are taken as unity, $(ML_n^{\;2+})$ may be taken as being equal to the total concentration of the metal present in solution. That is, because βn is large, $[M^{2+}]$ is so small that this approximation introduces no significant error. (L) is the concentration of the free uncomplexed ligand and may be calculated from the total concentration of ligand present in the solution and the total concentration of metal ions knowing n. The value of E^o for the complex ion $ML_n^{\;2+}$ referring to its reduction to metal and free ligand is obtained by setting $[ML_n^{2+}]$ that is the total concentration of metal equal to one molar and also (L) equal to one molar. Thus:

$$E^o_{ML_n^{2+},M} = E^o_{M^{2+},M} + \frac{2.303\ RT}{z\ F} \log \frac{1}{\beta_n} \qquad (22)$$

It is emphasised that the method of calculating electrode potentials given above is valid only if ML_n^{2+} is the sole complex ion containing the metal present in solution. If lower complexes such as $ML_{(n-1)}^{2+}$ are present it is not sufficient to calculate $[M^{2+}]$ using only the value of β_n.

2.2.1.3. Activity Coefficients

Finally, it has been assumed in the treatments above that since reduction of metal ions in solution to produce metal is carried out at concentrations of the order of one molar and large amounts of other salts are also present, the relevant equilibrium constants were those obtained using solutions of high total ionic strength. In order to calculate standard electrode potentials or free energies of formation of the complexes it was supposed that activity coefficients were unity because the relevant equations refer to activities of species whereas equilibrium constants relate concentrations. Such a supposition is obviously absurd. However, very little information is available concerning the activity coefficients of complex species, in solutions of importance in hydrometallurgy. This is particularly true in the case of precious metals although knowledge of this data is less critical than the less electropositive elements.

2.2.1.4. Kinetics

Whilst thermodynamic treatment indicates the feasibility of a reaction taking place it gives no indication of its rate. In the case of a simple reaction such as (16) the rate will be expected to depend on the activities and so on the concentrations of the metal ion, hydrogen gas and hydrogen ion in solution. If the rate of the reverse reaction between the metal and the hydrogen ions is significant in determining the overall reaction rate, then the surface area of metal available for reaction will also be important. When a complex metal ion, such as an ammine, is to be reduced, the concentration of the complexing agent will usually have to be included in the rate equation.

Some metals, such as nickel and cobalt will not form as a result of reduction of aqueous solutions of their salts by hydrogen unless some suitable surface is already present at which the reaction can take place. In such cases the reduction reaction is hetero-geneous and the area of the catalytically active surface is important. Even when the reaction is homogeneous, the fact that a solid is produced raises the usual problems as to whether fresh nuclei can be formed by the metal atoms produced by the reaction between molecules in solution, or whether the metal will collect only on a pre-existing nucleus of solid.

Good reviews of the fundamental thermo-dynamic and kinetic considerations in the reduction of metals in solution have been given by Wadsworth [84], by Meddings and Mackiw [85], by Forward and Halpern [86] and by Schaufelberger [83].

2.2.2. Commercial Applications of Gaseous Reduction of Metals

At the present time there are six commercial installations where pressure-hydrometallurgical processes have found an application in the routine large-scale production of nickel, cobalt and copper.

Sherrit Gordon Mines Ltd., operates in Fort Saskatchewan, Alberto, Canada, a refinery where an ammonia leaching process is used for the recovery of nickel and cobalt from sulphidic nickel concentrates and an acid leaching process is applied for the treatment of roasted calcines and high temperature alloy scrap, in conjuction with hydrogen reduction [87, 88].

A commercial plant is under construction by Ontokumpu Dy. in Finland for the recovery of cobalt from cobaltiferons pyrite concentrates.

Operation of the former Freeport Nickel Co. plant at Moa Bay in Cuba is being continued by the Castro Government. The lateritic ore is treated there in a high pressure sulphuric acid leach circuit to produce a high-grade nickel cobalt sulphide concentrate at a capacity equivalent to 25,000 tons of nickel per year. Refining of this concentrate to pure metal, originally to take place at the Louisiana refinery, is being carried out either in the Soviet Union of Czechoslovakia.

In the U.S.A. the Universal Minerals and Metals Co. operates a plant in Kansas City to produce 10 tons of copper powder per day from various copper bearing scrap metals, and the Arizona Chemcopper Co. has recently completed the construction of a plant to produce 25 tons of copper powder per day from impure cement copper. Reviews of the operating characteristic of all these plants are given by Mackiw, Benz and Evans [89], and by Evans [82].

3. PREVIOUS WORK

3.1. Solvent Extraction of the Platinum Metals

In their review of the application of solvent extraction to metal extraction, Smithson et. al. [20] remarked that no references to the liquid-liquid extraction of precious metals could be found. They suggested that "Opportunities may exist for the use of this technique in the recovery of gold from certain solutions but these have apparently not been seriously explored. There seems to be scant likelyhood whatever" - they continued - "that liquid-liquid extraction will ever find use in the treatment of cyanide solutions from gold ore leaching operations, owing largely to the efficiency and relative cheapness of present precipitation methods. There is some possibility" they suggest "that special cases may arise where liquid-liquid extraction would be competitive with other methods - for example if it became necessary to selectively remove gold from plating solutions or solutions resulting from secondary precious metals recovery processes."

While it is true that all applications of liquid-liquid extraction in the refining of platinum metals up to now have strictly concerned analytical procedures, recently work has been published indicating that the application of these techniques, at least to purification of anode slimes is being seriously considered on a commercial basis. Dolgikh and co-workers in Russia have examined the possibility of extracting noble metals from copper and nickel anode slimes with aminated alcohols and amines produced by reduction of technical nitroparaffins [45, 46, 52]. In England Morris and Ali Khan have published preliminary work on the application of solvent extraction to the separation of several noble metals from precious metal concentrates. They have recommended that the separation of gold by dibutyl carbitol [5], of ruthenium by carbon tetrachloride [44], and of rhodium by the cation exchanger dinonylnaphthalene sulphonic acid [69] could have several advantages over traditional methods in industrial processing.

For the purposes of this work a review was made of some sixty references to the application of various solvent extraction processes in the analytical chemistry of the platinum metals. In this, the review has been restricted to solvation and ion association systems. Chelating systems which have been comprehensively studied and reviewed [2, 70] have not been examined here. Whilst chelates in the form of substituted oximes have been specifically designed for copper extraction, it was considered that it would be more profitable initially to explore the possibility of using reagents which were intrinsically cheaper and had a simpler chemistry than chelating agents.

3.1.1. Solvating Systems

A summary of the principle characteristics of techniques developed for separation of platinum metals by means of a solvating system is shown in Table 1. The principle systems examined or recommended chiefly for analytical separations are ethers, ketones and neutral or basic phosphorous compounds, i.e. oxygenated compounds.

(a) Ketones: Palladium has been shown to be virtually completely extracted by isobutyl methyl ketone from solutions contaminated with niobium and zirconium [29]. Success was attributed to the aptitude of palladium to form a complex iodide PdI_4^{2-} whereas neither niobium or zirconium forms a stable iodide in aqueous solution. This evidence tends to suggest that extraction may be by an ion-association mechanism. Similarly osmium has been shown to be quantitatively separated as a thiocyanate complex in octanone [26].

(b) Ethers: Gold in the form of the bromoaurate may be extracted free from contaminating iron and other noble metals except osmium by extraction into isopropyl ether [32], but rhodium had been shown to be unextractable by the same solvent over a large range of pH from chloride solution [35]. Successful introduction of extraction by means of diethyleneglycol dibutyl ether (dibutyl carbitol) has been made into refining trials on gold from chloroauric acid solution [5]. Complete separation from iron, arsenic and other contaminants is achieved and it was observed that extraction improved with increasing gold (III) concentration in the aqueous phase.

(c) Basic Phosphorous Compounds: Palladium may be efficiently extracted by triphenylphosphine as a $PdI_2.2(C_6H_5)_3P$ complex from weakly acid media although the arsenic and antimony analogues are better [28], and ruthenium(IV) may be extracted by tri-octyl phosphine oxide but not quantitatively.[39] In their systematic investigation of the extraction by tri-octyl phosphine oxide of 60 elements from chloride and nitrate solutions Ishimori and co-workers showed that only osmium and platinum could be quantitatevely extracted and then only from chloride complexes [36].

(d) Tributyl Phosphate: Much work has been reported on the solvent extraction of platinum metals by Berg and co-workers by tributyl phosphate (TBP) from thiocyanate [27], bromo [33], chloro [34, 41] complexes. Their results indicated that TBP could, by multiple countecurrent extraction, be used to separate binary mixtures of rhodium and iridium, rhodium and platinum, platinum and palladium. Similar work by Faye and Inman showed that by employing iodide complexes platinum and palladium could be separated from rhodium and iridium by TBP [30]. However, results of work by Ishimori et al. on TBP extraction from nitrate solutions show that only Ru(IV) and Os (VI) may be considered as being quantitatively extracted [42]. A later paper by Meier et al. on the solvent extraction of osmium reports a systematic study on the extraction of this element by TBP and confirms these results [40].

3.1.1.1. Physical Dissolution Finally in this solvation section consideration should be given to the extraction of ruthenium and osmium tetroxides by carbon tetrachloride (Table 2). It is condidered that, due to the high coordination state of these compounds, they are "physically dissolved" in solution as RuO_4 and OsO_4 molecules. The distribution ratios for osmium and ruthenium between carbon tetrachloride and water have been determined by Martin as 12 and 59 respectively and are independant of the concentration of the tetroxides over considerable ranges [43]. These results have been used by Morris and Ali Khan as the basis for developing a solvent extraction technique in the refining of Ru and Os. They conclude that advantages of this process could ensue from the incorporation of a scaled up version in the commercial refining of ruthenium [44].

3.1.2. Ion Association Systems

3.1.2.1. Anion Exchangers

It is only in the last ten years that attention has been turned to the possibility of exploiting the anion forming tendencies of the noble metals by separating them with liquid anion exchangers. They have been simultaneously studied as a method of analysis, in fundamental research into extraction mechanisms and as processing reagents.

A summary of the principle characteristics of solvent extraction processes using liquid anion exchangers for platinum metals is shown in Table 3. The anion exchangers used have involved all types of amine, quaternary ammonium compounds and extraction has almost invariably been made from solutions of chloro-complexes.

(a) Analytical Applications

Ishmori et. al. in their systematic work on the extraction of some sixty elements in hydrochloric acid solution by Primene JMT (trialkylmethylamine), Amberlite LA-1 (secondary alkylamine) and tri-iso-octylamine showed that none of the platinum metals could be considered to be quantitatively extracted by the primary amine although gold could be easily extracted at low (1-2M) hydrochloric acid concentrations in the aqueous phase.

The secondary amine was shown to have greater extraction powers although only quantitative for osmium and platinum in addition to gold [54, 55]. (A scheme for the separation of osmium by Amberlite LA-1 has been described by Meier [65]). The tertiary amine proved to be the most powerful extractant but, rhodium and iridium were still not effectively extracted and work performed later on rhodium showed that this metal was not extracted by any amine under any conditions[35]. Russian workers have come to similar conclusions that while gold palladium (II) and platinum (IV) may be quantitatively extracted rhodium (III) and iridium (III) were effectively not extracted at all [58, 60, 61]. However, it was also observed that iridium (IV) is extracted by a benzene solution of tri-n-oclylamine but that contact with the organic phase leads to partial reduction of the iridium (IV) to iridium (III) leading to a decrease of the quantity of metal extracted [47]. Work by Khattak and Magee also showed that rhodium (III) was reluctant to being extracted by tri-iso-octylamine although rhodium (III) - tin (II) complexes were amenable to a quantitative extraction [51]. A comprehensive study of extraction of ruthenium (III) by long chain amines has been made by Shanker et al. [50]. Their results show that extraction decreases in the order primary amines > secondary > tertiary amines, while within the tertiary amines, increasing chain length and decreasing branching leads to reduced extraction. Similarly extraction is increased by the use of diluents with higher dielectric constants and of a weakly basic rather than an acidic nature.

Some papers have been published on extraction of platinum metals by quaternary ammonium compounds and it has been found that these even more basic compounds give enhanced extractability [63, 64, 67]. In alkaline solutions platinum can be separated from all other metals; in weakly acidic media all the platinum metals are readily extracted and can be separated from base metals. Additionally in weakly acidic media the separation of platinum and palladium from other noble metals is possible and in strongly acidic media platinum may be separated alone.

Finally a paper by Deptula has demonstrated the antagonistic effect of di-n-butylphosphoric acid on the extraction of platinum(IV) by tri-n-octylamine from the chlorocomplex in sulphuric acid [52].

(b) Applications to Process Refining

The first attempts at applying solvent extraction techniques to the refining of platinum metals from anode slimes were made by Dolgikh and co-workers in Russia in the early 1960's. They extracted the noble metals by industrial amines from chloride solutions produced by chlorination of the slimes with chlorine gas. By use of multiple stage separation 99.9% of all precious metals in the slimes were removed and only 0.12% of all contaminants from a 6 M solution of hydrochloric acid [45, 46]. In this work primary amines were preferred to higher amines since in this case the reaction is chiefly one of inner complex amine formation whereas with tertiary amines the addition reaction is chiefly realised. The inner amine complexes obtained are extremely stable compounds which are not destroyed by mineral acids and alkalis but necessarily stripping or re-extraction of the metals is thus more difficult. A later paper has given an account of operating experience from a pilot plant using this technique [59]. As a result of this work a plant in Belgium has incorporated a solvent extraction technique in the recovery cycle of gold and platinum metals from anode slimes arising from the electrolysis of Dore metal [68].

Further work on the fundamental aspects of the reactions involved has shown the analogy of the extractions to ion-exchange resin mechanisms [56,57] and work has been extended to show the influence of other types of extractant [48] and the effect of sulphate ions in solution [62]. Shivrin et.al. have published work on the extraction refining of noble metals by quaternary ammonium compounds but difficulty was experienced due to the propensity of these highly surface active reagents to form stable emulsions. However, by careful control of conditions gold cyanide may be effectively extracted by these reagents of the type (CH_3R_3N) Cl and (R_4N) Cl [53].

In Japan Abe and Yazawa have also applied amine extractants to the separation of metals related closely to the hydrometallurgical processes and results show agreement with previous and subsequent work [66]. Finaly Ali Khan and Morris in preliminary work have shown the feasibility of tertiary amines to extract platinum metal nitrites [49].

A summary of the specific extractants used as liquid anion exchangers is given in Table 4.

3.1.2.2. Cation Exchangers

Presumably as a result of the reluctance of noble metals to form simple cationic species in solution little work has been done with liquid cation exchangers in precious metal chemistry. However, one paper by Ali Khan and Morris shows the possibility of extracting and separating rhodium by this means. They have used dinonylnaphthelenesulphonic acid to separate quasi effectively rhodium from contaminants and other platinum metals and recommend that if a barren aqueous phase scrub cycle is incorporated into the flow scheme, this process could be used to advantage in refining of rhodium from precious metal concentrates [69].

3.2. Gaseous Reduction of Platinum Metals

Some of the earliest investigations on the gaseous reduction of metals from solution were performed on the platinum group metals. During the period 1909 - 1931, the Ipatievs and co-workers studied the use of hydrogen under pressure to precipitate platinum, iridium and other metals and metal oxides from aqueous and organic solution [90]. The reactions were carried out in sealed unagitated tubes and the metallic products, when formed were frequently contaminated with stable oxides and basic salts which precipitated at the higher temperatures before the hydrogen could diffuse into solution and effect reduction. Although the products from this work were too impure for further development, the demonstrations of the feasibility of using hydrogen under pressure to effect reduction must be considered a major contribution in the development of these processes.

Later, still in the U.S.S.R., the pioneer work of the Ipatievs was continued over the period 1930 - 1948, by Tronev et. al. [91, 92, 93], primarily on the hydrogenation of aqueous salts of the precious metals and the precipitation of silver, gold, palladium, platinium, rhodium and iridium. The procedures developed enabled the platinum group metals to be separated by selective precipitation.

As a result of the literature survey on the chemistry of platinum metals and the various solvent extraction processes available it appeared that the most logical choice and the most promising system was that of the liquid anion exchangers. The theoretical aspects of amine extraction systems are given in papers published by Diamond [71] and Grinstead [72]. From these it was possible to decide upon the nature and range of process variables which were to be investigated.

4.1. Amine Extraction Systems

Let us consider the mechanism whereby amine extractants act as liquid anion exchangers and the factors which influence their extratability.

4.1.1. Formation of Anion Exchanger

The amine, which is usually dissoved in an organic diluent, is transformed into such an agent by reaction with an acid species which is introduced into the aqueous solution of the metal salts. The simplest expression that can be written for this type of reaction is:

$$R_3N_{(org)} + H_3O^+ \rightleftharpoons R_3NH^+_{(org)} + H_2O \qquad (23)$$

where a secondary or primary amine can be substituted for the tertiary amine. Although this is an oversimplification of the situation it nevertheless emphasises the base-acid nature of the reaction, the main driving force being the fact that the amine binds the proton more strongly than does a water molecule.

However, different acids show very different degrees of extraction under similar conditions and so extraction also depends on the anion. It must therefore be included in (23).How this should be done depends upon the nature of the ammonium species in the organic phase and upon the diluent. In dilute solution in the usual low dielectric constant diluent the salt becomes ion paired so (23) becomes:

$$X^- + R_3N_{(org)} + H_3O^+ \rightleftharpoons R_3NH^+.X^-_{(org)} + H_2O \qquad (24)$$

$$K_1 = \frac{[R_3NH^+X^-]_{org}}{[R_3N]_{org}\ a_{HX}} \qquad (25)$$

The ion pairing is not entirely electrostatic but may involve a weak hydrogen bond between the ammonium cation and the anion. This interaction is stronger the smaller and more basic the anion, but the ease of extraction shows just the opposite order e.g. $Cl^- < Br^- < I^- < ClO_4^-$. This is because it is the aqueous phase interactions of the ions and not the organic phase ones which dominate in determining the sequence. Water is the best anion solvating agent present, as so the ions leave the aqueous phase inversely with the order of increasing hydration.

4.1.1.1. Effect of Amine Class

When considering the extraction of a given acid under varying conditions, however, differences in the organic phase interactions readily show up. For simple acids the order of extraction by amine class is usually primary > secondary > tertiary. An explanation is that the increasing number of alkyl groups sterically hinder the approach of the anion to the ammonium hydrogen as well as cutting down the number of interacting hydrogens on the nitrogen. The cation-anion interaction is weakened for both reasons and so the extraction decreases. For the same reason the spread of selectivity among anions should be expected to increase in going from primary, secondary tertiary to quaternary ammonium salts. The cation-anion interactions partially neutralise or oppose the order of extraction dictated by the dominant aqueous phase hydration behaviour and so the latter shows its maximum effect with the quaternary salts and a minimum selectivity with the primary ammonium catrons.

4.1.1.2. Effect of Diluent

The diluent is not inert but interacts with both the amine and the ammonium salt through its functional groups (chemical properties) and with the salt through long range coulombic effects (dielectric properties).

(a) Dielectric Effects: In general the higher the dielectric constant of the diluent the better the extraction and this is understandable. A positive electrostatic free energy obstructs the transfer of ions from a medium of high dielectric constant (water) to one of lower value. An order of magnitude estimate of this term can be obtained by applying the Born charging expression to the transfer of a pair of dissociated spherical monovalent ions from water ($\epsilon_{aq} = 80$) to an organic diluent (ϵ_{org})

$$\Delta G_{aq \rightarrow org} = N_o e^2 (\tfrac{1}{2}r_+ + \tfrac{1}{2}r_-)(1/\epsilon_{org} - 1/\epsilon_{aq}) \qquad (26)$$

If the ions associate to a pair in the low dielectric constant medium the (positive) free energy of transfer is reduced by the energy of the ion pairing. With $1/\epsilon_{org} \gg 1/80$ the most favourable case is for two ions of equal radius and the value of $\Delta G_{aq \rightarrow org}$ is reduced to one-half the value for dissociated ions. So even for ion pairs the long range coulombic interactions with the diluent provide a positive free energy of transfer whose magnitude depends on the dielectric constant of the diluent. This term must of course be overbalanced by the acid-base reaction for the interaction to occur.

(b) Chemical Effects: The correlation between dielectric properties and extractability is not very vigorous however. Besides "electrostatic" solvation of the ions a short range chemical effect with the diluent must also be considered.

If the diluent is somewhat basic (e.g. aromatic compounds) there may be an interaction between it and the weakly acidic hydrogen of the ammonium cation, thus improving extractability. If on the other hand the diluent molecule is slightly acidic, one might expect it to interact with the basic extractant molecule effectively reducing the latter's concentration and so decrease the extraction. For example such behaviour is observed with the trialkyl phosphates , phospine oxides, etc. where extraction of acids is poorer in the slightly acidic diluent chloroform than in carbon tetrachloride. However, this is not true of tertiary amine extraction. For some reason the former does not react as strongly with small uncharged molecules such as chloroform as might be expected from its greater basicity. But the cholorform molecules may (hydrogen) bond with the anion of the ammonium salt, thus helping the extraction and do so more strongly the smaller and more basic the anion. For such anions, chloroform, or any other weakly acidic solvent becomes one of the best possible diluents for extraction.

4.1.1.3 *Association of Extractant* One of the most important and interesting features of amine extraction systems is the degree of association of the ammonium salt in the organic phase. The properties of the diluent, the nature of the ammonium cation and of the anion and their concentrations determine whether the salt is dissociated, ion-paired or still more highly aggregated in the organic phase. In a high dielectric constant medium such as nitrobenzene an ammonium salt with a large anion may be completely dissociated over a wide range of concentration. But with smaller anions the interionic attractions are larger and the salts, although dissociated at very low concentrations, ion-pair at higher concentrations. If the diluent has a very low dielectric constant and little chemical solvating ability, the ammonium salt may associate to still larger aggregates beyond the ion pair to ion quadrupoles thus leading to reduced extraction [73].

The degree of aggregation can also be correlated to the nature of the anion. For if the anion catron pair can hydrogen bond and thus solvate each other they will more readily form ion-pairs from the free ions but they will have less need to aggregate further. The order of this interaction is as expected from the size of the ions, $Cl^- > Br^- > I^-$ and they show the opposite tendency to aggregate beyond the ion-pair. In this respect quaternary ammonium salts which are incapable of such hydrogen bonded cation-anion interactions are more susceptible to aggregation than are tertiary ammonium salts.

this respect quaternary ammonium salts which are incapable of such hydro

However, it should be pointed out that at higher concentrations of ammonium salts in the diluent, the organic phase activity coefficients are no longer constant (i.e. > 0.1 M). The presence of such a large concentration of ions even though highly associated changes the properties of the diluent from those of, for example, cyclohexane to those of an entirely new substance which may have better extraction characteristics, despite aggregation of the extractant.

4.1.2. Ion Exchange with the Metallic Species

The ammonium salt ion-pair formed by reaction of the amine with an acid is now capable of exchanging the simple anion with a complex metallic anion, usually a halometallic complex.

$$R_3NH^+ \cdot X^- + MX^-_4 \rightleftharpoons (R_3NH^+) MX^-_4 + X^- \qquad (27)$$

The sequences of the order of extraction with these complex ions as a function of amine class, of increased branching of the amine alkyl groups and of the diluent tend to be opposite to those of the hydrohalic acids, since the latter are present and in competition with the complex metal ion, i.e. ion exchange.

4.1.2.1. Effect of Amine Class

As has already been mentioned the order of (hydrogen-bonded) interaction of Cl^- with the ammonium cation is 1RY > 2RY > 3RY > 4RY and extraction follows the same sequence. This means that a weakly interacting anion (ClO_4^- or MX_4^-) which does not depend as much on such hydrogen bonding to help its extraction as does Cl^-, will compete best with Cl^- in extraction with a 4RY anion, next best with a 3RY, and so on, yielding an order opposite to that for hydrochloric acid extraction itself.

4.1.2.2. Effect of Diluent

A similar argument holds for the inversion in extraction order between the hydro-halic acid and the(monovalent) halometallic complexes acids with change in diluent. The halide interacts more strongly with chloroform than does the larger, less basic anion, so that when both are present, the larger anion is relatively less strongly favoured and extracted than with a chemically more inert diluent such as cyclohexane. As a result chloroform is a good diluent for hydrochloric acid extraction but a poor one for the (ion exchange) extraction of halometallic complexes, while cyclohexane or the aromatic solvents have the opposite effects. Such inversions in extraction order become more marked the greater the disparity in size and basicity of the anions involved.

4.1.2.3. Role of Water

Large amines themselves do not appear to be very hydrated in the common diluents, but with most anions appreciable water is co-extracted with the ammonium salt and furthermore the presence of water increases the solubility of the salt in the diluent. The water acts as a bridge between the cation and the anion or is hydrogen bonded to the anion and varies as the need for solvation of the anion e.g. $Cl^- > Br^- > I^- > ClO_4^-$.

4.1.2.4. Excess Acid

A molecule of acid such as hydrochloric acid is a polar molecule which can hydrogen bond to an anion just as can water. Excess acid present in the system may thus solvate the anions according to their basic strength,

NO_3^- > Cl^- > Br > I^- > ClO_4^-, forming molecule-ions. The extraction of metal complex anions from aqueous hydrochloric or nitric acid solutions may be greatly influenced by the formation of these species as the latter are less easily hydrated and more readily extractable than the simple anions and so compete much better than the latter in ion exchange. Thus for a complex anion, the distribution curves from dilute hydrochloric acid solutions are almost identical to those from solutions of lithium chloride but they increasingly fall below the hydrochloric acid value as the concentration rises into the region where HCl_2^- and $H_2Cl_3^-$ can form and extract.

4.1.2.5. Basicity of Amine

Decreasing the basicity of the amine results in reduced extractability and if the amine becomes weak enough one molecule may not provide enough solvation for the proton leading to the formation of $(R_3N)_2H^+$ or even $(R_3N)_2H_3O^+$ complexes. Similarly the substitution of an aromatic group for an alkyl one in a tertiary amine causes a considerable reduction in its basicity and a marked drop in extraction, about a factor of 10^5 per aromatic group, due to steric hindrance.

4.1.2.6. Re-extraction of Metal Complexes

The amine extracts are usually amenable to one or more methods of stripping the extracted metal ions readily and into a relatively small product volume [99]. The methods include some reactions that affect mainly the extractant: hydrolysis of the (weak base)amine salt displacement by a strongly extracted stripping agent; some that affect mainly the extracted metal: change of oxidation state, dissociation of the extractable complex, competitive formation of a non-extractable complex, precipitation.

Hydrolysis of the amine salt, reversing equation(23) completely destroys its exchange capacity and strips nearly all extracted materials. Thus it is particularly useful for stripping strongly extracted solutes, for the last step of a selective stripping series, and for eliminating contaminants. Stripping by complete hydrolysis may impose a disadvantage if fresh acid and a special operation are needed to regenerate the amine salt for recycle. However, the extraction feed (leach liquor, dissolver solution, etc.) often contains excess acid for other reasons, sufficient to reform the amine salt in the last extraction stage without unduly raising the raffinate pH.

Stripping by competitive displacement can be a very simple and effective method, provided that the stripping agent can be tolerated in the extraction system as well as in the product, or can be satisfactorily removed before recycle.

Whenever a considerable degree of salting is required for extraction of a particular metal ion, water stripping should be effective for its removal. When the solute is subject to hydrolysis, a dilute acid solution (e.g. 0.01 M) is used instead of plain water. Enough acid may be automatically provided by excess acid extracted from the feed and transferred to the stripping section. When water stripping is desired in a process, only a moderately strong extractant should be used.

Formation of a non-extractable aqueous-phase complex can be used for stripping whether or not formation of a particular extractable complex is involved in the extraction. The stripping agent is not necessarily extractable. However, it is usually one of the common complex forming anions and thus may be extracted, if so, the same question of elimination or tolerance in the extraction system applies as in stripping by competitive displacement.

Sharply selective stripping can be obtained where a difference exists in the extractability of different oxidation states of a metal. Hence a metal extracted in one oxidation state may be stripped by contacting the extract with a stripping agent which reduces the metal to a lower oxidation state which is not extractable.

Finally stripping may be effected by precipitation methods either by a strip solution containing a reductant or by direct reduction from organic phase with a gas. However, these methods involve certain practical difficulties in separating solids from either one or two liquid phases.

4.1.3. Interpretation of Process Parameters

In his paper on liquid ion exchangers Hogfeldt concluded that "progress has been made in the field of amine extractions with regard to the identification of species in the organic phase. But the equilibria regulating the extraction processes are not well understood at present partly because of interfering aggregation equilibria." [73]

However the extraction of ferric thio-cyanate complexes by trinonylamine has recently been studied in order to determine to what extent extraction behaviour using this kind of solvent can be predicted from equilibrium data. It was shown that under normal conditions of iron-thiocyanate ratio the ion extracted is $Fe(SCN)^-_4$, giving a complex $(C_9H_{19})_3NH^+.Fe(SCN)^-_4$ which dissolves in the benzene-amine layer [10].

The relevant equilibrium constants are K_1 to K_4 and the important variables are the concentrations of iron and thiocyanate ions. Since the concentrations of other ions are not necessarily small, and the concentration of ferric and thiocyanate ions change during the extraction, the variation of these equilibrium constants with total ionic strength, I, must be calculated using the Debye-Huckel relationship, corrected for variation of the activity coefficients with concentration.

$$\log K^o_n = \log K_n - \frac{A \Delta z^2 \sqrt{I}}{1 + B\mathring{a} \sqrt{I}} - I \Delta C \qquad (28)$$

where K^o_n is the value of K_n at infinite dilution

A and B are fundamental constants

z is ionic charge

$\overset{o}{a}$ and C are arbritary parameters.

The values of the parameters were taken as $\overset{o}{a} = 4.5 \times 10^{-8}$, $\Delta C = 0.295$ and $B = 0.33 \times 10^{8}$, in the case of K_1. At 25°C, $A = 0.509$, $K_1^o = 1{,}070$. For K_1 the experimental data fit the equation reasonably well between $I = 0.1$ and 1.0, if $K_2 = 96.6$, $\Delta C = 0.044$, $\overset{o}{a}B = 1.5$. The few results for K_3 fit the equation

$$\log K_3 = \log K_3^o - 1.257\ I$$

with $K_3 = 32.2$. The value of K_4 is independant of I as long as the ratio of the activity coefficients of the SCN^- and $Fe(SCN)^-_4$ ions remain constant.

By using potassium nitrate solution as a base electrolyte, the total ionic strength was held constant; the pH was maintained at ~2 the actual value being measured. The equilibrium constants for the formation of iron-nitrate complexes and hydrolysis products were corrected in the same way as those for thiocyanate complexes, and it was then possible to calculate the amounts of extractable species present at any thiocyanate-iron ratio. Since only the extractable complex of iron present in any quantity of significance was $Fe(SCN)^-_4$, the extraction of ferric thiocyanate complexes may be represented as

$$R_3NH.SCN_{(org)} + Fe(SCN)^-_{4(aq)} \rightleftharpoons R_3NHFe(SCN)_{4(org)} + SCN^-_{(aq)}$$

where R is the nonyl group (C_9H_{19})

The particular partition coefficient of $Fe(SCN)^-_4$ is

$$P_4 = \frac{[R_3NHFe(SCN)_4]_{org}}{[Fe(SCN)^-_4]_{aq}}$$

and the equilibrium constant for the extraction is:

$$K_4 = \frac{[R_3NHFe(SCN)_4]_{org}[SCN^-]_{aq}}{[Fe(SCN)^-_4]_{aq}[R_3NH\ SCN]_{org}}$$

$$\text{Hence}\quad K_4 = \frac{P_4}{D_{SCN^-}} \qquad (29)$$

If it is assumed that hydrolysis and complexing by nitrate are negligible the iron distribution ratio in general is given by:

$$D_{Fe} = \frac{\sum_{n=4}^{n=6} [(R_3NH)_{n-3}\ Fe(SCN)_n]_{org}}{[Fe]_{aq}}$$

$$= \frac{\sum_{n=0}^{n=6} P_n \beta_n [Fe^{3+}][SCN^-]^n}{[Fe^{3+}] \sum_{n=0}^{n=6} \beta_n [SCN^-]^n} \qquad (30)$$

Therefore D_{Fe} should be independant of the concentration of iron. In order to predict D_{Fe} it is necessary to know the values of the equilibrium constants for formation of the complexes which give β_n, the values of K_n the way in which D_{SCN^-} varies with the concentration of free thiocyanate ions, and the free thiocyanate ion concentration itself.

It was shown that if hydrolysis and complex formation by nitrate are taken into account there was a linear relationship between D_{Fe} and the concentration of free thiocyanate ions as long as the range of concentration studied is small. However, K_4 was found to vary with the concentration of iron and it was suggested that this was due to cationic species and $Fe(SCN^-)_4$ ions in the aqueous phase forming polynuclear complexes. The value of K_4 also increased with increasing total ionic strength due to a salting-out effect.

From the above example it can be seen that even in the simplest amine extraction systems, attempt to rationalise partition data from fundamental relationships leads to a somewhat intractable result needing large amounts of fundamental data to resolve it. Any attempt to apply this approach to situations as complex as those involving the noble metals about which there is little information of this kind would be unjustifiable. The aqueous equilibria in solutions of these metals is not known with any certainty due to multiple valency states and to the co-existance in solution of several complex species in mutual equilibrium including products of hydrolysis.

Alternatively more empirical methods may be adopted such as the approach of LLoyd and Oertel [74] who have attempted to correlate extraction isotherms obtained from various liquid anion exchange processes with the aim of establishing a general mathematical relationship between the characteristics of each.

They suggested that if one assumes that there are m molecules of amine associated with each molecule of the extracted species, then the molecules involved in the complex will be equivalent to a solvent concentration of mY where Y is the organic phase molarity of the extracted species. The free solvent concentration is thus (M - mY) where M is the total solvent molarity. If it is then assumed that the solvent-metal salt complex is of constant composition at all levels less than saturation, then (M-mY) will be the free solvent concentration at all levels of the concentration of the extracted species in the organic phase.

Also it was found that in the extraction of most single species, the equilibrium isotherm, relating concentration of the extracted species in the aqueous and organic phase is one in which the distribution ratio is proportional to some power of the free solvent concentration

i.e. $$\frac{Y}{X} = E(M - mY)^n \qquad (35)$$

where: X = molarity of the extracted species in the aqueous phase

: E = extraction factor

Of particular interest since it occurs in many systems is the case where the distribution ratio Y / X is directly proportional to the free solvent concentration i.e. $n = 1$

$$\text{then } \frac{1}{X} = \frac{EM}{Y} - E\,m \tag{36}$$

The usefulness of this relationship is that a plot of 1 / X versus 1 / Y should yield a straight line of slope EM. Moreover the intercept with the 1 / X axis should be $- E\,m$ and the intercept with the 1 / Y axis should be m / M. Thus m and E may be found graphically.

The significance of the factors n, m, E, is that they can together completely satisfy the specification of the loading and extraction characteristics of any particular amine in a given system. The loading factor m will be a true measure of the saturation capacity of the amine regardless of the concentration while the extraction factor E will be constant throughout the range of concentrations of the extracted species at all amine concentrations.

From their own results and correlations with those of other workers most of whose work was found to concern systems where n = 1, Lloyd and Oertel found good agreement between the equations developed and extraction isotherms determined experimentally.

Similarly equations were developed and tested for the simultaneous extraction of two species. They assumed that the extraction and the loading factors remained constant whether one species is extracted alone or in the presence of another, and set up two equations relating the organic and aqueous phase concentrations of the two extracted species at equilibrium.

$$\frac{Y_1}{X_1} = E_1(M - Y_1m_1 - Y_2m_2)^{n_1}$$

and

$$\frac{Y_2}{X_2} = E_2(M - Y_1m_1 - Y_2m_2)^{n_2}$$

then if $n_1 = n_2$ the selectivity factor β, defined as the ratio of the distribution ratios of the two species will be constant, that is

$$\frac{Y_1}{X_1} \Big/ \frac{Y_2}{X_2} = \frac{E_1}{E_2} = \beta \qquad (37)$$

However, if $n_1 \neq n_2$ it should be noted that the selectivity factor will not be constant but will vary with the organic phase concentrations of the extracted species. In this case it may be expected that if $n_1 > n_2$ separation between species 1 and 2 will improve with increasing organic phase concentration if $E_1 > E_2$ but will decrease if $E_1 < E_2$ and vice versa. Results showed that equations give a good semi-quantitative expression to the extraction isotherms of two species extracted in the presence of each other.

Results obtained in the correlation of these equations with experimentally determined isotherms allow analytical solutions for the number of stages required in attaining optimum extraction performance.

4.2. Experimental Programme

On the basis of the theoretical aspects of amine extraction processes and knowledge of the solution chemistry of platinum group metals a preliminary experimental programme was drawn up. This was devised so that potential processes could be isolated and identified by investigation of the following process variables.

(a) Metallic valencies: the extraction of noble metals in their most probable valency states

Ru(III)
Os(IV)
Rh(III)
Ir(III),(IV)
Pd(II)
Pt(IV)
Au(III)

(b) Metal concentrations: the extraction of noble metals in a range 10^{-1}M to 10^{-4}M.

(c) Metal complexes: study of chloro-complexes in hydrochloric acid and in comparison to other common anionic ligands.

(d) Anion concentration: the extraction of noble metals from solutions of varying anionic strengths.

(e) Amine reagents: extractability of primary, secondary, tertiary amines and quaternary ammonium compounds of varying chain length.

(f) Diluents: extractability of amines in aromatic diluents and in comparison to some aliphatic diluents.

(g) Concentration of Extractant: extraction performance at varying amine loadings.

For the purposes of this work branched 2 - amino-octane and dodecane primary amines (improved phase disengagement properties over straight chain amines) di-pentyl,-octyl,and -dodecylamines, and tri-pentyl,octyl,and dodecylamines were obtained from B. Newton- Maine Ltd., (Norfolk) and tetrapentyl and tetraheptyl ammonium chloride was obtained from Kodak Ltd., (Liverpool). All amines and diluents were used without further treatment.

4.2.1. Analytical Techniques

Traditional methods may be employed for the quantitative determination of the metallic species in either phase after contacting but these have certain drawbacks. Spectrophotometric absorption techniques and polarographic methods require that the nature of the metallic species in solution remains constant. This implies precise knowledge of the types of metallic complexes present and the proportions of particular species in equilibrium under any given conditions. In the case of the noble metals this amount of control is not possible to maintain in a real situation. However, some spectrophotographic work was done on platinum metal solutions both before and after extraction and whilst in the organic phase itself in order to determine whether or not any changes were taking place in the metal species under extraction conditions.

A more effective and accurate method of determination is by means of radiochemical tracersadded to the aqueous phase before extraction. Providing the mixed labelled solution undergoes a chemical treatment to ensure that the radioactive metallic ions are of the same species and in the same equilibrium proportion as those of non-radioactive ions it is merely necessary to measure the subsequent physical dilution of the radioactive component. Investigations into the solvent extraction of platinum metals by Ali Khan and Morris [5, 44, 69], and Ishimori[35, 54, 55] were carried out using radiotracer techniques.

4.2.1.1. Radioactive Tracer Analysis

The principles of normal radioisotope tracer methods are given in various reviews [79, 80]. Solutions of the platinum metals labelled with radionuclides were made up into chemically homogeneous solutions and extraction performed until near equilibrium conditions were achieved. Having then allowed the two phases to disengage aliquots of an equal amount of each were counted under identical geometry using a γ-scintillation assembly. This comprised a NaI (Tl) 25 mm x 25 mm well-type scintillation tube and a Nuclear Enterprises SR3 ratemeter with a discrimination capability. By use of this equipment not only could individual radionuclide activities be measured under peak energy conditions but by variation of bias control, two activities due to different labelled metals present in the same solution could be measured simultaneously providing there was a significant difference in principle γ-photon energies. In this way it was possible to determine the separation factors between pairs of metals in a single solution.

All radionuclides were obtained from The Radiochemical Centre and were subjected to γ-spectrometry before use to ensure radiochemical purity. Table 5 shows the principle characteristics of the radio-tracers used to determine distribution data.

4.2.2. Experimental Procedure

4.2.2.1. Kinetics of Extraction by Amines

Before commencing the distribution studies, two kinetic factors appeared to be of importance in the liquid anion extraction of the platinum metals. The first was simply concerned with the rate of approach to equilibrium concentrations of the metal species between the organic and aqueous phases. Simple shake-up tests over varying periods of time showed that contacting for about 2 minutes would give a satisfactory approach to equilibrium. (See Fig. 2)

The second factor involved the attainment of consistant results between platinum metal aqueous solutions of different concentrations and chloride ion concentration. It was found necessary to heat the solutions, once made up, for about 30 minutes to attain equilibrium of aqueous metal solutions. To confirm this a solution of Ir (III) was made up in 6.7M HCl and extracted with a 1RY amine at intervals over a period of months. Equilibrium appeared to be obtained after 5 - 6 weeks at room temperature (see Fig. 3) indicating that the species of platinum metals take a considerable time to come to equilibrium after changes in concentration and pH.

4.2.2.2. Preparation of Iridium Solutions

As already described it was decided to use a radioisotopic tracer technique to determine the equilibrium concentrations of the metallic species in the organic and aqueous phases. In the case of iridium 1 mCi of Ir ^{192} was obtained from the Radiochemical Centre Amersham ostensibly as a chloro-complex, so it was considered quite satisfactory to spike a solution of hexachloroiridate (IV) with the tracer to obtain a labelled solution. The mixed solution was treated with chlorine gas to ensure a homogeneous solution of Ir (IV). However, upon subjecting this solution to extraction by organic solvents the radiometric results differed widely from those anticipated by visual inspection, spectrophotometry, and gravimetric analysis. γ-spectrometry showed 100% radioisotopic purity and yet various chemical and electrochemical treatments on the solution failed to effect a change. Finally bromate hydrolysis was performed followed by redissolution of the ppt of Ir $(OH)_4$ and this gave results in agreement with other analytical methods. It was therefore deduced that the tracer was not in the stated chemical form, but as a result it was decided to perform a precipitation and redissolution treatment on all labelled solutions as a general procedure to ensure homogeneity.

A 0.1 M stock solution of iridium was made up by redissolution of 10 grams of labelled $Ir(OH)_4$ containing 500 μCi of Ir ^{192} to give hexachloroiridate (IV).A .01 M solution was used to discern the effect of amine class, chain length and diluent. The optimum diluent and chain length was then fixed and the effect of variation in HCl concentration (1 - 10 M) and iridium concentration (.05 M,.01M,.002 M) determined with varying amine class. Iridium (III) chlorocomplexes were prepared by reduction of some of the stock iridium (IV) solution with silver powder and diluting as required. Similarly bromo-complexes and sulphatocomplexes were made up to examine the effect of the nature of the competing anion. Finally aqueous solutions of constant pH were prepared with varying chloride ion concentrations using NaCl and $AlCl_3$ to investigate the effect of this variable independently of acidity.

In all cases 10 mls of aqueous phase were equilibrated with 10 mls of organic phase in a separating funnel and shaken vigorously for a period of 2 minutes. Distribution ratios were then determined by measuring the radioactivity of 1 ml each of aqueous and organic phase by scintillation counting.

4.2.2.3. Preparation of Rhodium Solutions

Preparation of labelled solutions of rhodium was complicated by the need to chemically separate the Rh^{105} isotope from the ruthenium target material containing active Ru^{97}, and Ru^{103} following irradiation. In addition the short-half-life (36 hrs.) of the Rh^{105} required rapid execution of both purification and shake up tests before the radioisotope became relatively inactive. A small portion of the 5 grams of Rh needed for completion of the experimental programme was labelled with the target material containing 15 mCi of Rh^{105} as $Rh(OH)_3$, in a glove box. NaOH and NaOCl were added to the labelled precipitate and the slurry warmed. Hydrochloric acid was added and the solution boiled to distill off the contaminating ruthenium as RuO_4. γ -spectrometry showed the distillate was pure Ru^{97} and Ru^{103} but despite several attempts it proved impossible to distil off all the ruthenium from the rhodium, before significant decay had occurred.

As a result a new target was prepared and irradiated and isolation of Rh^{105} effected by the method of Kobayashi [96]. This involved production of an aqueous solution of ruthenium tetroxide as before but followed by a fast extraction of all ruthenium isotopes into carbon tetrachloride. Two shake-ups with fresh solvent were all that was required to give a raffinate containing only activity due to Rh^{105} as measured by γ-spectrometry. Aqueous solutions of Rh(III) chlorocomplexes were now made up in the same way as the previous iridium solutions and distribution data determined in a similar manner.

4.2.2.4. Preparation of Palladium Solutions

The preparation of labelled solutions was less problematic with palladium since the tracer Pd^{103} of 17 day half-life was obtained carrier free.

A small proportion of the 5 gms of palladium (as $PdCl_4^{2-}$) necessary for the programme of work was taken, as with the iridium and rhodium, and the tracer solution (1mCi) was added. The metal was precipitated with an ammoniacal hydrazine solution and the remainder of the palladium, as metal, was added. The whole precipitate was then redissolved in aqua regia and a stock solution 0.1 M in palladium (II) made up, after destruction of any remaining nitric acid. γ-spectrometry showed isotopic purity with a very low intensity peak at365 Kev and a very high intensity at 40 Kev. This latter peak is in fact due to the 57 minute $Rh^{103\,m}$ daughter of Pd^{103}. While this was obviously the most convenient activity to measure due to its intensity its utilisation imposed two restrictions. Firstly it was necessary to measure the activity of the solutions following extraction only after sufficient time had elapsed (about 10 half-lives of the daughter Rh^{103m}) so that selective separation of the rhodium might not interfere. Secondly the low energy of the γ-ray being measured would be significantly less attenuated in the organic phase, of low density, than in the aqueous phase. It was thus necessary to measure the activity of the aqueous phase before and after extraction to give a measure of the distribution ratio.

Preparation of solutions and measurement of activities was otherwise the same as that employed in iridium and rhodium extractions.

4.2.2.5. Preparation of Platinum Solutions

Solutions of labelled platinum (IV) were produced in a very similar way to those of palladium in which the bulk platinum solution and the radio tracer solution (2 mCi) were precipitated down with hydrazine and redissolved in aqua regia to give a stock solution of 0.1 M hexachloroplatinate (IV) in 1.0 M HCl. The radioisotope employed was the metastable Pt^{195m} which has a 4 day half-life and a very intense γ-ray peak at 99 Kev due solely to the isometric transition to the ground state. The use of this isotope therefore did not involve those problems encountered with Pd^{103} although measurement was again made only on aqueous solutions as the γ energy was still relatively low. Otherwise the preparations of solutions and measurements was similar to those in Ir(III), Rh(III) and Pd(II) extractions.

4.2.2.6. Preparation of Ruthenium Solutions

Preparation of labelled solutions of ruthenium (III) was effected by oxidising a Ru^{106} spiked solution of the metal chlorocomplex to ruthenium tetroxide and extracting into carbon tetrachloride from a solution just acid with dilute sulphuric acid. This was then stripped back as the chlorocomplex by contacting the organic phase with concentrated hydrochloric acid. The volume of the solution was decreased by evaporation and then made up into various concentrations of metal ions and hydrochloric acid as before.

As with the palladium extractions the γ energy of the Ru^{106} tracer was so low that distribution ratios were determined by activity measurements in the aqueous phase before and after extraction.

4.2.2.7. Preparation of Osmium Solutions

Labelled osmium (IV) solutions containing $Os^{191+185}$ tracer were produced in a very similar way to the previous ruthenium solutions by extraction of osmium tetroxide into carbon tetrachloride. However, in the case of osmium, SO_2 gas was bubbled through the hydrochloric acid strip solution to reduce the osmium (VIII) ions to osmium (IV).

Measurement of Os^{185} activity presented no problems as a high intensity peak exists at 640 Kev

4.2.2.8. Preparation of Gold Solutions

For the sake of completeness gold (III) was investigated to see how its extraction performance compared with the platinum group metal solutions of gold labelled with Au^{195} were produced by precipitation of a spiked solution of the metal with sulphur dioxide, redissolution in aqua regia, and taking up crystals of $AuCl_3$ with hydrochloric acid.

The γ-energy of Au^{195} being rather low (99Kev) activity measurements were again made on aqueous solutions before and after extraction.

4.2.2.9. Binary Solutions

(a) Palladium - Iridium Mixture

Solutions of chlorocomplexes of palladium and iridium in different proportions (10:1 and 1:10) were made up from stock solutions of Pd(II) and Ir(III) and made up to IM and 8.5 M in HCl. Extraction was performed using all four classes of amines of fixed chain length in a benzene solution. By selectively discriminating against either one or other of the characteristic γ-energy peaks, electronically, the presence of both elements was determined simultaneously without needing to resort to chemical analysis methods. It was found that under the optimum conditions for measurement of Ir^{192} activity, activity due to Pd^{103} (Rh^{103m}) was undetectable. However, 10% of activity of Ir^{192} was detected under conditions optimised for measurement of Pd^{103} (Rh^{103m}). By subtracting this activity it was considered that it would be possible to assess both the distribution ratios of iridium and palladium and hence the separation factor of the metals in the presence of each other.

(b) Platinium - Iridium Mixtures

The method used was the same as that adopted for the synthetic palladium-iridium solutions using all classes of octylamines in benzene. 10:1 and 1:10 solutions of Pt:Ir were used as before but only in 1.0 M HCl as it appeared from results of Pd - Ir separations that the iridium (III) became oxidised to the IV-state at high acid concentrations.

In the case of platinum-iridium solutions it was found again that the

was practically undetectable at the optimum measure

activity due to Pt^{195m} was practically undetectable at the optimum measurement conditions for Ir^{192}, while 19.3% of the activity of Ir^{192} measured under these conditions showed up under optimum Pt^{195m} measurement conditions. As before this amount of activity was subtracted from the platinum activity, thus to give both distribution ratios simultaneously.

4.2.2.10. Stripping and Scrubbing

Experiments were designed to test the ability of the metal complexes to strip or be scrubbed from the organic phase to determine whether or not there were any limitations to the use of certain reagents as extractants in continuous processing. The various methods examined, were hydrolysis, acid stripping and anion exchange.

4.2.3. Results and Discussion

4.2.3.1. Simple Metal Solutions

The results of distribution studies on amine extraction of platinum group metals are given in Tables 6 - 14. For convenience the solvent concentration chosen for investigation of process variables was fixed at 10% v/v in the diluent giving a molar concentration of 0.3M-0.6M, depending upon the molecular weight of the extractant. At the metal concentrations used this exceeded the anticipated stoichiometric loading capacity of the amine according to equation (27).

In the preliminary tests carried out on each metal not surprisingly it was found that the aromatic diluents gave a better extraction performance than aliphatic ones not only in terms of higher distribution ratios but also enhanced phase separation properties and a greater solubility for the metal-amine complex (no third-phase formation). Benzene was thus used as diluent for all further tests. However, the order of extraction of platinum metals with class of amine varied from that expected in theory. Where differences are small, some of this variation may be accountable for on a concentration basis i.e. amines were not all of same molar strength due to difference in molecular weight between differing classes. Nevertheless on the basis of results obtained the order of extraction of platinum metals by amines was found to be

Ir(III) - 1RY > 2RY > 3RY > 4RY
Rh(III) - 1RY > 2RY > 3RY > 4RY
Pt(IV) - 4RY > 2RY > 1RY > 3RY
Pd(II) - 2RY > 4RY > 3RY > 1RY See Figs. 4-9
Os(IV) - 1RY > 2RY > 3RY > 4RY
Ru(III) - 1RY > 2RY > 3RY > 4RY
Au(III) - 4RY > 3RY > 2RY > 1RY

Thus whilst platinum, palladium (and gold) as expected are increasingly more extracted as the degree of substitution increases; iridium (III), rhodium, osmium and ruthenium show completely the opposite trend. This may simply be a reflection of the more complex solution chemistry of the latter four metals.

The values for distribution ratios obtained under differing thermodynamic conditions may be discussed qualitatively in terms of the chemical equations derived earlier for anion-exchange reactions. Assuming that extractions of chlorocomplexes takes place according to equation (27) then,

$$n(Am)Cl + MCl_x^{n-} \rightleftharpoons (Am)_nMCl_x + nCl^-$$

where Am = RNH_3, R_2NH_2, R_3NH, or R_4N.

therefore
$$K = \frac{[(Am)_nMCl_x][Cl^-]^n}{[(Am)Cl]^n[MCl_x^{n-}]}$$

but Distribution Ratio
$$= \frac{[\text{concentration of metal}]_{org}}{[\text{concentration of metal}]_{aq}}$$

$$= \frac{[(Am)_nMCl_x]}{[MCl_x^{n-}]}$$

therefore
$$D.R. = \frac{K[(Am)Cl]^n}{[Cl^-]^n} \tag{31}$$

Thus increasing chain length of the alkyl radical (R) lowered extractability in all cases since this increased the molecular weight of the amine and therefore lowered its molar concentration. Similarly increasing chloride ion concentrations of the aqueous phase generally lowered the distribution ratios particularly in the case of platinum and palladium where the distribution ratio was lowered by about two orders of magnitude when chloride ion concentration rose by one order of magnitude (Figs. 6 and 7). This corresponds to an 'n' value of 2 which is to be expected with bivalent $PtCl_6^{2-}$ and $PdCl_4^{2-}$ ions. The corresponding value for iridium and rhodium however appeared to be only unity compared to the anticipated value of 3 when $IrCl_6^{3-}$ and $RhCl_6^{3-}$ ions are present. But this trend was only observed when iridium and rhodium were extracted by secondary and tertiary amines and quaternary ammonium chloride. When extracted by primary amines both metals showed a peak distribution ratio at about 6 - 7 M HCl which may indicate that at lower concentrations lower valent hydrated complexes, such as $RhCl_5(H_2O)^{2-}$ are present, which are less extractable (Figs. 4 and 5). Similarly ruthenium and osmium whose complexes are known to exist as lower chloride species at HCl concentrations less than 6 M showed peak distribution ratios with all classes of amines when extracted from aqueous solutions greater than 6 M in HCl (Figs. 8 and 9)

Extractions performed on both iridium (III) and platinum to determine the effect of chloride ion concentration at constant pH by use of Na Cl and $AlCl_3$ confirmed that the decrease in distribution ratios is independant of acidity as predicted in equation (31). Using NaCl results were very similar in value to those using hydrochloric acid but there was a significant increase in extraction when the chloride ion source was due to trivalent aluminium. (Figs. 4a, 7a)

Little systematic difference was noted in distribution ratios with varying metal concentration although platinum did show a surprising drop at very low concentrations (10^{-4}M). This is understandable since at the low loading of metal in organic phase in these tests the free amine concentrations was almost constant and therefore altered the equilibrium of the reaction very little. Thus at these low loadings, distribution ratio was also independant of metal concentration.

Whilst increasing concentration of extractant in the diluent increased distribution ratios systematically the order of increase in all cases except gold, was less than that anticipated. Log-log plots of concentration of 2-amino octane in benzene vs distribution ratios of all six platinum metals and gold were computed by linear regression analysis and gave "n" values shown in Table 15. These once again demonstrated the difficulty of quantifying distribution data of platinum group metals from theoretical assumptions.

Distribution data was also determined using iridium (III) solutions for extraction of alternative anionic complexes of platinum metals. Bromo-complexes for example showed higher values than chloro-complexes under comparable conditions possibly due to weaker association of the amine with simple bromide ions than chloride ions and reduced aqueous solvatability of the bromo complex. Sulphato-complexes however showed very poor extractability.

Determination of distribution data on iridium (IV) solutions had to be discontinued when it was discovered that the tetravalent ion is significantly reduced to iridium (III) during extraction thus invalidating the results. This was later confirmed by spectrophotometry. Since iridium (IV) was apparently more strongly extracted than iridium (III) attempts were made to maintain the higher state by addition of oxidising agents, but these did not prove very successful.

Finally, results indicated that platinum group metals were increasingly extracted by all amines in the order Pt/Pd > Os/Ru > Ir/Rh the heavier metal in each pair being more extractable than the lighter, indicated separation factors between each pair were high enough to suggest that under certain conditions good separation could be obtained whilst under other conditions all six metals could be extracted simultaneously.

4.2.3.2. Binary Solutions

(a) Palladium - Iridium Separation

In view of the indicated high separation factor (β) between Pd(II) and Ir(III), in low $[Cl^-]$ concentration, of about $10^2 - 10^3$ a series of extractions from mixed solutions using different classes of amines was attempted, and the results of these are shown in Table 16. As can be seen, the separation factors achieved from 1.0 M solutions of HCl are similar to those predicted from results of extraction of the individual metals. The order of increasing separation is 1RY $<$ 2RY $<$ 4RY $\leqslant$ 3RY. However, at high acid concentrations and where the amount of iridium ions are in a minority compared to the palladium ion, the iridium was extracted with an abnormally high distribution ratio. This was most notably so in the case of 2RY, 3RY and 4RY amines.

(b) Platinum - Iridium Separation

Simultaneous measurement of distribution ratios and hence separation factors (β values) of synthetic Pt(IV) - Ir(III) solutions computed similarly to Pd - Ir mixtures also showed results in good agreement with those predicted from simple solutions. (Table 17) Values increased in the order 1RY $<$ 2RY $<$ 3RY $<$ 4RY with values falling an order of magnitude between high and low concentrations of platinum. At 1.0 M HCl, quaternary heptyl-ammonium chloride gave β values of 1600 when platinum concentration was high with respect to iridium (10:1) and 145 when low (1:10), indicating the possibility of very high separation.

4.2.3.3. Stripping and Scrubbing

Various reagents were used to investigate the strippability of the metal amine complexes. The results shown in Table 18 are for primary, secondary and tertiary amines where significant extraction into the organic phase has taken place. Quaternary amine complexes were found to be effectively unstrippable.

From the results obtained it appeared that the most promising method would be by hydrolysing the amine complex by an alkaline solution such as sodium hydroxide although sodium carbonate was considered a more economic method, less severe on the solvent and has less tendency to precipitate platinum metal hydroxides or hydrated chlorides in the stripped solution.

4.2.4. Spectrophotometry

Spectrophotometry using a Unicam S.P. 800 was carried out on all platinum metal solutions to give an indication of the types of complex metal ions present and to see whether or not any changes were taking place in the metal species under extraction conditions. Spectra were taken of the aqueous phase before extraction, the raffinate after extraction, and the amine-metal chloro-complex in the organic phase. This was carried out during extraction with a primary amine (2 - dodecylamine) and a quaternary ammonium compound (tetraheptylammonium chloride).

It can be seen from Figures 10 - 21 that generally there is a shift of absorption peaks to longer wave lengths when the metal complex is in the organic phase but that the metal species remains essentially the same type of chloro-species. In all cases the raffinate also remains in the same chemical form before and after extraction except in the case of iridium IV which is reduced almost entirely to iridium(III.)

In the case of palladium (II) extraction into primary amine however, the organic metal complex has a shorter wavelength absorption peak and this fact coupled with the resistance of this complex to hydrolysis suggests that a different type of amine-metal bond may be occurring, possibly an inner orbital coordination reaction.

5. Testing of Proprietary Reagents

5.1. Systems

From the work on chemically pure reagents it was concluded that the most profitable areas of application of amine extractants to the refining of platinum group metals were likely to be as follows:

(a) Separation of platinum group metals from base metals by primary amines.

(b) Separation of Pt/Pd from Rh/Ir using tertiary amines or quaternary ammonium compounds.

(c) Separation of Rh from Ir using tertiary amines or quaternary ammonium compounds providing iridium is retained in the (IV) state.

Similarly it appeared that several criteria could be layed down about the organic extractant systems.

(a) Aromatic diluents give enhanced extraction performance over aliphatic and there is less tendency to third phase formation.

(b) Primary amine should contain as many carbon atoms as possible commensurate with high solubility in diluent, to ensure low solvent losses to aqueous phase.

(c) A long chain alcohol should be present to assist in coalescence and obviate any tendency to third phase formation.

(d) Tertiary amines were to be preferred to quaternary ammonium compounds as stripping from organic phase is easily effected.

(e) Tertiary amines need not contain more than about 24 carbon atoms to give high extraction with low solvent losses.

(f) Chloride ion concentration of aqueous feed should be about 3 - 5 M for optimum extraction of all platinum metals from base metals by primary amines and for Pt/Pd separation from Rh/Ir with minimum scrubbing of coextracted Ir/Rh

(g) High metals concentrations in feed solutions give high process efficiency but the high amine concentrations necessary to maintain high loading of organic phase must be commensurate with good phase separation behaviour and low solvent losses.

5.2. Reagents

5.2.1. Diluents

Due to the inherent health and fire hazard involved in the use of simple benzene type diluents these were considered unsuitable for use in industrial processing. Therefore attention was turned to proprietary alkyl benzenes manufactured as petroleum by-products the criteria being high flash point and low viscosity. Four of the most suitable types are shown in Table 19.

5.2.2. Amine Extractants

Choice of a suitable tertiary amine proved to be a simple one, the General Mills Co. Alamine 336 being a well tested reagent from that commany's range of amines and quaternary ammonium compounds (Table 20). Finding a suitable primary amine however proved difficult. Reagents of this type manufactured by Armour Hess Chemicals and Kraft Chemicals as flotation reagents proved to be quite unsuitable due to a strong propensity to emulsion formation. This was eventually considered to be due to their straight chain normal structure whereas the primary amines used in the screeningwork had been of the 2-amino type. Eventually two reagents produced by Rohm and Hass, Primene 81-R and Primene J-MT were adopted as they were of the branched chain tertiary carbon type with very high phase separation properties (Table 20).

5.2.3. Modifiers

Decanol was adopted as a modifier for the organic phase to ensure good phase separation and reduce the tendency to third phase formation. This was the shortest carbon chain length alcohol which is effectively insoluble on aqueous solution. Alcohols of greater chain length appeared to be less effective in coalescence. However, it appeared that using Primene and Alamine reagents, phase separation was very good even in the absence of alcohol.

5.3. Selection of Specific Solvent System

In view of the fairly wide choice of extractants and diluents available a comparative test was carried out to fix the components of the two amine systems offering the greatest potential in full-scale processing. The two primary amines Primene 81-R and Primene JMT were each made up into 10% solutions in the four diluents, BP·180, Solvesso 100, Solvesso 150, and Dobane JNX. Extraction tests were then carried out on solutions of iridium III chlorocomplex in 1.0 M hydrochloric acid. Results showed that Primene 81-R performed better than Primene JMT on a weight for weight basis although very similar mole for mole (Table 21). In view of its high flash point Solvesso 150 was selected as the best diluent although giving similar results to Solvesso 100 and B.P. 180. Dobane JNX however gave the highest extraction performance but due to its high viscosity was slow to promote phase disengagement. Therefore, despite its lower flash point, Solvesso 150 was selected.

Thus the two specific organic solvents chosen for examination were

1. PRIMENE 81-R in SOLVESSO 150 (5% decanol)
2. ALAMINE 336 in SOLVESSO 150 (10% decanol).

5.3.1. Distribution Studies

5.3.1.1. Base Metals

In view of the possibility of employing primary amines in refining of platinum metals as a group from base metals, tests were made on the extractability of common base metals Fe, Ni, Cu, Pb and Ag from chloride solutions. Solutions of the chlorides of these metals were made up in various concentrations of hydrochloric acid and distribution ratios determined gravimetrically for Cu and Ni and by radiotracer methods for Fe using Fe^{59}, for Ag using Ag^{110m} and Pb using Pb^{210}. In all concentrations of Cu and Ni up to 5M hydrochloric acid distribution ratios were less than 0.01 in Primene 81-R. The very low solubility of Pb and Ag in chloride solutions effectively obviated any need to worry about the extraction of these elements but distribution ratios of tracer levels were about 0.1 at 3M HCl. The situation with Fe (III), however, is very different. At low chloride ion concentrations the distribution ratio of Fe (III) is very low but rises very rapidly at higher concentrations (Table 22). It thus appeared that chloride ion concentration of the aqueous feed solution should be kept as low as possible to give maximum separation of platinum metals from iron. In view of the fact that the previous work shows peak extractability for Ir, Rh, Os and Ru at about 6 M HCl, solutions at a compromise concentration of 3M in hydrochloric acid appeared to be indicated.

5.3.1.2. Platinum Group Metals

Solutions of Ir(III) Ir(IV), Rh(III), Pd(II), Pt(IV), Ru (III), Os(IV) and Au(III) were prepared in exactly the same manner as the previous experimental work using the same methods for production of homogeneous radioactively labelled solutions. Distribution studies were made on metal solutions between 10^{-1}M and 10^{-4}M and the extraction isotherm plotted, for the solvent system employed.

Whilst solutions 3M in hydrochloric acid appeared to be the optimum concentration for both separation of base metals, and separation of Pt/Pd from Rh/Ir, the effect of HCl concentration was also investigated further on the proprietary reagents. Similarly the effect of reagent concentration was determined over the range 2%-20% amine in the diluent on a volume for volume basis.

5.3.2. Results and Discussion

5.3.2.1. Extraction

Results of extraction of platinum metals and gold by Primene 81-R and Alamine 336 are shown in Tables 23-28. It was found that Primene 81-R was a much less potent extractant than the primary amine 2-aminododecane used in the screening tests althoug both are of very similar molecular weight. But this was overcome by using a higher concentration (20%) of the extractant to determine a more useful equilibrium diagram. Similarly ruthenium and osmium appeared to be unsuitable to treatment by this reagent as the metal complex produced in the solvent phase was of quite a different colour from that in the aqueous phase suggesting something more than a simple ion-association complex. Stripping back from the organic phase also proved very difficult, so it was decided to discontinue at this time further work on amine processing of these two metals.

It was also discovered that, when using Primene 81-R for the primary amine extraction of rhodium and iridium (III), increasing chloride ion concentration of the aqueous feed continuously lowered the distribution ratio (Fig. 22) rather than reaching a peak value at about 6M HCl observed in the screening tests (Figs. 4, 5). Thus a more effective separation of platinum metals from base metals can be made with Primene 81-R at low chloride ion concentrations since distribution ratios of platinum metals are increasing whilst those of base metals, particularly iron, are decreasing. The equilibrium diagram shown in Fig. 23 was plotted from results obtained with an aqueous phase HCl concentration of 1.0 M.

Once again at low loading of the organic phase, distribution ratios were relatively independant of metal concentration but began to fall at high concentrations. Similarly iridium (IV) solutions showed a strong tendency to be reduced to iridium (III) in the presence of the extractant and attempts to maintain the iridium in the higher valency state which again appeared the more extractable, were not very successful.

The effect of Primene 81-R in the solvent on distribution ratios more closely agreed with that predicted by theory although iridium was again an exception. (Table 29). "n" values computed by linear regression analysis correlated fairly well with the metallic species assumed to be present in the aqueous solutions. Since most of the platinum metals showed an "n" value of about 2 significant improvement in extraction can be made by increasing Primene concentration. Thus separation factors over base metals with "n" values of less than 2, increase with increasing Primene 81-R concentration.

Distribution ratios determined from extraction of platinum metals by Alamine 336, as expected, gave results in very good agreement with those obtained with trioctylamine due to their very close chemical structure. The effect of hydrochloric acid concentration on distribution ratios shown in Fig. 24 again indicated a high separation factor between Pt/Pd and Rh/Ir. The approximate inverse square dependance of distribution ratio on chloride ion concentration supported the "n" values of around2.0 determined from the effect of Alamine concentration in the solvent phase. This suggested that no improvement in separation factors between these pairs of metals could be effected by altering the Alamine concentration, providing it was never less than the requirements of the stoichiometry of the anion-exchange equation.

Apart from platinum which again showed a slight drop in distribution ratios at low metal concentrations (although still of very high value) these two factors appeared relatively independant of each other until the loading of the amine by platinum and palladium significantly affected the free

Alamine concentration. This gave a very satisfactory equilibrium diagram (Fig. 25) for a clean mutual separation of Pt/Pd from Rh/Ir. from an aqueous solution of 3M HCl. This was supported by results of distribution data determined simultaneously on synthetic binary solutions of one metal from each pair using the γ-activity discrimination method of radio tracer scintillation counting described before (Table 30).

An attempt was made to correlate distribution data obtained from amine extraction of platinum metals to the empirical equation derived by Lloyd and Oertel to describe extraction isotherms. However in most cases the level of metal concentrations which was of interest was so low that the loading of the amine was not significant enough to cause systematic lowering of distribution ratios with increasing metal concentration in the aqueous feed solution. Similarly since "n" values had already been found to mostly approximate to a value of 2.0 this would have made calculation of extraction factor "E" and loading factor "m" in equation (35) difficult.

Nevertheless an analysis of the distribution data for the extraction of palladium by Alamine 336 was made using this method. The "n" value already determined from slope analysis of a log-log plot of amine concentration vs distribution ratio was substituted into equation (35) so that

$$\text{Distribution Ratio } \frac{Y}{X} = E(M - mY)^{2.25}$$

Thus $\sqrt[2.25]{\frac{Y}{X}}$ was plotted against Y, the equilibrium organic phase metal concentration the intercept being $\sqrt[2.25]{E.M}$ and the slope $-\sqrt[2.25]{E.m}$. Since amine concentration, M was known, E the extraction factor and hence m, the loading factor could be calculated. From the best straight line "m" was found to be 1.85, and "E" to be 700 (Fig. 26).

The equation $\frac{Y}{X} = 700\ (M - 1.85Y)^{2.25}$

was found to fit the experimentally determined isotherm fairly well which correlated with the simple anion exchange equation

$$2R_3N\ HCl + PdCl_4^{2-} \rightleftharpoons (R_3NH)_2\ PdCl_4 + 2Cl^-.$$

It may also be noted that at very low metal loadings the free amine concentration is approximately equal to the total amine concentration.

Thus $\frac{Y}{XE}$ is then constant and a maximum for any given amine concentration. Simple calculation showed that for a 10% Alamine 336 solution (0.25M) maximum distribution ratio should have a value of ~30 which was in fact the experimentally determined value at very low palladium concentrations.

5.3.2.2. Stripping

Stripping of all metal chlorocomplexes from organic solutions of Primene 81 - R and Alamine 336 was easily effected by hydrolysis of the amine the most useful stripping solution being a 0.5M Na_2CO_3 solution little tendency being shown to formation of precipitates or cruds. However, it proved impossible to strip palladium from the Primene 81 - R solutions although reduction to the metal from organic phase by hydrazine was effective. Similarly very small amounts of palladium remained in the organic solutions of Alamine 336 after stripping, although this was minimal when alcohol was absent. This may be due to the presence of 1 - 2% primary amine in the tertiary Alamine as impurity.

5.3.2.3. Scrubbing

Scrubbing of co-extracted Ir(III) and Rh(III) during separation of Ir/Rh from Pt/Pd was easily effected by aqueous hydrochloric acid of the same strength as the feed solution. This again was most effective in the absence of decanol.

6. Continuous Testing of Solvent Extraction Systems

Following the distribution data obtained from the testing of proprietary reagents two specific systems were chosen as being worthy of consideration for continuous processing, where total metal concentration did not exceed 10 g/L.

(a) Extraction of platinum metal chlorides from a dilute hydrochloric acid solution (1M) containing base metals by 20% solution of Primene 81-R.

(b) Separation of platinum and or palladium from a strong hydrochloric acid solution (3M) containing iridium and or rhodium by 10% solution of Alamine 336.

For safety reasons the diluent for the organic reagents was required to be Dobane JN-X as this had the highest flash point, and did not appear to have any effect upon the extractive power of the amines.

First, however it was necessary to have some understanding of the chemical engineering aspects of the process in order to be able to optimise the choice and operation of testing equipment.

6.1. Process Theory

6.1.1. Process Types

In principle, it might be possible to effect a reasonable purification of a rare metal in solution by a single batch extraction, if either the distribution ratio or the solvent-to-aqueous ratio were high. However a fairly high process cost would usually have been borne by the previous ore leaching or dissolution stages, etc. and this would be sufficient to justify a number of successive extractions with solvent in order to reduce the rare metal concentration in the aqueous phase to an economic reject level. It is clearly necessary to optimise the number of extractions and volume of solvent in each, so as to obtain the maximum amount of product extracted by a given total quantity of solvent [75].

(a) Multiple Batch Extraction

Assuming a solute with a constant distribution ratio, D then it can be shown that after n successive extractions

$$(C_A)_n = (C_A)_o \left[\frac{V_A}{V_A + D.V_o}\right]^n \tag{32}$$

where C_A = concentration of solute in aqueous phase

V_o = volume of solvent phase

V_A = " " aqueous "

Equation (32) shows that if the total volume of the solvent (nV_o) is constant, then the greatest reduction in concentration is obtained when it is large and V_o is small, i.e. by means of a large number of small volume extractions.

(b) Counter-Current Batch Extraction

In practice it is inconvenient to carry out a large number of successive batch extractions with fresh solvent. In counter current batch processes, portions of aqueous phase containing the solute are extracted with successive portions of organic solvent phase in such a way that the fresh solvent always extracts from the weakest aqueous phase, and the most concentrated solvent extracts from the solute rich aqueous feed. Although this type of process may be suitably improved by mechanisation of mixing, settling and separating this is rarely done since it is considerably more practical to allow the phases to flow continuously, for which there is a considerable amount of equipment available on an industrial scale.

(c) Continuous Counter-Current Extraction

Equipment for continuous counter-current extraction takes the form of vertical columns, and horizontally mounted mixer-settler extractors. In practice, although the flow to a mixer settler (or some types of columns) is continuous, true continuous counter current operation is not obtained. This type of behaviour is best classed as continuous multiple contact. True continuous counter-current operation is obtained when the two phases pass continuously in opposite directions as in a simple packed or unpacked column. As in the case of batch extraction it is possible to relate mathematically the feed concentrations to the final aqueous (or solvent) concentration in an elementary manner via the distribution ratio, the number of stages and the solvent and aqueous volumes or flow rates. Assuming both constant flow rates and distribution ratio it can be shown[100] that

$$Fa = a\frac{(1 - E^{n+1})}{1 - E} \qquad (33)$$

where Fa = initial aqueous feed concentration

a = final " raffinate "

n = number of stages

E = Extraction factor (= distribution ratio x solvent - to-aqueous flow ratio).

The extraction of a solute from an aqueous to solvent phase is often not a process which is entirely specific to one particular solute. The system is chosen so that the distribution ratio of the desired solute is fairly high, but other solutes may also have appreciable distribution ratios and thus tend to extract. In these circumstances, a scrub section is commonly employed which washes the loaded organic phase with a suitable aqueous phase, thus returning the contaminating solute back to the extract section. The effect of the scrub solution, however, must be such that it does not remove an undue amount of the desired solute. This may be determined mathematically in a similar way to that for extraction

i.e.

$$F_s = a\,\frac{(1 - S^{n+1})}{1 - S} \qquad (34)$$

where F_s = initial aqueous scrub concentration

S = scrubbing factor ($= \frac{\text{solvent-to-aqueous flow ratio}}{\text{distribution ratio}}$)

A similar approach can be made to determine the optimum conditions for stripping the desired solute back into an aqueous phase.

6.1.2. Equilibrium Diagrams

In practice the distribution ratio is rarely constant throughout the system, thus invalidating the simple methods of relating feed to extract or raffinate concentrations by calculation. Consequently extraction systems are usually designed by the graphical method of McCabe and Thiele [101].

The equilibrium diagram as shown in Fig. 27 is first drawn from distribution data and the desired flow rates which are selected on the grounds of economy compatatible with a satisfactory process. Line OC is known as the equilibrium line and is the extraction isotherm under the desired process conditions. Line AB is known as the extraction operating line where B is the initial aqueous feed concentration at E. A is the desired raffinate concentration, and the slope is the ratio of solvent to aqueous feed flow rates. Line BCD represents the extract operating line where B is the solvent concentration in the final extraction stage, D is the solvent concentration after scrubbing, and the slope is the ratio of solvent to scrub feed flow rates. The point C is known as the "pinch point" which introduces an element of stability into the system in that it absorbs extra stages and fixes a maximum solvent concentration thereby compensating for any changes in the equilibrium line caused by changes in solution composition. Stages are stepped off graphically from the solvent and aqueous exit ends of the two sections where it may be important to allow sufficient stages for a low aqueous raffinate concentration or to have a number of stages in the scrubbing section which is adequate for scrubbing back impurities, which can only be decided by referring to the equilibrium diagram for each solute.

Most solvent extraction systems have a strip section to remove the solute from the solvent phase. Here a low distribution ratio is required and this may be effected by various chemical means. Fig. 28 shows anequilibrium diagram for a strip section where the solute concentration in solvent at B is reduced to that at A.

6.1.3. Process Kinetics

The rate at which solvent extraction processes proceed is dependant upon chemical reaction rates and or mass transfer rates. In most systems, the diffusional mechanisms of solutes through phases and across phase boundaries are complicated by a chemical reaction such as solvation occurring at the phase boundary itself. Fortunately in most practical systems these reaction rates are found to be very fast compared to mass transfer rates, so they may conveniently be ignored.

The dispersion of one phase in the other as droplets during the mixing period both shortens the diffusion paths inside the two phases and increases the interfacial area. Once droplets of dispersed phase have been formed great benefits to the rate of mass transfer are also derived from the eddy diffusion effects arising from turbulence created by impellors or baffles which causes frequent coalescence and re-formation of drops. However, the decrease in droplet size below a certain level may bring disadvantages, since it might reduce the degree of internal recirculation within the droplets, would decrease the free rising velocity of the drops and would in any case demand greater power usage. There is thus an optimum droplet size for most solvent extraction systems [102].

6.1.4. Coalescence of Dispersions

In all extraction processes after contact of the liquid phases and interphase mass transfer has been completed, the phases must be separated. In multiple stage contact processes this separation has to be carried out after each stage and contributes significantly to the overall efficiency of the process.

Liquid-liquid dispersions, like all other dispersed systems, are usually thermodynamically unstable. This is because the free energy associated with the large interfacial area between the dispersed and continuous phases in these systems can decrease by aggregation or coalescence of the dispersed phase. Energetically then coalescence of a liquid dispersion would be expected particularly, in binary systems until ultimately two liquid layers had been formed. However it is the kinetics of this process which are of paramount importance in the design and operation of separation equipment. In order to promote coalescence within a dispersion turbulence within the liquid must first be suppressed so that the droplets can migrate to form a heterogeneous zone at the phase boundary between the bulk liquid phases. The rate of migration of flocculation of the droplets is determined by such properties as the density difference between the phases, continuous phase velocity and droplet size. Droplets coalesce within this zone to complete phase separation [103].

The process of coalescence is essentially one of drainage of the film of continuous phase trapped between the droplet and the "plane" liquid-liquid interface. In the absence of mass transfer the thinning of this film is caused by the action of bouyancy forces but in the presence of mass transfer, movements in the interface will result, directed either into or out of the film, thereby accelerating or retarding the draining process [104]. In the negative direction of transfer drainage will be accelerated,'rest times short' and coalescence rapid . In the case of positive direction of transfer, liquid will be drawn into the film thus retarding drainage,increasing rest times and slowing down coalescence.

Frequently coalescence is observed to be a two stage process in which there is a relatively rapid coalescence of large droplets (primary dispersion) followed by a slow coalescence of a very fine haze of droplets. Often this separation is not completed before the phases pass out of the process causing high solvent losses in aqueous raffinates and contamination by entrained aqueous phase in the solvent extract. This situation is usually avoided by operating the process organic continuous i.e. aqueous phase dispersed in organic, although it is not always practicable [105].

Whilst much work has been done recently in an attempt to quantify and predict coalescence behaviour in systems from fundamental data, results show that knowledge is still very much in the development stage and that design of equipment for phase separation must be based on observing behaviour of the system of interest under static and dynamic conditions.

6.1.5. Response Characteristics and Control of Extraction Processes.

An aspect of any solvent extraction process which is of increasing significance in the adoption of this technique in industry is process optimisation and control. In designing a solvent extraction process it is desirable first to know the effect of extraction conditions such as number of stages, feed and scrub compositions, flow ratio of solvent/feed/scrub, kinetics of mixing and settling, etc. on the yield and purity of the product [107]. As described earlier the classical McCabe-Thiele methods for the calculation of the number of theoretical stages required in a solvent extraction system employ equilibrium data and graphical analysis. However, these methods cannot cope satisfactorily for the optimisation of systems containing more than two extractable macro-components. Methods for the calculation of stage wise data for multi-component systems have thus been devised which involve "guessing" a possible set of operating conditions and interpolating the equilibrium data. A typical example of this was the method of Lloyd and Oertel described earlier [74].

However, methods of this type are very time consuming and the use of computers has considerably shortened the time required to make these calculations. Several computer programmes inspired by the nuclear power programme have been produced in the last few years and have been reviewed [106].

All the above work however concerns only the steady state behaviour of processes, that is the relationships of certain input variables and the corresponding output variables, when they are constant and do not change with time. The dynamic behaviour of processes on the other hand must also be known, as this involves the relationships between time dependant inputs and the output variables which also vary with time, such as how stage concentrations will change with time following a sudden step change in the feed concentration.

The unsteady state characteristics of processes are important in two classes of problem, viz:

(a) Start-Up Problems - in which it is desired to predict the rate at which a process proceeds to equilibrium from a given initial state, e.g. the rate at which a mixer-settler initially filled with pure solvent and solute free phases approaches equilibrium after the feeds have been put on.

(b) Control Problems - in which information is required on the open-loop response of the controlled variables in a process to uncontrolled disturbances in certain input streams, deliberate changes in load and to changes in the corrective actions which it is proposed to use in the control of the process [108]. Methods for determining the hydrodynamic behaviour of processes are usually quite simply undertaken by effecting disturbances in input feeds of a known extent on a process plant and making on-line analysis of stage concentrations and output feeds over a period of time. These results can then be related to an analysis of the behaviour on a theoretical basis, and control algorithms derived.

6.1.6. Process Economics

In considering the optimisation of solvent extraction processes these should not only be a technical success but also an economic one. As a solvent extraction process is commonly not the only way of achieving a particular separation, it is particularly important to make an accurate financial assessment of any proposed new process involving a solvent extraction stage as well as ensuring that the design of the extraction process is optimised [109].

In comparing the process involving solvent extraction with one that does not, it is important to compare the economics of the whole process and not merely the two different separation stages, which may produce products of differing purity or involve differences in other stages of the process, for example in effluent treatment requirements.

In general, the economics of solvent extraction processes are dependant upon the "up-stream" and "down-stream" portions of the plant and economic considerations may be divided into capital costs and operating costs. [110].
The factors having a significant effect on the capital cost are:

a. Number of mixer-settler stages required.
b. Settler area per stage
c. Mixer volume per stage.
d. Solvent inventory.
e. Solvent recovery equipment.
f. Ancillary equipment including pumps, pipe work, etc.

Similarly operating costs are made up of:

a. Cost of solvent loss.
b. Cost of acid/base loss.
c. Cost of power to mixing.
d. Cost of power to pumping.
e. Operating labor cost.

In addition the economics of the process are greatly affected by the extraction efficiency achieved, which determines the value of unextracted metal in the raffinate. Some of these costs are minor but although frequent stress is given to the costs due to solvent losses [114], the most significant factor is very often the cost of the chemical treatment of the solvent in stripping, scrubbing, etc. Warner [111] has indicated typical cost ranges for hydrometallurgical processes per ton of metal processed as

Capital Costs	£2 - £50
Solvent Recovery	£30 - £120
Solvent Losses	£1 - £10

Work has been carried out by several authors in an attempt to optimise processes on an economic basis. Jenson and Jeffries considered the hourly profit as a function of the cost of contactor (operating and fixed costs and depreciation) and of the solvent (recovery make up, and capital charges), the relative magnitudes of the two being functions of the solvent treatment. They give charts having contour lines, showing how the profit varies with the choice of operating parameters. From these the conditions for maximum profit for a particular application can be determined [112].

An assessment of the economic considerations in the operation of amine extraction systems has been made in comparison with other processes [113]. The economic advantages were noted that a wide choice of stripping agents is available and the final choice is dependant on cost and consumption subsequent processing steps, and the form and purity of the final product. Also it has been shown that amine extractants possess the power to maintain their activity irrespective of extractant concentration in the diluent. Herein lies an important property which allows amine extraction to be applied to both concentrated and dilute leach liquors in that the metal carrying capacity of the organic may be changed without affecting the extraction power of the amine. Since the cost/litre of solvent decreases as the extraction concentration decreases some control of organic loss is therefore possible through control of the extractant concentration as organic losses are dependant only upon the total volume of aqueous feed.

When liquors more concentrated in metal values are treated, organic losses become an almost negligible factor in processing costs. As more dilute liquors are treated, a range in metal value concentration is reached where organic losses become an important consideration. In this range it is normally advantageous to reduce extractant concentration to minimise this cost.

As the extractant concentration is lowered, the organic to aqueous flow rate ratio must be increased to compensate for the decreased metal carrying capacity of the organic phase. Obviously a point is reached where the increased organic flow rate will necessitate increased design capacity, and could completely offset the advantage of decreased solvent loss costs.

6.2. Design and Construction of Continuous Testing Plant

Visits were made to several authorites and manufacturers (British Nuclear Fuels Ltd., Leeds University, Warren Springs Laboratory and Power Gas Co.) in order to obtain advice on the choice and design of equipment.

6.2.1. Types of Contactor Available

There are three major classes of equipment available for continuous counter-current solvent extraction [20, 75, 115, 116].

a. Columns: these are simply towers in which the dense phase enters at the top and contacts the light phase rising from the bottom. Mass transfer may be effected by spraying, baffles, sieve-trays, packed porous membranes, or by rotating discs. The number of stages is determined by the height of the column.

b. Centrifugal extractors: in which the two phases enter through the axis of the centrifuge, the lighter phase emerging at the ends of the arms and contacting the heavier phase on its way to the centre, while the heavier phase emerges from the centre and contacts the lighter phase on its way to the periphery.

c. Mixer-Settlers: in which the two phases are mechanically mixed and flow to a separate settling area where they disengage. The separated phases may then flow in opposite directions to adjacent mixers, for further contacting, in their next respective stage.

By unanimous choice of all the authorities visited, the system most suitable for continuous counter-current testing was that using mixer-settler type contactors. The advantages of these are:

a. Each mixer-settler is a discrete stage and the characteristics of any process may be investigated as such.

b. Flexibility: any number of stages and configurations of extraction and stripping may be incorporated as required.

c. Operation and flow of the phases can easily be observed visually particularly if perspex is used as the structural material.

d. No interstage pumping is required as phases will flow by gravity.

e. Cheap and simple construction especially compared to centrifugal equipment.

f. Can easily handle crud formation and any unfiltered solids.

g. Failure of any one stage does not require shut down of whole plant.

6.2.2. Factors Affecting Cost and Performance of a Mixer-Settler

In order to determine the most efficient and economic design of a mixer-settler system for a given process it was necessary to consider and investigate all those factors given in 6.1.6. which affect both the capital and operating costs of the system.

In view of these, it was necessary, having established the optimum chemical and thermodynamic conditions from shake-up tests, to determine the effect on the mass transfer and phase separation operations of the following independent variables.

a. Mixer configuration

b. Agitator speed

c. Residence time in mixer

d. Phase continuity

e. Organic/Aqueous ratio

f. Specific settler flow

g. Settler configuration.

6.2.3. Choice of Equipment

It was considered that the best assessment of the above factors on the systems of interest could be made by obtaining mixer-settlers from Power Gas Corporation who have developed a standardised design for laboratory and pilot-scale testing (Plate 1). These contactors which employ a pump-mix impellor system have been developed from actual operating experience and incorporate good hydrodynamic features which allow considerable flexibility in both the type and operation of process being investigated:

a. Pump-mix impeller obviates any need for interstage pumping.

b. No back-mixing of phases, leading to high stage efficiency, due to separate mixer and settler boxes and pump-mixing.

c. Totally independent stages allow great flexibility in flow sheet development and good visual observation of process conditions.

d. Separate settler allows greater variation in settler surface area geometry critical to good settling characteristics.

e. Design of mixer box prevents air entrainment during mixing which adversely affects phase separation.

f. Settler inlet baffle maintains discrete phase boundaries in settler.

g. Variable height raffinate wier allows investigation of dispersion band thickness in settler.

h. Mixer input design allows hydrostatic pressure measurement in mixer.

6.2.4. Determination of Plant Capacity

The size and throughput capacity of the plant was dependant upon several factors. The main criterion was the fact that owing to the high intrinsic value of the metals being processed only a limited amount was available for use. The capacity of the mixer box, which determines the maximum flow rates, had therefore to be fixed at a size which would give a useful amount of data over a reasonable operating time (6 - 12 hours per run). The smallest mixer available had a capacity of 340 mls/minute and with a volume of 350 mls this meant a minimum mixing time of about one minute. Shake-up tests showed that kinetics of extraction, scrubbing and stripping were fast (see Fig. 2) and that a minimum mixing time of this length should give a satisfactory approach to equilibrium.

The size of settlers required was determined by the settling time of various mixed phases of differing composition and with either aqueous or organic phase continuous. 25 mls of each phase were mixed and the time taken for a satisfactory separation to occur (primary break time) was noted (see Table 31). On the basis of a maximum throughput of 340 mls/min a minimum settler volume of 1 - 1.5 litres was required for an organic continuous dispersion and substantially less for an aqueous continuous one. The settler available had a volume of 4 litres which could be reduced by filling with perspex blocks, so that spare capacity was available. The geometry of the settler had also been optimised in design so as to give a maximum surface area for the dispersion to settle whilst ensuring that sufficient head of separated organic and aqueous phases would be present to prevent mixed phase flowing over an outlet wier.

6.2.5. Flow Sheet Design

The design of a flow sheet and therefore the number of stages required to fully test the processes was limited due to financial reasons caused by the expense of each mixer settler unit. However the equilibrium diagrams for the two processes of interest suggested semi-quantitative separation between extractable and non-extractable solutes, requiring few stages to attain an effectively complete separation. The stripping process using dilute carbonate solution appeared to be virtually quantitative allowing a minimum of two stages in this section. Similarly two stages each of extraction and scrub for the tertiary amine separation of Pt/Pd from Rh/Ir were required as a minimum. These four stages could be then combined for the extract section in the primary amine separation of platinum metals from base metals since a scrub section did not appear to be necessary. Thus the unit comprised a total of six stages from which the process efficiency obtained was compared to that predicted theoretically from an equilibrium McCabe -Thiele diagram operating under the given conditions. It was then possible to predict the number of stages required for full pilot-trials on any process of given feed concentrations, purity, raffinate losses, etc. A flow sheet for the unit is shown in Fig. $\overset{29}{28}$ where the position of inputs and outputs can be changed according to the process being investigated.

6.3. Construction of Continuous Testing Plant

Having obtained the mixer-settler units these were now built into an integrated solvent extraction unit.

6.3.1. Materials of Construction

In view of the fact that both processes of interest involve the use of strong hydrochloric acid solutions and aromatic diluents the materials of construction were restricted as follows.

Wood for bench top, stirrer gantry, control panel, pump stands.

Glass for flow controllers, rotameter flowmeters (tantalum floats), valves (P.T.F.E. plungers), T-junctions.

Perspex for mixer settler units and impellors.

P.V.C. for all pipework

Tufnel for impellor drives to stirrer motors and wier height control screws on settlers

6.3.2. Ancilliary Equipment

In addition to the mixer settler units the following ancilliary equipment was used.

8 x 45 litre polythene reservoir tanks

6 Gallenkamp variable speed stirrer motors

12 Q.V.F. Quickfit Rotary valves with PTFE plungers

1 M.P.L. 'K'-Twin metering pump (polypropylene heads) for organic and aqueous feeds

2 Multifix variable speed peristaltic pumps for strip and scrub feeds

4 Rotameters (Tantalum floats) for metering flow rates

12 Glass float flow controllers for controlling flow of phase between adjacent mixers and settlers.

6.3.3. Plant Layout

A wooden bench standing on trestles was specially constructed on which the mixer settler units were mounted (Plate 2). This consisted of a 10 mm plywood base surrounded by 100 mm deep pine edging forming a shallow bath. A false bottom of formica was placed inside, moulded and sloping away to one end of the bench where a drain plug was placed. This made for greater cleanliness when spilling and flooding occurred and any overflow was collected and returned to the appropriate reservoir or to waste. Above the formica a wooden lattice was built on which the mixer-settler units were placed in two rows of three lengthways-on to afford easy access. Above the mixer settlers two pine gantries were built to which the stirrer motors were fixed and along which, the feed pipework was layed. All the woodwork was protected by Bosticote chemical resistant paint. A plywood control panel was constructed (Plate 3) onto which rota meters, stirrer motor speed controllers and pump switches were affixed, and below which the feed pumps were placed on a small table (Plate 4)

6.3.4. Flowsheet Flexibility

All the feed and interconnecting pipework in the plant was made in such a way that by use of the appropriate valves it would be possible to employ 2, 3 or 4 stages in the extract sections, 0, 1 or 2 stages in the scrub section and 2, 3 or 4 stages in the strip section up to a total of 6 stages (see Fig. 29). Similarly a controlled recycle of organic phase into the mixer of all stages where an aqueous phase might leave the process was incorporated. This allowed an organic continuous condition in the mixer to be maintained, to control solvent losses.

In order to be able independently to assess operating characteristics of extract and scrub sections, the outgoing aqueous scrub phase was not fed into the first extract stage, since variation in scrub flowrate would then have influenced extraction flowrate simultaneously.

6.4. Commissioning of Plant

6.4.1. Calibration of Flowmeters

Following completion of the construction work it was necessary only to calibrate the rotameters against flow rate before start-up could begin. This was effected simply by pumping the various feeds by the appropriate pump through the respective rotameters at varying pumping rates and measuring the time taken to fill a 250 ml volumetric flask. The flow rate (in mls/min) was then plotted against float height (Fig. 30). In the case of the flows from the metering pump which works by means of a deforming diaphragm, the height was taken as the maximum height of the float at the end of each pump stroke.

6.4.2. Start-Up Procedure

The plant was started up using two stages in each of the extract, scrub and strip sections and Dobane as the organic phase and water as all the aqueous phases. The settlers were filled with equal volumes of Dobane and water to speed up the start-up process, water (the heavier phase) being poured in first to prevent phases emerging at the wrong output wier. The pumps were started and controlled at a flow rate of 100 mls/min and the flow controllers positioned at approximately the height of the settler output wiers. As the phases began filling the mixer boxes, the stirrer motors were turned on slowly at first to prevent any air entrainment and then the speed increased when full until the pumping action of the impellor produced a sufficiently negative hydrostatic pressure to draw in phases from adjacent settlers. After 1-2 hours organic phase was circulating the whole plant and being returned to the feed reservoir, and similarly with aqueous feeds to the extract, scrub and strip sections. Those mixers which were running aqueous continuous due to the impellor being started-up in the aqueous phase produced very cloudy separated phases in the settlers as predicted but the dispersion band was almost non-existant indicating a very fast settling rate. Those mixers running organic continuous however produced very clean separated phases and dispersion band 30-50 mm in depth. Where the aqueous continuous condition existed the organic phase was recycled from the settler to the mixer of the same unit until an organic continuous dispersion was obtained so that all aqueous phases had minimum solvent entrainment. At flow rate ratios of unity this situation was maintained indefinitely, once the systems had achieved hydrodynamic equilibrium. When flow rate ratios were less than one in favour of the aqueous phase the intrinsic hysteresis in phase continuity changes allowed the organic continuous condition to be maintained until the ratio was 1.5 - 2.0 and then phase continuity reversal could only be avoided by continuous recycle of organic.

Having established the behaviour of the plant with diluent and water these phases were then replaced by 10% V/V solution of Alamine 336 in Dobane as the organic phase and 3M HCl solutions as the aqueous feed and scrub solutions, and a 0.5M Na_2CO_3 strip solution. Similar operating conditions were noted although the aqueous strip solution did not maintain the same clarity as the aqueous raffinate and scrub solutions, and there was a greater tendency to form a light interfacial crud in the settler. It was also noted that dispersion band depth was significantly less in the strip section than either the scrub or extract sections which agreed well with the theoretical considerations already discussed [117]. Increased impellor speed had the tendency to produce deeper dispersion bands undoubtedly as a result of the production of smaller droplets with slower coalescence rates. Increasing flow rates above a total of 300 mls/min tended to cause flooding of the mixer unless excessive stirrer speeds were used.

6.4.3. Response Characteristics

Before embarking on the experimental programme it was desirable to have some understanding of the hydrodynamics of the multistage unit so that it would be possible to estimate the time required to attain equilibrum in a process after start up or following any changes in plant operation. In order to do this, it was decided to continuously monitor variations in hydrochloric acid concentration of the raffinate solution following step wise changes in hydrochloric acid concentration of the feed solution by simple acid-base titration.

First however it was important to ensure that the take up of excess acid by Alamine 336 did not change with acid concentration of the feed. A 10% V/V solution of Alamine 336 in Dobane JN-X (0.25M) was shaken with an equal volume of varying concentrations of HCl in water for a period of one minute. The phases were separated and the aqueous raffinate was titrated against 3.0M NaOH using phenolphthalein. The concentration of HCl in the organice phase was thus calculated by difference between aqueous phase concentration before and after extraction. It was found that the amount of hydrochloric acid taken up by the organic phases remained an approximately constant 0.25M over a range of feed concentrations of 1 - 6M. (The extraction of HCl by 10% Alamine 336 in Dobane thus corresponds to a theoretical stoichimetry of 1:1; R_3N:HCl)

6.4.3.1. Response Testing

At the beginning of response testing the situation in the plant was as follows:

2 stages extraction

Feed concn.(HCl)	1.8M (by titration)
Raffinate " "	1.65 " "

2 stages scrub

Feed concn.(HCl)	2.6M " "

Raffinate concn.(HCl) 2.6M (by titration)

2 stages strip

Feed concn.(Na_2CO_3) 0.7M " "

Stripped organic " (HCl) 0.006M " ".

A dilute solution of HCl (0.9M) was then substituted as feed for the extract section and the raffinate titrated against NaOH approximately every 15 - 20 mins. Equilibrium having been attained the dilute (0.5M) HCl solution was then fed into the scrub section giving effectively a four stage extraction section and the raffinate again monitored. The variation in HCl concentration with time following these step changes can be seen in Fig. 31.

The aqueous and organic feed flow rates were approximately a constant 100 mls/min throughout and the volume of each phase held up in any stage was between 2 - 2.2 litres. Simple calculation showed that in both cases equilibrium was reattained after 2 - 3 changes of volume.

On this basis, at a nominal flow rate of 100 mls/minute and with a total plant hold-up volume of approximately 14 litres, 40 litres of feed solution would be necessary to achieve equilibrium under any given operation conditions. In view of the relatively shallow dispersion band in the settler even when operating organic continuous, it was decided to halve the settler volume by means of perspex blocks positioned on the bottom of each settler vessel. This allowed a greater utilisation of the platinum metal solutions available.

6.5. Plant Trials

6.5.1. Preparation of Solutions

a. Aqueous Solutions

Stock solutions of platinum and palladium were made up by dissolving 400 grams of each metal as chloride in 1 litre of concentrated hydrochloric acid and 200 grams each of iridium (IV) and rhodium chlorides in 1 litre of concentrated hydrochloric acid. These solutions were then added pro rata to 40 litres of the appropriate hydrochloric acid solution (1M or 3M) as required to form the feed solution in the extract section. Where iridium (III) solutions were required the stock solution of iridium (IV) was diluted 10:1 with water and reduction of iridium (IV) to iridium (III) effected by silver powder, and then the excess silver and silver chloride removed.

Stripped solutions of platinum and palladium were subjected to reduction by hydrazine and the resulting metal sponge redissolved and recycled to the stock solution. Iridium and rhodium containing raffinates and scrub solutions were bulked up to high concentration by evaporation and similarly re-cycled.

Scrub feeds were made up in 40 litre vessels of the appropriate concentration of hydrochloric acid and strip solutions similarly produced by dissolving anhydrous sodium carbonate in water to give a 0.5M solution.

b. Organic Solutions

30 litres each of 10% V/V Alamine 336 in Dobane and 20% V/V Primene 81 - R in Dobane were made up. 5% decanol was added to the Alamine solution to prevent third phase formation. The organic solutions were continuously recycled, the feed being taken from the top of the reservoir to allow aqueous entrainment to settle.

6.5.2. Operation of Plant

The operation of the plant was effected in a very similar manner to the methods adopted during commissioning trials with metal-free solutions. Aqueous feed solutions were made up to investigate the process efficiency with varying combinations of metals, flow rates, flow rate ratios, number of stages of extraction and scrubbing and to measure the solvent losses under these conditions of operations. Runs were continued until the throughput of organic phase at the flow rates being used was equal to approximately 3 times the total held-up volume of the organic phase in the plant. From a knowledge of the response characteristics determined earlier, the process was then considered to have reached equilibrium and samples were taken for analysis.

6.5.3. Sampling and Analysis

After equilibration of a run 25 mls each of the feed solution, raffinate solution, scrub solution and strip solution were removed and analysed for the constituent metals being separated, by atomic absorption analysis. Occasionally further aqueous soltions were taken from settlers of intermediate stages in a process to give an extraction profile of the whole system. Unfortunately it was not possible to obtain analysis of organic phases directly using this method.

Solvent losses were estimated by the method of Ashbrook [118]. This is a spectrophotometric method based on the formation of a complex between the amine and cobalt thiocyanate. The complex is developed in dilute sulphuric acid and extracted with carbon tetrachloride.

6.5.4. Results and Discussion

6.5.4.1. Alamine Extraction Process

The results of continuous testing of Alamine 336 for separations of Pt/Pd from Rh/Ir are shown in Tables 32--35. Both platinum and palladium were quantitatively extracted in two stages from all concentrations of feed solution. This was in good agreement with the equilibrium diagram, but neither metal showed any tendency to be scrubbed out of the organic phase. However both rhodium and iridium (III) were co-extracted to a greater extent than anticipated from their distribution ratios which indicated 6% and 15% co-extraction respectively (Equation 33). By reducing the organic:aqueous flow ratios in the extract section from 1:1 to 1:2 the co-extraction of iridium (III) and rhodium was significantly reduced without influencing the quantitative nature of platinum and palladium extraction whilst still maintaining an "organic continuous" mixing operation. Similarly, reducing the phase ratio in the scrub section effected a more effective washing out of the contaminating rhodium and iridium (III) from the organic phase. It appeared that by employing more stages in the scrub section a complete removal of these two metals from the platinum / palladium rich organic phase might be made. In addition to improving the separation factors, reducing organic to aqueous phase ratio also conferred the advantage of producing a concentration effect on the extracted metal.

However, stripping the platinum and palladium from the amine was not quite as satisfactory as had been anticipated from static tests. Palladium began to precipitate a basic complex upon prolonged existence in the 0.5M sodium carbonate strip solution and although virtually quantitative removal of palladium from the amine was effected, a serious solids problem arose which blocked the settler of the first strip stage.

Similarly stripping of platinum whilst not producing any significant precipitation of platinum metal salts also provoked a gradual build up of crud but this time apparently of an organic nature in the form of a fine transparent film which prevented complete phase separation in the settlers. This again led to serious flooding problems and had to be removed periodically to enable the process to continue. Changing the concentration of the strip solution had no effect on the production of this phase, nor did the addition of sodium chloride which it was thought might help by stabilising the existence of the chloro-complex species of platinum in the alkaline stripped solution. Samples of this interfacial crud were removed in an attempt to try and discern its nature by gas-liquid chromatography but great difficulty was experienced in its isolation. The alternative solution to this problem which would allow a continuous cycle of operations is an anion exchange stripping technique, e.g. by NO_3^- ions (providing such solutions are acceptable to downstream processes) since acid or neutral stripping has a very unfavourable distribution equilibria. This would undoubtedly involve many more strip stages of operation.

The only reported work on the application of tertiary amines for commercial processing of platinum metals describes how Alamine 336 was used to extract gold, platinum and palladium from other precious metals and base metals resulting from nitric acid treatment of slimes from Dore metal electrolysis [98]. The nature of this process was thus quite different in that co-extraction of both Rh/Ir and base metals had to be avoided simultaneously which in anion exchange systems requires contradictory conditions. Thus at high HCl concentrations base metals tend to form strongly extractable anionic complexes whilst extraction of anionic Rh/Ir complexes becomes unfavourable due to the competing chloride ions, and vice versa at low HCl concentrations. Consequently the use of very low (0.5M) HCl concentration is far from the optimum conditions for the mutual separation of Pd/Pt from Rh/Ir due to significant Rh/Ir co-extraction particularly at the high amine concentrations used (25%) due to the power factor ('n' value) on distribution ratio with amine concentration of about 2.0 for platinum metals. Since the extraction of gold, palladium and platinum is virtually quantitative under these conditions it is also surprising that the extraction of platinum is not reported as being complete when as many as six stages of extraction were used. Similarly the very low figures quoted for Rh/Ir co-extraction would not be expected from an inspection of the distribution data particularly taking into account the relatively ineffective scrub conditions (2 stages 0.5M HCl). In fact co-extraction of Rh/Ir appeared from the results of the work reported here in the continuous testing to be greater than anticipated and therefore requires very effective scrubbing by strong HCl solutions. Possibly an even higher HCl concentration in the feed solutions (say 6M when Pt/Pd extraction is still highly favourable) would achieve a nearer approach to a mutual separation of the two pairs of metals.

Finally, the reported use of xylol (flash point 65°F) cannot be recommended for commercial application due to the potential fire hazard it provides particularly when high flash point alkyl benzenes such as Dobane JN-X (flash point 252°F) proved satisfactory as diluents both chemically and physically (from the hydrodynamic point of view) in the present work.

6.5.4.2. Primene Extraction Process

The results of continuous testing of Primene 81-R for extraction of platinum metals from base metals are shown in Table 36. In these tests, iridium in the feed solution was present as iridium (IV) as this is more extractable and although partially reduced to iridium (III) by contact with the amine, since both valency states are extracted this does not alter the nature of the process. It was found that extraction of both iridium and platinum was almost quantitative with the limited number of stages available (palladium was not used due to the stripping problems already encountered with Alamine which would have made continuous operation difficult).

Rhodium however showed very poor extraction characteristics under the operating conditions. Shortage of time prevented further investigation of this aspect although increasing the number of stages, increasing organic to aqueous flow ratio, or improving the chemical conditions by lowering pH or increasing solvent concentration would undoubtedly assist in its extraction. Co-extraction of base metals was virtually non-existant giving a very clear cut separation of platinum metals.

As with the Alamine process a transparent solid film was produced in the strip section in the mixed phase emulsion which hindered complete phase separation. The nature of this phase was again difficult to resolve but appeared to be a product of the amine and the sodium carbonate solution since it was noticed in further simple shake up tests that it formed in the absence of diluent and platinum metal although the presence of the latter did aggravate the situation possibly by encouraging and trapping any fine precipitates of platinum metal salts, at the interface between the organic and aqueous phases. It was also observed that the effect was much worse when an organic contiunuous condition existed in the mixer perhaps as a result of the longer separation times. However this operating condition was much to be preferred due to the very much more effective stripping action this had. As with the Alamine process the only alternative continuous process would appear to be by anion stripping using NO_3^- ions ideally in an acidic solution to prevent hydrolysis of the platinum metal salts. However the palladium amine complex which as has already been observed appears to be a stable inner orbital complex is still singularly resistant to this form of attack. Nevertheless possibly use could be made of this to effect a primary separation of palladium from platinum by stripping back the latter and then reducing the palladium complex to metal in situ from the organic phase.

The use of Primene 81-R was found to have one very significant drawback to its use on a continuous basis. It was noted that whilst quite insoluble in neutral or slightly acid aqueous solutions, there appeared to be a strong tendency for the amine hydrochloride formed during extraction to be leached out into the raffinate solution. This occurred despite the fact that Primene 81-R possesses an alkyl radical containing more carbon atoms than the primary amines examined in the screening tests whose almost quantitative extraction of platinum, palladium and gold did not suggest the possibility of such solvent loss characteristics. However the immiscibility of alkyl chains of this length could be effectively reduced when in the form of tertiary carbons such as the case of Primene reagents. Thus whilst Primene 81-R(12-14carbons) was preferred originally to Primene JMT (18-22 carbons) because of marginally greater extractability on a weight for weight basis the latter must be substituted in any further work on continuous testing of this process, if an economical and pollution free process is to be developed.

These observations on the primary amine platinum metal extraction process revealed some anomalies in the reported Russian work [60,45,46] using nitroparaffins. Whilst the general extraction characteristics are very similar to those observed in this work their use of straight chain amines makes no mention of any emulsion problems which were encountered when early attempts to isolate a suitable commercial reagent used almost identical compounds. Similarly no mention is made of solvent losses into process streams despite the use of amines having almost identical chain lengths to Primene 81-R whose hydrochloride was found to be strongly leached out into the raffinate. Additionally no mention was made of the stripping techniques investigated or adopted.

6.5.4.3. Amine Stability

Solutions of Alamine 336 and Primene 81-R in Dobane were kept in continuous contact for several months with aqueous hydrochloric acid and sodium carbonate solutions and samples removed periodically to investigate the chemical stability of the amines under the process conditions. Both N.M.R. and I.R. spectrophotometry failed to reveal any breakdown of the reagents although there was a visible tendency for the amines to become golden brown in colour particularly when in contact with alkaline solutions. Similarly samples of the organic process streams were removed after continuous operation of the testing rig following many cycles of extraction and stripping and their I.R. spectra compared to those of the unused solvent. Whilst Alamine 336 again revealed no evidence of any breakdown (Fig. 34), it was here that the leaching of the hydrochloride of Primene 81-R was noted since there was a severe diminution of the characteristic amine peaks at A (3200-3600 cm^{-1} -N-H stretching), B (1600 cm^{-1} N-H bond), and C (650-900 cm^{-1} N-H bond) (Fig. 35). It was by examination of these spectra and from volume changes during shake up tests that an estimate of the solvent loss was made.

6.5.4.4. Solvent Losses

Figures for typical solvent losses for both the Alamine and Primene processes are shown in Table 37. All these results refer to organic continuous processes as this produced far clearer separated phases with significantly less organic entrainment. This is possibly a surface tension effect, in which a liquid of high surface tension (i.e. aqueous solution) dispersed in one of low surface tension (i.e. organic solution) has both a lower tendency to produce very fine droplets having poor buoyancy characteristics, and a greater tendency for dispersed droplets to coalesce, but this is a phenomenon which is not well understood at present.

The method of Ashbrook [118] was found only to be applicable to the estimation of the losses of Alamine 336. Here it will be noted that the solvent losses are of such a low order of magnitude that they would have little significance upon the overall economics of the tertiary amine process.

It proved very difficult to find a simple method for the direct analysis of the loss of Primene 81-R into the raffinate but as this appeared to be substantial (due to the leaching of the amine hydrochloride) it was indirectly estimated to be of the order of 10-20,000 ppm. As already mentioned this is excessively high and Primene JMT for which solvent losses were estimated to be only of the order of a few hundred ppm would appear to be the preferred extractant.

7. General Discussion and Conclusions

The major part of this work has attempted for the first time to make a systematic investigation of the application of amine extraction processes to the platinum group metals. Most of the previous work reported on this subject was found to be orientated towards specific analytical separations or investigations into the nature of inorganic co-ordination complexes rather than towards gaining an overall picture of the characteristics of liquid anion exchange of this group of metals when using amine type extractants.

Generally it was found that the platinum metals as a whole behaved in a way which correlated closely with the true anion exchange process described in equation (27). Whilst most of this work was confined to acid chloride solutions due to the requirements of upstream refinery operations, the effect of metal concentration, amine concentration in the diluent chloride ion concentration and pH showed approximate quantitative agreement with the stoichiometric requirements of the classical anion exchange equation. The exceptions to these general observations were (a) the anomalous behaviour of 2-amino alkyl primary amine (as compared to the normal primary amine, Primene) which showed a peak extraction of rhodium and iridium at around 6M HCl concentration: (b) the very low 'n' values that 2-amino alkyl primary amines gave with all platinum metals: (c) the maximum extractability of osmium and ruthenium above 6M HCl which correlated well with the known tendency for these metals to become totally anionic above this point: (d) the stability of the primary amine complex of palladium evidenced by resistance to stripping and its spectroscopy suggesting the formation of an inner orbital complex.

As expected aromatic diluents were found to enhance the performance of the amine extractants whilst increasing alkyl chain length reduced their extractive power. The fact that 'n' values of n-primary amine (Primene 81-R) and n-tertiary amine (Alamine 336) were approximately of the order of 2.0

showed that unlike many liquid anion exchange processes where $n \simeq 1.0$ the extractive power of amines varies with concentration. The order of extraction with substitution of the amine with the exception of platinum and palladium was found to be at variance with the theoretical predictions however.

The suggested application of amine extraction of platinum metals to industrial refining required several other criteria to be met particularly with regard to satisfactory reagent compatability in continuous mixing and separation operations and a suitable technique for removing the metal ions from the organic phase. Hence the use of commercial straight chain primary amines which have a relatively high extractability for all platinum metals over base metals could not be adopted due to the strong tendency for emulsion formation with hydrochloride solutions. Thus the weaker tertiary carbon primary amines ideally with at least 20 carbon atoms (such as Primene JMT) to avoid losses due to leaching of the hydrochloride were found to be of much more practical importance. Similarly re-extraction or stripping by neutral or very strong HCl solutions from amine metal complexes was not practicable due to the unfavourable distribution equilibria under these conditions. The application of hydrolysis stripping, whilst appearing to offer a quantitative removal of the metals from the organic phase was found to have severe drawbacks when in continuous operation and its use cannot be recommended. It thus appeared that anion exchange stripping, by for example NO_3^- ions, although by no means quantitative may be the only solution to the problem of a suitable continuous strip operation other than by gaseous reduction to the metal in situ in the organic phase.

However, the extraction and scrub cycles of operation were found to operate technically very well and at high HCl concentrations Pt/Pd and Ir/Rh may be mutually separated with very few stages of operation whilst at low HCl concentrations all platinum metals may be very clearly separated from base metals providing sufficient stages of extraction are available to ensure complete extraction of the weakly extracted rhodium ions.

A brief examination of the economics of the processes showed the relative importance and magnitude of the three major factors of capital costs, operating costs and solvent losses to be very similar to those given by Warner. In the present work it was calculated that for a plant using 15 - 18 stages in the primary amine process operating continuously at flow rates of 1 litre/minute at metal concentration of 10 g/l the approximate costs including solution make up and with a 5 - 10 years amortization of capital costs were estimated to be:

Capital Costs - £3 / Kg metal processed
Solvent Recovery - £1 -£2 / Kg metal processed
Solvent Losses - 1p / Kg metal processed

for the tertiary amine process using 10 - 12 stages and operating under similar conditions:

Capital Costs - £2 /Kg metal processed
Solvent Recovery - £2 - £3 /Kg metal processed
Solvent Losses 1p / Kg metal processed

In conclusion it is suggested that:

(a) Further work be done to establish a more satisfactory stripping process using anion exchange.

(b) Subsequently that a pilot plant be built designed for use with actual refinery feed liquors using Alamine 336 and Primene JMT as extractants.

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Extractant	Diluent	Separated Metals	Impurity Metals	Aqueous Phase	Acid pH/M	Common ion	Reference No.
Isobutyl Methylketone	–	Pd	Nb, Zr	$(PdI_4)^{2-}$	H_2SO_4 20%	KI:Pd 4:1	29
Octanone	–	Os	Other Nobles	Thiocyanate	HCl 1.0 M	NaSCN	26
Isopropyl Ether	–	Au	Fe and Other Nobles	Chloro-Aurate	HBr 2.0 M	–	32
Ethers, + (TBP + TOPO)	Various	Ru	–	$(SO_4)^{2-}$ Complex	H_2SO_4 or HCl	–	35
Dibutyl Carbitol	–	Au	Other Nobles	Chloro-Aurate	HCl 4.0 M	–	5
Tri-Phenyl Phosphine	Cyclo-Hexane	Pd	Other Nobles	Complex Halide	–	Iodide	28
Tri-n-Octyl Phosphine Ox.	n-Hexane	Ru	–	Nitrate Complex	–	–	39
Tri-n-Octyl Phosphine	Toluene	Noble Metals	–	Chloride or nitrate	HCl and HNO_3		36
T.B.P.	–	Binary mixtures of Pd,Pt,Rh,Ir from each other		Thio-cyanate	HCl 1.0 M	KSCN	27
T.B.P. + Amylacetate	Benzene	Pt,Pd,Ir Rh	–	Complex Bromides	HBr 4.4 M	–	33
T.B.P.	–	Rh and Ir	–	Complex Chloride	HCl	NaCl	34
T.B.P.	–	Noble Metals	Noble Metals	Chloro-Complexes	HCl	NaCl	41
T.B.P.	Hexane	Noble Metals	Noble Metals	Complex Halides	HCl 6.0 N	–	30
T.B.P.	–	Noble Metals	–	Nitrate Complexes	HNO_3	Nitrate	42
T.B.P.	Various	Os	–	Chloro-Complex	HCl + HBr	–	40
Mesityl Oxide	–	Pt (IV) + Pd (II)	–	$PdCl_4^{2-}$ + Chloro complex	HCl 5.6 M	2.3 M $AlCl_3$	31
Amyl Alcohol							38
Kerosene	–	Pt + Pd	Pd + Pt	Complex Chloride	HCl	–	37

SOLVATING SYSTEMS

INVESTIGATED

ON

PLATINUM GROUP METALS

TABLE 2

Extractant	Diluent	Separated Metals	Impurity Metals	Aqueous Phase	Acid pH/M	Common ion	Reference No.
Carbon Tetrachloride	-	Ru(VIII)	-	Tetroxide	-	Alkali Metal Salts	43
Carbon Tetrachloride	-	Ru(VIII)	Os and Others	Tetroxide	-	-	44

Physical Dissolution Systems Investigated on Platinum Group Metals

TABLE 3

Extractant	Diluent	Separated Metals	Impurity Metals	Aqueous Phase	Acid pH/M	Common ion	Reference No.
Primary Amines	Xylene	Noble Metals	-	Chloride Complexes	HCl Various	-	54
Tri-n-Octylamine	Xylene	Noble Metals	-	Chloride Complexes	HCl Various	-	55
Amberlite LA-1	Chloroform	Os	-	Chloride Complex	HCl	-	65
Various Amines	Xylene	Rh	-	$(SO_4)^{2-}$ or Cl^- Complexes	H_2SO_4+ HCl	-	35
Tri-n-Octylamine	-	Pt, Rh	-	Chloride Complexes	HCl Various	-	58
Primary Amines	-	Noble Metals	-	Chloride Complexes	HCl Various	-	60
Aliphatic Amines			-	Chloride Complexes	HCl Various	-	61
Tri-n-Octylamine	Benzene	Rh, Ir	-	Chloride Complexes	HCl 6 M	-	47
Tri-n-Octylamine	Benzene	Rh(III) Pt(IV),Pd(II)	-	Chloride Complexes	HCl	-	51
Tertiary Amines	Various	Ru III	-	Sulphato Complexes	H_2SO_4	-	50
Quaternary Amines	-	Noble Metals	-	Chloride Complexes	HCl	-	63
Alkyl Amines	Various	Noble Metals	-	Chloride Complexes	HCl	LiCl	64
Tetraoctyl Ammonium Br	Toluene	Noble	-	Halide Complexes	HCl	-	67
Tri Octyl Amine	Benzene	Pt(IV)	-	Chloride Complex	H_2SO_4	-	52
Aliphatic Amines	Kerosene	Noble Metals	Ni, Fe, Cu	Chloride Complexes	HCl 2.0	-	45
Aliphatic Amines	Kerosene	Noble Metals	Non-Ferrous	Chloride Complexes	HCl	-	46
Primary Amines	Kerosene	Noble Metals	Ni, Fe, Cu	Chloride Complexes	HCl	-	59
Alamine 336	Xylol	Pt, Pd	Cu, Te, Bi, Pb	Chloride Complexes	HCl	-	68

(Continued)

Extractant	Diluent	Separated Metals	Impurity Metals	Aqueous Phase	Acid pH/M	Common ion	Reference No.
Primary Amines	–	Ir(IV)	–	Chloride Complexes	HCl	Various	56
Dimethyl dialkyl Ammonium Cl	–	Pt(IV)	–	Chloride Complexes	HCl Various	–	57
Quaternary Amines	–	Noble Metals	–	Chloride Complexes	H_2SO_4	–	62
Tri-Iso-Butylamine	–	Pt,Pd, Ir	Rh	Chloride Complex	HCl	–	48
Quaternary Amines	Decyl Alcohol Tetradecane	Au,Ag	–	Cyanide Complexes	8-9	–	53
Various Amines	Kerosene	Pt Pd Rh	–	Halide Complexes	HCl + HBr	–	66
Tri-n-Octylamine	Toluene	Pd,Pt,Ru	Rh Ir	Nitrito Complexes	HCl 7	$NaNO_2$	49

Anion Exchange Systems Investigated on Platinum Group Metals

TABLE A

Primary Amines	Secondary Amines	Tertiary Amines	Quaternary Ammonium Compounds
ANP-1 (Russian)	Amberlite LA-1 (1)	Tri-n-Butylamine	Trialkylmethyl –
ANP-2 (Russian)	Amberlite LA-2 (1)	Tri-iso-Butylamine	Dialkyldimethyl-
Primene J.M.T. (1)	Di-n-Octylamine	Tri-n-Hexylamine	Trialkyl Benzyl –
Aminated Alcohols	Di-n-Decylamine	Tri-n-Octylamine	Dialklmethylbenzyl
4-Aminooctane	Dibenzylamine	Tri-iso-Octylamine	Alkyldimethylbenzyl
		Tri-n-Nonylamine Tri-n-Dodecylamine N-Alkyl Dimethyl Amine	Octyldimethylbenzyl Tetraoctyl Aliquat 336 (2)
		Cyclohexyldidodecyl Amine	
		Adogen 381 (2)	
		Adogen 364 (2)	
		Alamine 336 (2)	

(1) Rohm and Hass Ltd., Trade name

(2) General Mills Co. Ltd., Trade name.

Amines Employed in Solvent Extraction of Platinum Metals

TABLE 5

Element	Isotope	Half-life	Principle γ-Energies MeV
Ruthenium	106	1 year	0.51, 0.62 (from Rh 106)
Osmium	185	94 days	0.65
Rhodium	105	36 hours	0.321, 0.308
Iridium	192	74 days	0.30, 0.31, 0.47
Palladium	103	17 days	0.040 (from Rh 103m)
Platinum	195 m	4 days	0.099
Gold	195	192 days	0.099
Iron	59	45 days	1.1, 1.3
Lead	210	22 years	0.047
Silver	110 m	253 days	0.66, 0.90, 1.38

Radioisotopes
used in
Distribution Studies
of
Amine Extraction
of
Platinum Metals

Distribution Ratios Determined for Iridium Chlorocomplex.

Amine		Diluent		
Class	Chain Length	Benzene	Toluene	Cyclohexane
1RY	Octyl	12.6	11.0	7.9 (3rd Phase)
	Dodecyl	13.0	10.6	9.4
2 RY	Pentyl	1.99	1.49	1.77 (3rd Phase)
	Octyl	1.17	0.86	1.08
	Dodecyl	0.07	0.07	0.15
3 RY	Pentyl	0.21	0.20	0.34 (3rd Phase)
	Octyl	0.13	0.08	0.17
	Dodecyl	0.05	0.04	0.07
4 RY	Pentyl	0.10	0.10	0.11 (3rd Phase)
	Heptyl	0.11	0.09	0.04

Table 6(a) Aqueous phase - 0.01M Ir(III) in 3.5M HCl; organic phase - 10% V/V.

Amine	Metal Conc.	HCl Concentration (Moles/Litre)				
Class	Moles/Litre	1.2	2.4	4.6	6.9	9.2
1 RY	5×10^{-2}	2.5	5.1	12.2	15.2	5.4
	10^{-2}	2.4	4.6	9.3	11.0	3.2
	2×10^{-3}	3.0	7.0	11.0	14.7	3.4
2 RY	5×10^{-2}	0.69	0.60	0.33	0.13	0.08
	10^{-2}	0.68	0.70	0.39	0.14	0.05
	2×10^{-3}	0.69	0.72	0.77	0.19	0.07
3 RY	5×10^{-2}	0.24	0.09	0.03	0.02	0.01
	10^{-2}	0.12	0.07	0.03	0.02	0.01
	2×10^{-3}	0.11	0.07	0.04	0.02	0.01
4 RY	5×10^{-2}	0.08	0.05	0.04	0.03	0.01
	10^{-2}	0.05	0.06	0.03	0.02	0.01
	2×10^{-3}	0.05	0.07	0.04	0.02	0.01

Table 6(b). Aqueous phase - Ir (III) ; organic phase - 10% V/V octylamines in Benzene.

Solvent Concentration	Distribution Ratio
5% V/V	17.3
10% V/V	23.0
15% V/V	27.1
20% V/V	31.7
25% V/V	34.7

Table 6 (c) Aqueous phase - 0.01M Ir (III) in 3.5M HCl ; organic phase 2-aminooctane in bebzene

TABLE 6 (Continued)

Amine Class	Metal Conc.	$[Cl^-]$ Concentration due to NaCl				
		0.1M	1.1M	2.1M	3.1M	4.1M
1 RY	.01M	1.90	2.33	3.40	6.00	8.53
3 RY	.01M	0.062	0.08	0.06	0.05	0.04

Amine Class	Metal Conc.	$[Cl^-]$ Concentration due to $AlCl_3$				
		0.1M	1.3M	2.5M	3.7M	4.9M
1RY	.01M	1.78	3.18	5.75	14.10	23.30
3RY	.01M	0.067	0.12	0.06	0.05	0.04

Table 6 (d). Effect of chloride ion concentration on distribution independent of pH. Aqueous phase - 0.01M Ir (III) in 0.1M HCl; organic phase - 10% V/V octylamines in benzene.

TABLE 7

Distribution Ratios Determined for Iridium Bromocomplex

Amine Class	Metal Concentration M	HBr Concentration				
		0.8M	2.0M	3.2M	4.4M	5.6M
1 RY	5×10^{-2}	30.0	18.7	15.9	11.5	10.0
	10^{-2}	59.0	67.0	21.0	8.3	3.2
3 RY	5×10^{-2}	0.24	0.05	0.03	0.02	0.02
	10^{-2}	0.33	0.04	0.02	0.01	0.01

Aqueous phase - 0.01M Ir (III) in HBr: organic phase - 10% V/V dodecylamines in benzene.

TABLE 8

Distribution Ratios Determined for Iridium Sulphatocomplex

Amine Class	Metal Concentration	H_2SO_4 Concentration				
		3.6M	7.2M	10.8M	14.4M	18.0M
1 RY	.01M	1.4	0.40	0.19	0.08	0.03
3 RY		0.03	0.01	0.02	0.01	0.01

Aqueous phase - 0.01M Ir (III) in H_2SO_4; organic phase - 10% V/V dodecylamines in benzene.

Distribution Ratios Determined for Rhodium Chlorocomplex

Amine		Diluent
Class	Chain Length	Benzene
1 RY	Octyl	1.65
	Dodecyl	2.10
2 RY	Pentyl	0.51
	Octyl	0.44
	Dodecyl	0.04
3 RY	Pentyl	0.12
	Octyl	0.08
	Dodecyl	0.04
4 RY	Pentyl	0.16
	Heptyl	0.03

Table 9 (a) Aqueous phase - 0.01M Rh (III) in 3.5M HCl
Organic Phase -- 10% V/V

Amine Class	Metal Conc'n (Moles/Litre)	HCl Concentration (Moles/Litre)				
		1.2	2.3	4.5	6.7	9.1
1 RY	5×10^{-2}	2.4	1.90	5.35	6.43	4.11
	10^{-2}	1.33	1.85	3.89	5.18	3.60
	2×10^{-3}	0.34	1.57	2.08	2.50	2.60
2 RY	5×10^{-2}	0.78	0.72	0.74	0.27	0.09
	10^{-2}	0.37	0.44	0.41	0.18	0.01
	2×10^{-3}	0.31	0.35	0.27	0.22	0.05
3 RY	5×10^{-2}	0.43	0.23	0.09	0.03	0.01
	10^{-2}	0.12	0.09	0.05	0.02	0.02
	2×10^{-3}	0.11	0.09	0.05	0.03	0.01
4 RY	5×10^{-2}	0.29	0.22	0.09	0.05	0.01
	10^{-2}	0.08	0.09	0.11	0.03	0.01
	2×10^{-3}	0.05	0.05	0.04	0.02	0.01

Table 9 (b) Aqueous Phase - Rh (III)
Organic Phase - 10% V/V Octylamines in Benzene

Solvent Concentration	Distribution Ratio
5% V/V	1.50
10% V/V	2.52
15% V/V	3.68
20% V/V	4.00
25% V/V	4.61

Table 9 (c) Aqueous Phase - 0.01M Rh (III) in 3.5M HCl
Organic Phase - 2-aminooctane in benzene.

Distribution Ratios Determined for Palladium Chlorocomplex

Amine		Diluent		
Class	Chain Length	Benzene	Toluene	Kerosene
1 RY	Octyl	12.8	8.9	5 (3rd Phase)
	Dodecyl	12.9	9.5	5.2
2 RY	Pentyl	141	86.5	22 (3rd Phase)
	Octyl	49.1	52.7	19.3
	Dodecyl	11.8	2.68	1.01
3 RY	Pentyl	50.1	29.3	24 (3rd Phase)
	Octyl	16.5	17.0	12.3
	Dodecyl	16.3	5.5	5.7
4 RY	Pentyl	62.1	56.5	13 (3rd Phase)
	Heptyl	32.2	45.8	11 (3rd Phase)

Table 10 (a) Aqueous Phase - 0.01M Pd(II) in 3.5M HCl
Organic Phase - 10% V/V

Amine	Metal Conc'n	HCl Concentration (Moles/Litre)				
Class	(Moles/Litre)	1.1M	2.2M	4.4M	6.7M	9.1M
1RY	5×10^{-2}	101	25.8	9.4	5.8	5.45
	2×10^{-3}	100	32.1	12.5	6.2	3.8
	10^{-4}	100	36.5	15.1	6.34	2.62
2 RY	5×10^{-2}	>1000	72	17.6	7.65	5.35
	2×10^{-3}	493	55	21.5	10.0	6.4
	10^{-4}	555	146	40.5	11.72	7.19
3 RY	5×10^{-2}	117	16.4	5.0	2.90	2.51
	2×10^{-3}	125	32.0	15.5	3.5	2.4
	10^{-4}	108	85.0	17.5	5.8	2.22
4 RY	5×10^{-2}	240	41.5	13.8	5.35	2.55
	5×10^{-3}	380	47.5	18.1	2.64	0.53
	10^{-4}	242	45	20.5	7.25	0.88

Table 10 (b) Aqueous Phase - Pd (II)
Organic Phase - 10% V/V Octylamines in benzene

Solvent Concentration	Distribution Ratio
5% V/V	3.41
10% V/V	7.76
15% V/V	12.75
20% V/V	19.85
25% V/V	23.50

Table 10 (c) Aqueous Phase - 0.01M Pd (II) in 4.5M HCl
Organic Phase - 2 aminooctane in benzene

Distribution Ratios Determined for Platinum Chlorocomplex

Amine		Diluent
Class	Chain Length	Benzene
1 RY	Octyl	49.5
	Dodecyl	67.0
2 RY	Pentyl	69.5
	Octyl	58.5
	Dodecyl	46.3
3 RY	Pentyl	238.0
	Octyl	67
	Dodecyl	38.8
4 RY	Pentyl	527.0
	Heptyl	182.2

Table 11 (a) Aqueous Phase - 0.01M Pt (IV) in 3.5M HCl
Organic Phase - 10% V/V

Amine Class	Metal Conc'n (Moles/Litre)	HCl Concentration (Moles/Litre)				
		1.1	2.2	4.4	6.6	9.0
1 RY	5×10^{-2}	115	85	40.7	28.8	19.3
	2×10^{-3}	88.0	69.3	43.5	29.1	12.8
	1×10^{-4}	10.75	8.52	4.48	2.60	1.13
2 RY	5×10^{-2}	144	94.0	46.0	31.8	22.8
	2×10^{-3}	87.0	82.7	71.0	54.1	37.8
	1×10^{-4}	22.7	8.55	9.8	7.15	5.15
3 RY	5×10^{-2}	99.5	61.3	24.4	18.8	11.1
	2×10^{-3}	92.1	40.4	53.5	36.2	11.0
	1×10^{-4}	20.1	19.1	8.7	5.56	8.75
4 RY	5×10^{-2}	471	350	171	47.8	13.0
	2×10^{-3}	450	315	149	61.1	10.4
	1×10^{-4}	95.1	88.7	46.9	30.1	7.35

Table 11 (b) Aqueous Phase - Pt (IV)
Organic Phase - 10% V/V Octylamines in benzene

Solvent Concentration	Distribution Ratio
5% V/V	25.5
10% V/V	55.5
15% V/V	84.5
20% V/V	95.5
25% V/V	114

Table 11 (c) Aqueous Phase - 0.01M Pt (IV) in 3.5M HCl
Organic Phase - 2--aminooctane in benzene

TABLE 11 (Continued)

Cl^- ion Source	Metal Concn.	$[Cl^-]$ Concentration				
		0.1M	1.1M	2.2M	3.1M	4.1M
NaCl	0.01M	370	154	139	87.5	72.5

Cl^- ion Source	Metal Concn.	$[Cl^-]$ Concentration				
		0.1M	1.3M	2.5M	3.7M	4.9M
$AlCl_3$	0.01M	392	132	126	166	154

Table 11 (d) Effect of chloride ion concentrations on distribution independent of pH. Aqueous phase - Pt (IV) in 0.1M HCl; organic phase - 10% V/V trioctylamine in benzene

Distribution Ratios Determined for Ruthenium Chlorocomplex

Amine		Diluent		
Class	Chain Length	Benzene	Toluene	Carbon Tetrachloride
1 RY	Octyl	8.15	9.73	8.90
	Dodecyl	8.75	9.85	11.70
2 RY	Pentyl	3.14	4.05	4.31
	Octyl	1.81	1.96	1.47
	Dodecyl	0.37	0.31	0.39
3 RY	Pentyl	2.49	2.64	0.87
	Octyl	0.72	0.31	0.09
	Dodecyl	0.17	0.26	0.06
4 RY	Pentyl	2.99	2.04	0.62
	Heptyl	0.99	0.83	0.33

Table 12 (a) Aqueous Phase - 0.005M Rh (III) in 3.5M HCl

Organic Phase - 10% V/V

Amine Class	Metal Conc'n (Moles/Litre)	HCl Concentration (Moles/Litre)				
		1.1	2.3	4.5	6.7	9.1
1 RY	2.5×10^{-2}	2.05	4.93	9.23	31.5	13.5
	2.5×10^{-3}	1.74	3.36	13.10	38.4	9.60
	2.5×10^{-4}	1.43	3.27	9.90	47.0	7.22
2 RY	2.5×10^{-2}	0.54	1.04	2.02	1.56	1.08
	2.5×10^{-3}	0.39	1.22	2.81	1.83	0.70
	2.5×10^{-4}	0.50	0.73	2.52	1.69	0.26
3 RY	2.5×10^{-2}	0.23	0.48	0.35	0.32	0.50
	2.5×10^{-3}	0.21	0.69	0.50	0.21	0.33
	2.5×10^{-4}	0.37	0.35	0.70	0.16	0.07
4 RY	2.5×10^{-2}	0.37	0.80	0.35	0.16	0.47
	2.5×10^{-3}	0.69	1.01	0.47	0.15	0.08
	2.5×10^{-4}	0.62	0.75	0.32	0.15	0.02

Table 12 (b) Aqueous Phase - Ru (III)

Organic Phase - 10% V/V Octylamines in benzene

Solvent Concentration	Distribution Ratio
5% V/V	5.19
10% V/V	8.65
15% V/V	13.50
20% V/V	17.50
25% V/V	20.40

Table 12 (c) Aqueous Phase - 0.005M Ru (III) in 3.5M HCl

Organic Phase - 2-aminooctane in benzene

Distribution Ratios Determined for Osmium Chlorocomplex

Amine		Diluent
Class	Chain Length	Benzene
1 RY	Octyl	3.66
	Dodecyl	3.89
2 RY	Pentyl	1.66
	Octyl	1.30
	Dodecyl	1.04
3 RY	Pentyl	1.34
	Octyl	1.30
	Dodecyl	1.04
4 RY	Pentyl	1.69
	Heptyl	1.33

Table 13 (a) Aqueous Phase - 0.01M Os (IV) in 3.5M HCl
Organic Phase - 10% V/V

Amine Class	Metal Conc'n (Moles/Litre)	HCl Concentration (Moles/Litre) 1.1	2.3	4.5	6.7	9.0
1 RY	5×10^{-2}	12.1	17.8	26.5	41.1	29.1
	5×10^{-3}	1.67	2.36	4.76	12.3	12.5
	5×10^{-4}	1.07	1.77	2.02	4.02	6.69
2 RY	5×10^{-2}	5.17	5.71	7.00	33.7	33.8
	5×10^{-3}	0.66	0.73	0.75	4.31	6.15
	5×10^{-4}	0.62	0.56	0.89	1.35	2.70
3 RY	5×10^{-2}	3.87	4.09	4.44	27.1	21.1
	5×10^{-3}	0.53	0.56	0.62	2.74	6.17
	5×10^{-4}	0.80	0.64	0.70	0.87	2.87
4 RY	5×10^{-2}	5.47	5.34	5.60	42.3	27.3
	5×10^{-3}	0.93	0.85	0.80	3.30	6.55
	5×10^{-4}	0.77	0.65	0.74	0.91	3.43

Table 13 (b) Aqueous Phase - Os (IV)
Organic Phase - 10% V/V Octylamines in Benzene

Solvent Concentration	Distribution Ratio
5% V/V	3.00
10% V/V	4.85
15% V/V	6.08
20% V/V	6.37
25% V/V	9.16

Table 13 (c) Aqueous Phase - 0.01M in 3.5M HCl
Organic Phase - 2-aminooctane in Benzene

Distribution Ratios Determined for Gold Chlorocomplex

Amine		Diluent
Class	Chain Length	Benzene
1 RY	Octyl	263
	Dodecyl	250
2RY	Pentyl	475
	Octyl	395
	Dodecyl	490
3 RY	Pentyl	>1000
	Octyl	>1000
	Dodecyl	>1000
4 RY	Pentyl	>1000
	Heptyl	>1000

Table 14 (a) Aqueous Phase -- 0.01M Au(III) in 3.5M HCl
Organic Phase - 10% V/V.

Amine Class	Metal Conc'n (Moles/litre)	HCl Concentration (Moles/Litre)				
		1.1	2.3	4.5	6.7	9.0
1 RY	5×10^{-2}	215	184	153	89	43
	5×10^{-3}	102	165	308	115	54
	5×10^{-4}	12.4	54	820	61	40
2 RY	5×10^{-2}	534	466	430	430	382
	5×10^{-3}	505	445	334	445	455
	5×10^{-4}	45.5	120	94	226	71
3 RY	5×10^{-2}	>1000	>1000	>1000	>1000	>1000
	5×10^{-3}	668	>1000	>1000	>1000	>1000
	5×10^{-4}	273	204	107	455	93
4 RY	5×10^{-2}	>1000	>1000	>1000	>1000	>1000
	5×10^{-3}	>1000	>1000	>1000	>1000	>1000
	5×10^{-4}	43.2	94	46.7	46.7	79

Table 14 (b) Aqueous Phase - Au (III)
Organic Phase - 10% (V/V) octylamines in Benzene

Solvent Concentration	Distribution Ratio
5% V/V	77.0
10% V/V	210.0
15% V/V	228.0
20% V/V	369.0
25% V/V	422.0

Table 14 (c) Aqueous Phase - 0.01M Au (III) in 3.5M HCl
Organice Phase - 2-aminooctane in Benzene

TABLE 15

Metal	"n" Values		Nominal Composition of Complex
	Experimental	Theoretical	
Ir(III)	0.43 ± 0.01	3	$IrCl_6^{3-}$
Rh(III)	0.74 ± 0.04	3	$RhCl_6^{3-}$
Pd(II)	1.22 ± 0.04	2	$PdCl_4^{2-}$
Pt(IV)	0.93 ± 0.08	2	$PtCl_6^{2-}$
Ru(III)	0.87 ± 0.04	3	$RuCl_6^{3-}$
Os (IV)	0.65 ± 0.08	2	$OsCl_6^{2-}$
Au (III)	1.10 ± 0.11	1	$AuCl_4^{-}$

"n" values determined for the extraction of platinum group metals by 2-aminooctane in benzene from 3.5M HCl solutions.

Amine Class	HCl Conc'n	Pd:Ir Ratio	Distribution Pd (II)	Distribution Ir (III)	Separation Factor
1 RY	1.0	10:1	65	3.0	21.7
		1:10	56	1.75	32
	8.5	10:1	3.14	10.6	0.34
		1:10	1.2	9.12	0.13
2 RY	1.0	10:1	236	1.6	148
		1:10	200	0.62	322
	8.5	10:1	6.05	22.1	0.21
		1:10	7.90	0.35	22.6
3 RY	1.0	10:1	116	0.39	300
		1:10	119	0.14	850
	8.5	10:1	1.68	5.95	0.24
		1:10	2.2	0.06	36.8
4 RY	1.0	10:1	305	2.11	150
		1:10	296	0.4	750
	8.5	10:1	2.8	27.5	0.07
		1:10	0.9	16.0	0.06

Distribution ratios and separation factors between Pd (II) and Ir (III) determined in presence of each other. Extractant - 10% V/V octylamines in benzene. (Metal concentrations : 10 = 2×10^{-2}M, 1 = 2×10^{-3}M, Pd (II) or Ir (III).)

TABLE 17

Amine Class	Pt:Ir Ratio	Distribution Ratio Pt (IV)	Distribution Ratio Ir(III)	Separation Factor
1 RY	10:1	30.4	2.19	13.9
	1:10	4.50	2.43	1.85
2 RY	10:1	115	0.76	152
	1:10	4.27	0.80	5.34
3 RY	10:1	75.5	0.23	305
	1:10	8.35	0.28	29.8
4 RY	10:1	225	0.14	1605
	1:10	10.2	0.07	145

Distribution ratios and separation factors between Pt (IV) and Ir (III) determined in presence of each other. Extractant - 10% V/V octylamines in benzene. (Metal concentrations : 10 = 2×10^{-2}M, 1 = 2×10^{-3}M Pt (IV) or Ir (III) in 1.0M HCl).

Strip Method		Ir(III)	Ir(IV)	Rh(III)	Pd(II)	Pt(IV)	Ru(III)	Os(IV)
Acid Strip	HCl	Qualitative	Qualitative	Qualitative	Qualitative	Qualitative	Qualitative	Qualitative
Hydrolysis	NH_4OH	Quantitative D.R. 0.01	Quantitative reduces to Ir(III)	Ammine PPT formed	Ammine Complex formed	Ammine PPT formed	Does not strip	Does not strip
	NaOH	Quantitative DR<0.01	Quantitative reduces to Ir(III)	Quantitative DR < 0.01	Does not strip 1 RY Amine.	Quantitative D.R.<0.01	Does not strip	Does not strip
Anion Exchange	H_2SO_4	Does not strip	Does not strip					
	HNO_3	Oxidises to Ir(IV)					Qualitative	
	$HClO_4$	Qualitative D.R. = 0.5	Qualitative DR = 0.1	Qualitative	Qualitative	Qualitative		

Stripping of platinum metals from primary and tertiary amine complexes

Reagent	Manufacturer	Flash Point	Viscosity
B.P. 180	B.P.	92°F	0.80 cps
Solvesso 100	Esso	100°F	0.72 cps
" 150	"	152°F	1.5 cps
Dobane JNX	Shell	252°F	5.2 cps

Proprietary Diluents

TABLE 20

Reagent	Manufacturer	Type	Number of Carbon Atoms	Molecular Weight	Flash Point
Primene 81-R	Rohm & Hass Co.	1 RY	12 - 14	~200	205°F
Primene JMT	" "	1 RY	18 - 22	~300	265°F
Amberlite LA-1	" "	2 RY	24 - 26	~370	353°F
Amberlite LA-2	" "	2 RY	24 - 26	~370	355°F
Alamine 336	General Mills	3 RY	24 - 30	392	355°F
Aliquat 336	" "	4 RY	32 - 36	442	270°F

Proprietary Amine Extractants

TABLE 21

Amine	Diluent	Distribution Ratio
Primene 81 - R	Solvesso 100	2.26
	" 150	2.06
	B.P. 180	1.92
	Dobane JNX	2.40
Primene JMT	Solvesso 100	1.23
	" 150	1.22
	B.P. 180	0.97
	Dobane JNX	1.22

Extraction of $IrCl_6^{3-}$ by various 10% solutions of primary amines and diluents from 3M HCl solution.

TABLE 22

HCl Concentration	1.2M	2.6M	4.2M	6.2M	8.0M
Distribution Ratio	0.0007	0.005	0.05	1.78	19.5

Distribution of Fe(III)(0.04M) into 10% Primene 81 - R in Solvesso 150 at various Hydrochloric acid concentrations.

Metal	HCl Concentration Moles/Litre						
	0.3	1.0	2.3	3.0	4.3	6.3	8.3
Rh(III)	0.63	0.51	0.32	0.26	0.22	0.08	0.04
Ir(III)	1.64	1.42	0.81	0.60	0.46	0.21	0.09
Pd(II)	9.2	4.08	2.31	1.54	1.01	0.72	0.41
Pt(IV)	19.3	9.60	6.56	3.80	2.13	1.04	0.62

Distribution ratios determined in extraction of 0.01M platinum metal solutions by 10% V/V primene 81-R in Solvesso 150.

TABLE 24

Metal	Amine Concentration (V/V)					
	2%	4%	6%	8%	10%	20%
Rh(III)	0.04	0.16	0.24	0.38	0.51	2.00
Ir(III)	0.26	0.48	0.66	0.92	1.42	3.54
Ir(IV)	0.62	1.00	1.80	2.16	3.76	8.75
Pd(II)	0.16	0.24	1.42	2.16	4.08	24.6
Pt(IV)	0.48	1.72	3.30	5.88	9.60	41.8
Au(III)	21.2	38.8	64.8	81.0	100.6	197.0

Distribution ratios determined in extractions of 0.01M platinum metal solutions by Primene 81-R in Solvesso 150 from 1.0M HCl

TABLE 25

Metal	Metal Concentration (Moles/Litre)						
	.001	.002	.005	.010	.020	.050	0.100
Rh(III)	1.44	1.64	1.94	2.00	2.01	1.44	1.40
Ir(III)	3.90	3.54	3.96	3.54	3.90	3.42	2.84
Ir(IV)	8.45	9.20	9.01	8.75	8.01	6.50	4.45
Pd(II)	25.1	25.1	26.6	24.6	22.1	24.5	16.4
Pt(IV)	35.2	40.7	45.1	41.8	36.3	24.2	18.7
Au(III)	83.6	134.0	179.0	197.0	210.0	216.0	204.0

Distribution ratios determined in extraction of platinum metals solutions by 20%(V/V) Primene 81-R in Solvesso 150 from 1.0M HCl.

Metal	HCl Concentration (Moles/Litre)					
	0.3	2.3	3.0	4.3	6.3	8.3
Rh(III)	0.82	0.09	0.07	0.05	0.02	0.01
Ir(III)	1.9	0.16	0.14	0.09	0.04	0.02
Pd(II)	956	43.5	29.6	16.2	5.08	2.10
Pt(IV)	2880	120	95	73.1	27.2	7.10

Distribution ratios determined in extraction of 0.01M platinum metal solutions in 10% (V/V) Alamine 336 in Solvesso 150.

TABLE 27

Metal	Amine Concentration (V/V)					
	2%	4%	6%	8%	10%	20%
Ir(IV)	0.82	1.83	1.93	2.02	2.23	3.02
Pd(II)	0.77	2.52	9.30	16.30	29.60	123.0
Pt(IV)	1.44	8.90	28.20	57.0	66.0	186.0

Distribution ratios determined in extraction of 0.01M platinum metal solutions by Alamine 336 in Solvesso 150 from 3.0M HCl.

TABLE 28

Metal	Metal Concentration (Moles/Litre)						
	0.001	0.002	0.005	0.01	0.02	0.05	0.10
Rh(III)	0.04	0.05	0.05	0.06	0.07	0.07	0.07
Ir(III)	0.12	0.12	0.12	0.14	0.16	0.16	0.16
Ir(IV)	0.63	0.92	1.46	2.23	2.14	1.89	1.67
Pd(II)	28.5	29.1	29.6	29.6	21.0	10.2	4.6
Pt(IV)	36.6	31.6	57.0	66.0	86.0	90.0	30.2

Distribution ratios determined in extraction of platinum metal solutions by 10% (V/V) Alamine 336 in Solvesso 150 from 3.0M HCl.

TABLE 29

Metal	"n" Values		Indicated Complexes Present
	Primene 81-R	Alamine 336	
Rh(III)	1.80 ± 0.10	-	$RhCl_5(H_2O)^{2-}$
Ir(III)	1.07 ± 0.07	-	$IrCl_4(H_2O)_2^{-}$ but
Ir(IV)	1.10 ± 0.09	-	probably $IrCl_6^{2-}$
Pd(II)	2.25 ± 0.26	2.26 ± 0.10	$PdCl_4^{2-}$
Pt(IV)	1.98 ± 0.11	2.20 ± 0.11	$PtCl_6^{2-}$
Au(III)	0.99 ± 0.04	-	$AuCl_4^{-}$

Computed "n" values of Platinum metal chlorocomplexes extracted by commercial amines.

TABLE 30

Bimetallic Solution			Distribution Ratio x	Distribution Ratio y	Separation Factor y/x
x	Ratio	y			
Rh(III)	10:1	Pd(II)	0.040	30.0	750
	1:10		0.030	10.5	340
Rh(III)	10:1	Pt(IV)	0.025	29.0	1080
	1:10		0.023	27.0	1260
Ir(III)	10.1	Pd(II)	0.060	29.0	480
	1:10		0.060	11.6	210
Ir(III)	10:1	Pt(IV)	0.030	24.0	800
	1:10		0.028	27.0	900

Distribution ratios and separation factors between platinum metals determined in the presence of each other. Extractant 10% V/V Alamine 336 in Solvesso 150. (Metal concentration: 10 = 10^{-1}M, 1 = 10^{-2}M in 3M hydrochloric acid solution.

TABLE 31

Organic Phase	Aqueous Phase	Settling Time Secs	Phase Continuity
10% V/V Alamine 336 in Dobane (5% Decanol)	3M HCl	30	Aqueous Continuous
	3M HCl 5g/L Pt	30	
	0.5M Na_2CO_3	45	
	3M HCl	180	Organic Continuous
	3M HCl 5g/L Pt	210	
	0.5M Na_2CO_3	150	
20% V/V Primene 81-R in Dobane	1M HCl	35	Aqueous Continuous
	1M HCl 5g/L Pt	35	
	0.5M Na_2CO_3	50	
	1M HCl	150	Organic Continuous
	1M HCl 5g/L Pt	180	
	0.5M Na_2CO_3	90	

Settling Rates of Mixed Phases

Run Number	Nominal Flow Rates mls/min.				Ratio of Flows			Feed Concentration		Equilibrium Concentrations g/L						Distribution Ratios		% Extraction	
										Raffinate		Scrub		Strip					
	Feed	Amine	Scrub	Strip	Feed/Amine	Scrub/Amine	Strip/Amine	Pt	Ir	Pt	Ir	Pt	Ir	Pt	Ir	Pt	Ir	Pt	Ir
1	105	100	120	110	1.05	1.2	1.1	1.075	0.82	<.001	0.450	<.001	0.120	1.050	0.235	$>10^3$	0.52	99.9	28.8
2	210	100	120	110	2.10	1.2	1.1	1.075	0.82	<.001	0.625	<.001	0.110	2.100	0.145	$>10^3$	0.23	99.9	17.7
3	105	100	120	110	1.05	1.2	1.1	0.335	0.225	<.001	0.155	<.001	0.040	0.295	0.070	10^3	0.45	99.9	32.1
4	105	100	120	110	1.05	1.2	1.1	0.390	0.295	<.001	0.145	<.001	0.030	0.375	0.150	10^3	1.03	99.9	51.0
5	105	100	120	110	1.05	1.2	1.1	1.375	0.130	<.001	0.075	<.001	0.025	0.165	0.035	$>10^3$	0.47	99.9	24.0
6	100	50	120	100	2.00	2.4	2.0	1.230	0.36	<.001	0.290	<.001	0.050	1.230	0.035	$>10^3$	0.12	99.9	9.7
7	100	50	110	100	2.00	2.2	2.0	0.145	0.34	<.001	0.250	<.001	0.045	0.145	0.035	10^3	0.14	99.9	10.3

Separation of platinum and iridium (III) with 10% (V/V) Alamine 336 in Dobane in continuous counter current tests. 2 stages in each section in all runs except run number 4 (3 stages extract 1 scrub). Feed and scrub solutions 2.8M in HCl.

Run Number	Nominal Flow Rates mls/min.				Ratio of Flows			Feed Concentration		Equilibrium Concentration g/L						Distribution Ratios		% Extraction	
										Raffinate		Scrub		Strip					
	Feed	Amine	Scrub	Strip	Feed/Amine	Scrub/Amine	Strip/Amine	Pt	Rh	Pt	Rh	Pt	Rh	Pt	Rh	Pt	Rh	Pt	Rh
1	105	100	120	110	1.05	1.2	1.1	0.965	1.000	<.001	0.725	<.001	0.200	0.895	0.060	$>10^3$	0.08	99.9	6
2	210	100	120	110	2.1	1.2	1.1	0.965	1.000	<.001	0.870	<.001	0.100	1.855	0.040	$>10^3$	0.05	99.9	4
3	105	100	120	110	1.05	1.2	1.1	2.400	0.360	<.001	0.270	<.001	0.065	2.400	0.005	$>10^3$	0.02	99.9	1.5
4	210	100	120	110	2.10	1.2	1.1	2.400	0.360	<.001	0.335	<.001	0.050	4.780	0.010	$>10^3$	0.03	99.9	2
5	210	100	225	110	2.10	2.25	1.1	2.400	0.670	<.001	0.650	<.001	0.030	2.330	0.020	$>10^3$	0.02	99.9	2
6	110	45	135	100	2.44	3.00	7.22	0.150	0.375	<.001	0.375	<.001	0.020	0.150	0.001	10^3	0.003	99.9	0.3
7	100	50	135	100	2.00	2.70	2.00	1.900	0.375	<.001	0.365	<.001	0.010	1.870	0.005	$>10^3$	0.01	99.9	1

Separation of platinum and rhodium with 10% (V/V) Alamine 336 in Dobane in continuous counter current tests. 2 stages in each section. Feed and scrub solutions 2.8M in HCl.

TABLE 24

Run Number	Nominal Flow Rates mls/min			Ratio of Flows		Feed Concentration g/L		Equilibrium Concentrations g/L						Distribution Ratios		% Extraction	
				Feed	Scrub			Raffinate		Scrub		Amine					
	Feed	Amine	Scrub	Amine	Amine	Pd	Rh	Pd	Rh	Pd	Rh	Pd	Rh	Pd	Rh	Pd	Rh
1	105	100	120	1.05	1.2	0.990	2.700	<.001	1.900	<.001	0.540	0.950	0.260	$>10^3$	0.1	99.9	10
2	210	100	120	2.10	1.2	0.975	0.340	<.001	0.290	<.001	0.050	1.650	0.010	$>10^3$	0.03	99.9	3

Separation of palladium and rhodium with 10% (V/V) Alamine 336 in Dobane in continuous counter current tests. 2 stages in each section. Feed and scrub solutions 2.8M HCl.

Run Number	Feed Concentration g/L			Equilibrium Concentrations g/L									Distribution Ratios			% Extraction		
				Raffinate			Scrub			Strip								
	Pt	Ir	Rh	Pt	Ir	Rh	Pt	Ir	Rh	Pt	Ir	Rh	Pt	Ir	Rh	Pt	Ir	Rh
1	1.015	0.205	0.700	<.001	0.160	0.615	<.001	0.040	0.080	1.160	0.025	0.010	$>10^3$	0.15	0.02	99.9	12	1.5
2	0.580	0.105	0.340	<.001	0.080	0.285	<.001	0.025	0.040	0.580	0.010	0.005	$>10^3$	0.12	0.02	99.9	10	2

Separation of platinum from rhodium and iridium (III) with 10% (V/V) Alamine 336 in Dobane in continuous counter current tests. 2 stages each section. Feed and scrub solutions 2.8M in HCl. Flow rates: feed 100 mls/min; Amine 50 mls/min; scrub 110 mls/min; strip 100 mls/min.

TABLE 36

Run No. 1

Metal	Feed Concentration g/L	Equilibrium Concentration g/L		Distribution Ratio	% Extraction
		Raffinate	Strip		
Pt	0.870	0.005	0.855	170	99
Ir	0.336	0.005	0.320	64	96
Rh	0.405	0.190	0.205	1.1	51
Fe	1.020	1.020	< 0.001	$> 10^{-3}$	$< 10^{-1}$
Ni	1.170	1.170	< 0.001	$> 10^{-3}$	$< 10^{-1}$
Cu	1.300	1.300	< 0.001	$> 10^{-3}$	$< 10^{-1}$

Run No. 2

Metal	Feed Concentration g/L	Equilibrium Concentration g/L		Distribution Ratio	% Extraction
		Raffinate	Strip		
Pt	0.435	0.006	0.420	70	98.5
Ir	0.045	0.001	0.040	40	97.5
Rh	0.095	0.055	0.045	0.8	46
Fe	0.415	0.415	< 0.001	$> 10^{-3}$	$< 10^{-1}$
Ni	0.345	0.345	< 0.001	$> 10^{-3}$	$< 10^{-1}$
Cu	0.395	0.395	< 0.001	$> 10^{-3}$	$< 10^{-1}$

Separation of platinum metals from base metals by 20% (V/V) Primene 81-R in Dobane in continuous counter current tests. 4 stages extract. 2 stages strip. Feed solutions 1.0M in HCl. Flow rates feed - 100 mls/min; Amine - 50 mls/min; strip 100 mls/min.

TABLE 37

Flow Rate mls/min	Solvent Loss ppm	
	Raffinate	Strip
200	6	15
100	5 - 6	10

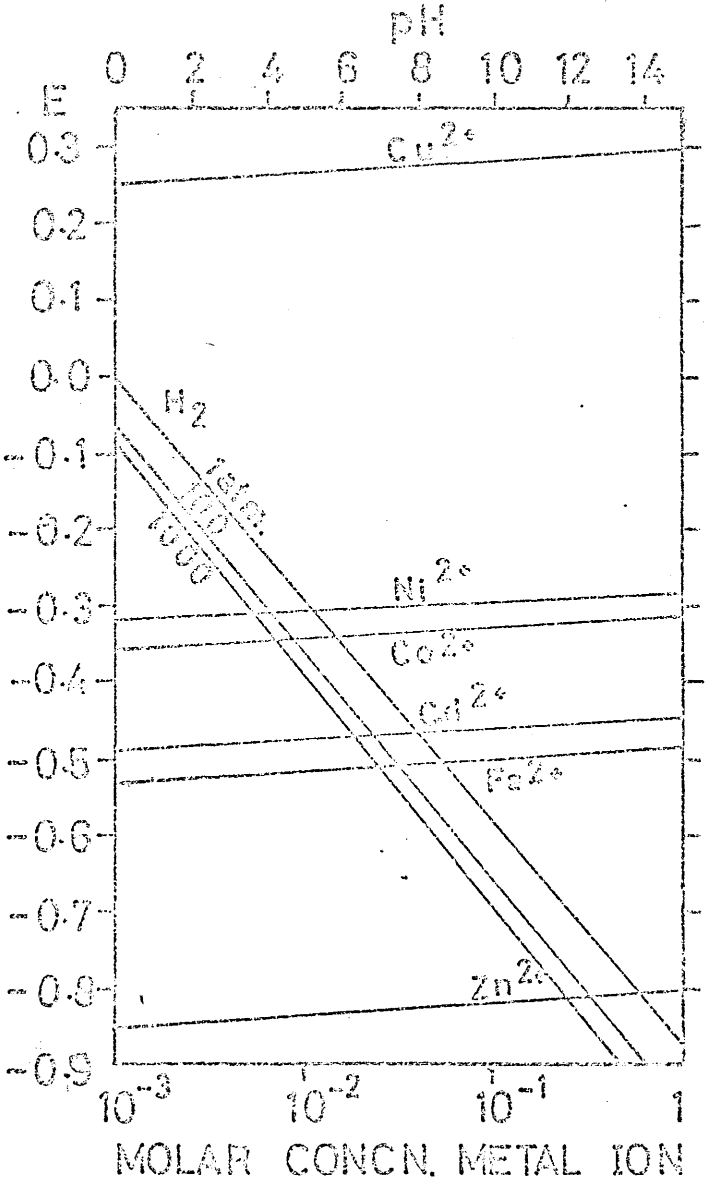
Solvent loss into aqueous process streams in continuous testing of 10% (V/V) Alamine 336 in Dobane extraction of platinum metals.

Flow Rate mls/min	Solvent Loss ppm	
	Raffinate	Strip
100	10-20,000	~ 100

Estimated

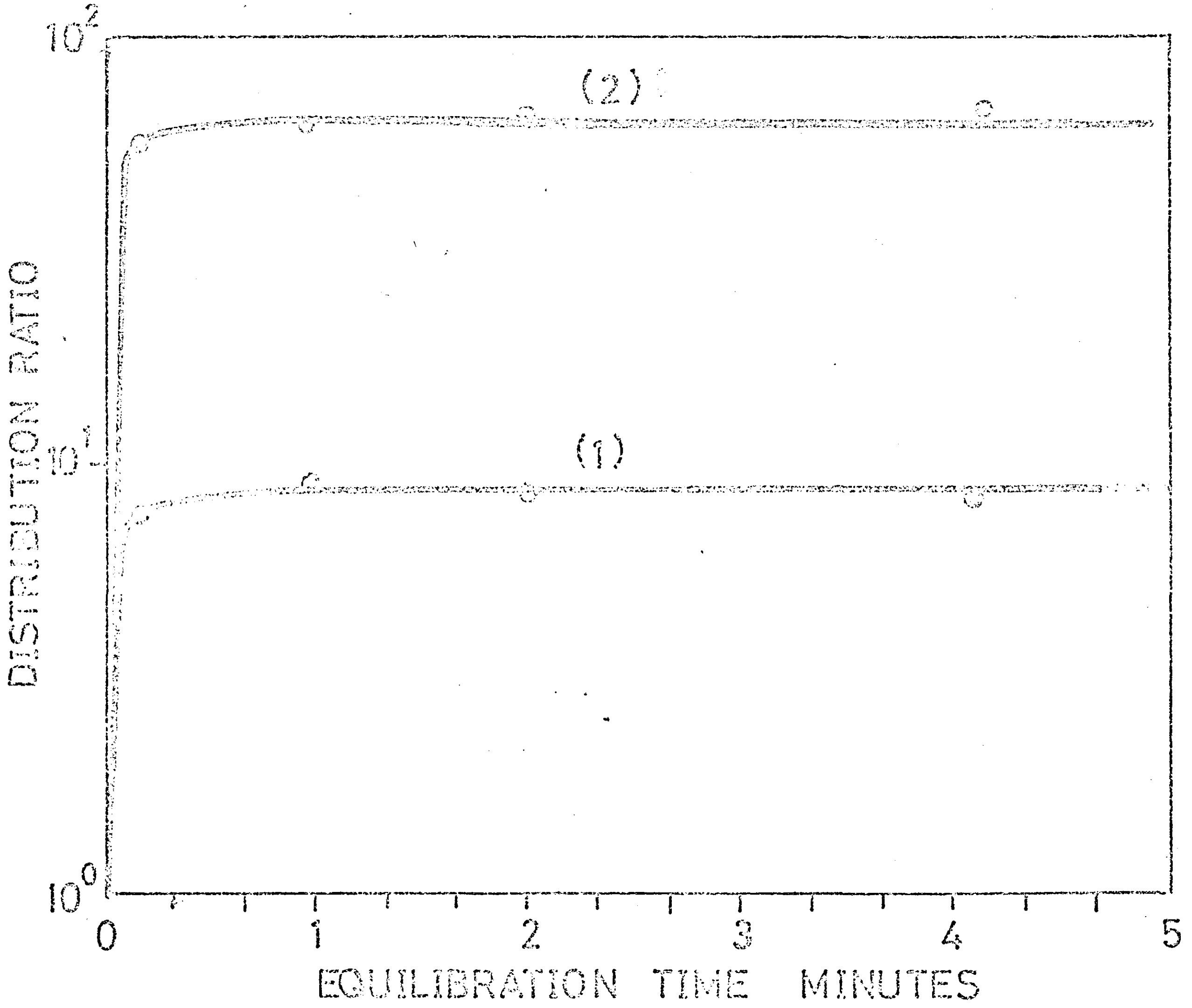
solvent loss into aqueous process streams in continuous testing of 20% V/V Primene 81-R in Dobane extraction of platinum metals.

FIG. 1.



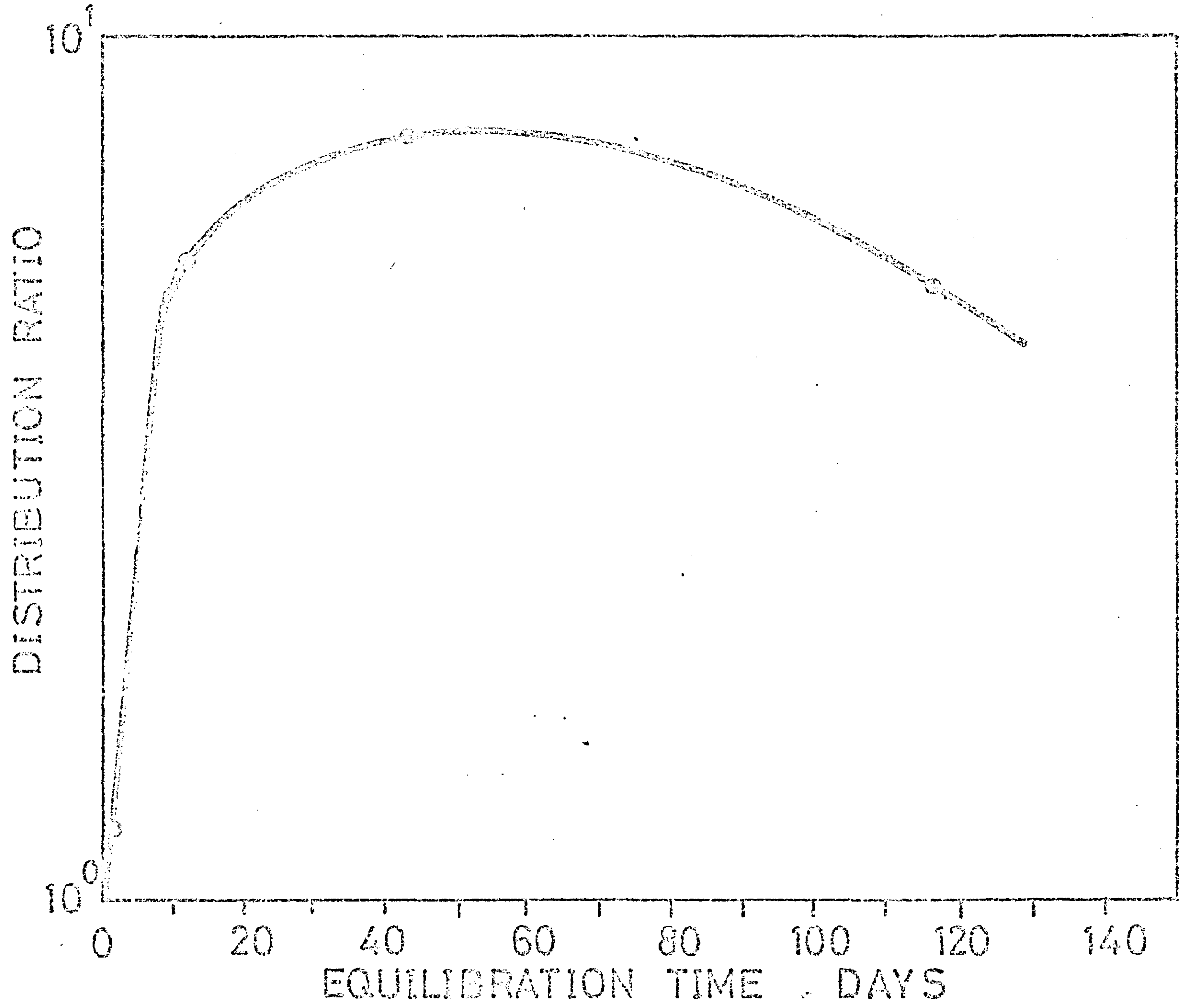
Variation of E with metal-ion concentrations for several metal sulphates. Similar lines for hydrogen are shown at pH values 0-14.

FIG. 2.



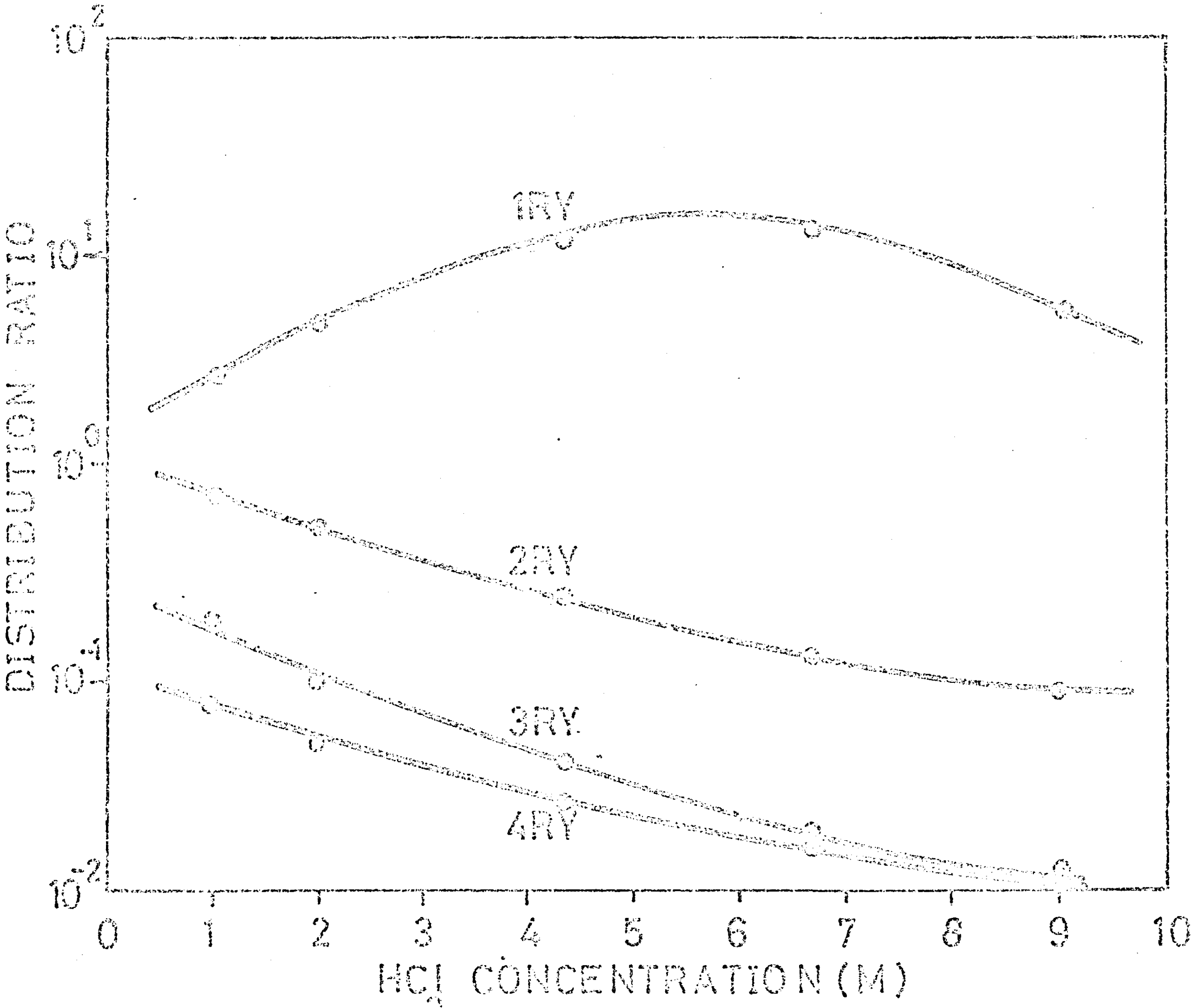
Kinetics of extraction .(1) Ir(III) by 10% 2-amino-octane in benzene;(2)Pt by 10% Alamine 336 in Solvesso150, from 3M HCl solution.

FIG. 3.



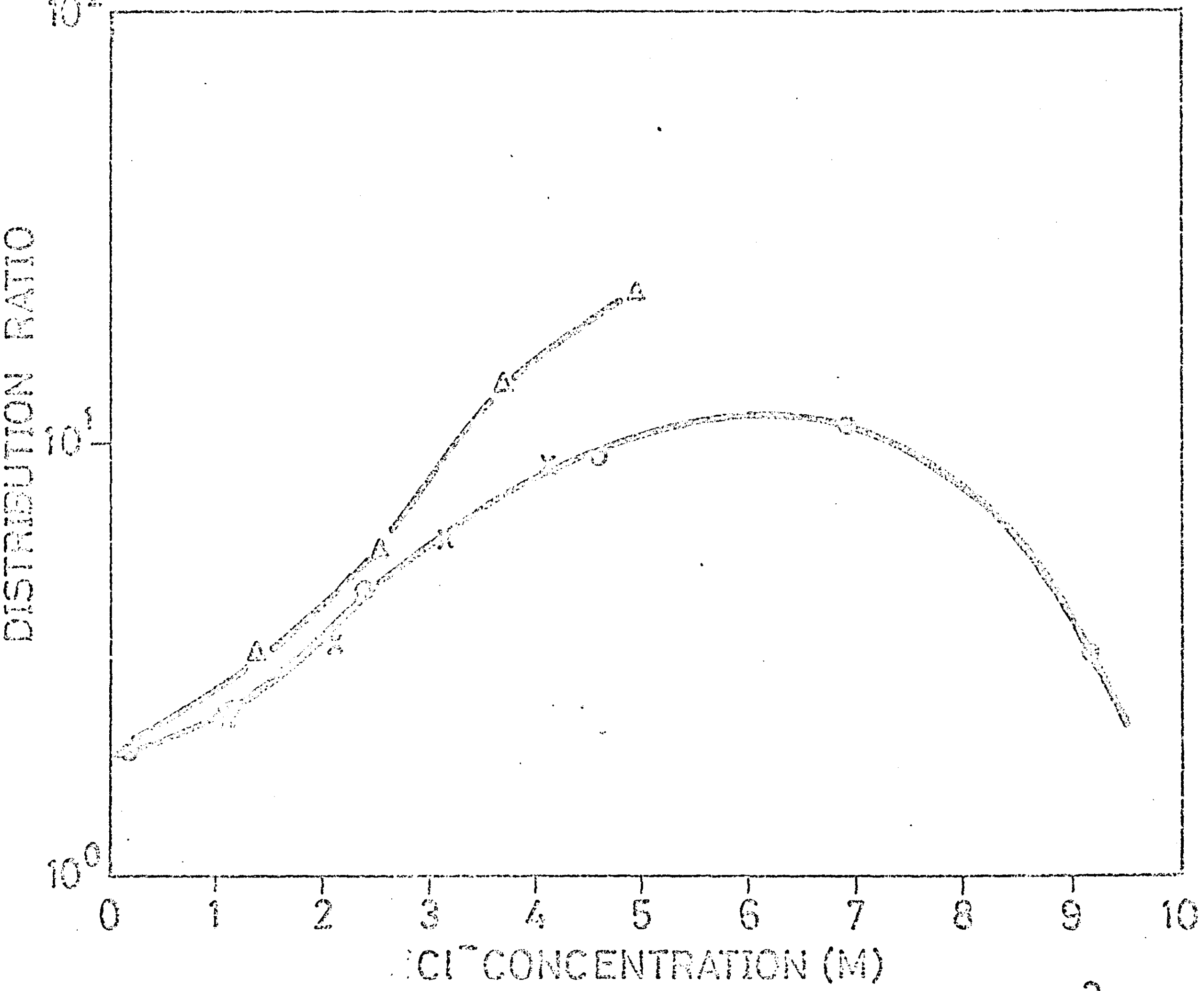
Kinetics of equilibration of aqueous solution of Ir(III) in 3M HCl. Extraction by 10% 2-amino-octane in benzene after fresh aqueous feed had been allowed to stand at room temp.

FIG. 4.



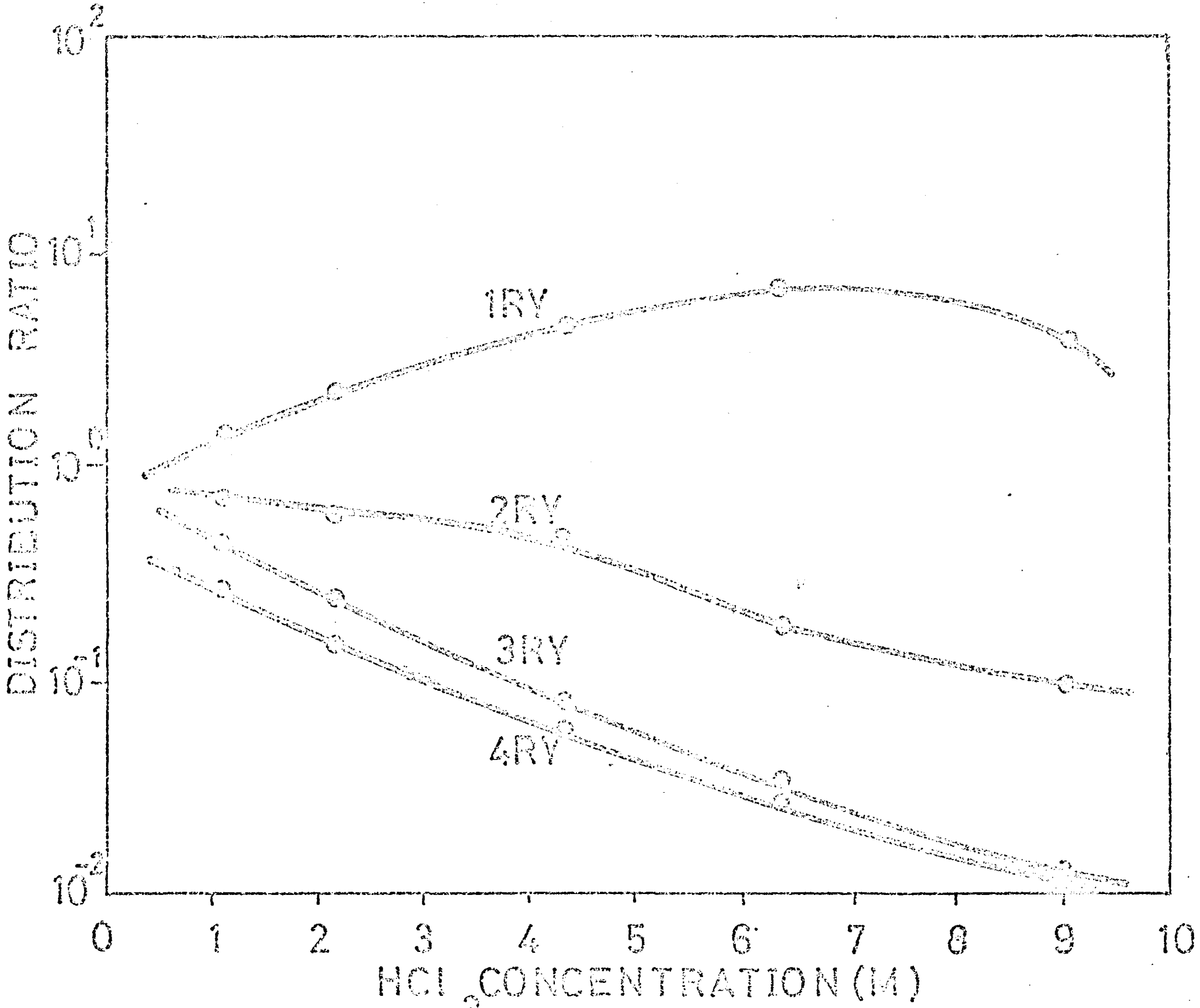
Extraction of $IrCl_6^{3-}$ (0·05M) by primary, secondary, tertiary octylamines, and quaternary heptyl ammonium chloride (10% v/v) in benzene

FIG. 4a



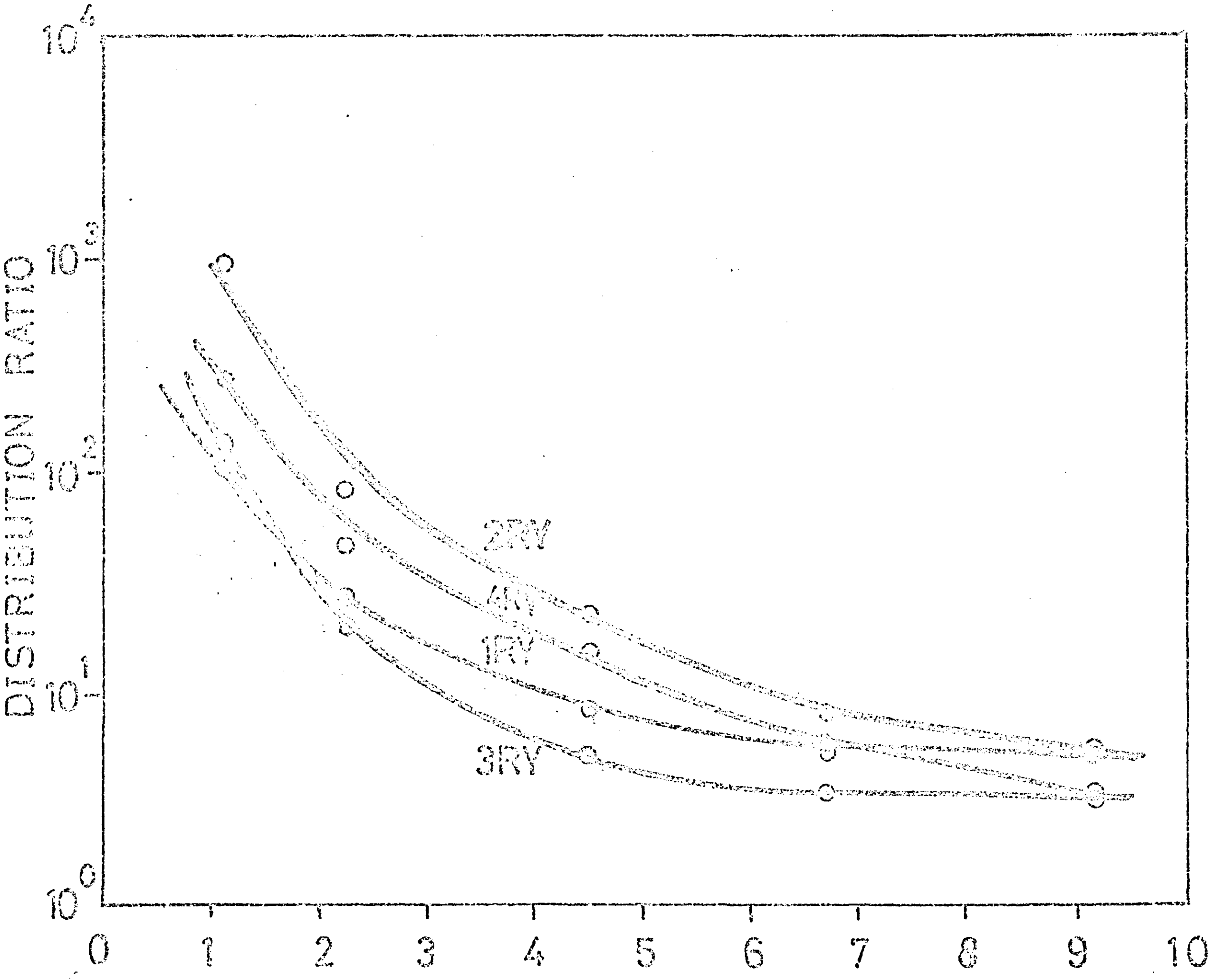
Effect of Cl⁻ concentration on extraction of $IrCl_6^{3-}$ by 10% 2-aminooctane in benzene independant of pH. o - HCl ; x - NaCl ; Δ - $AlCl_3$.

FIG. 5



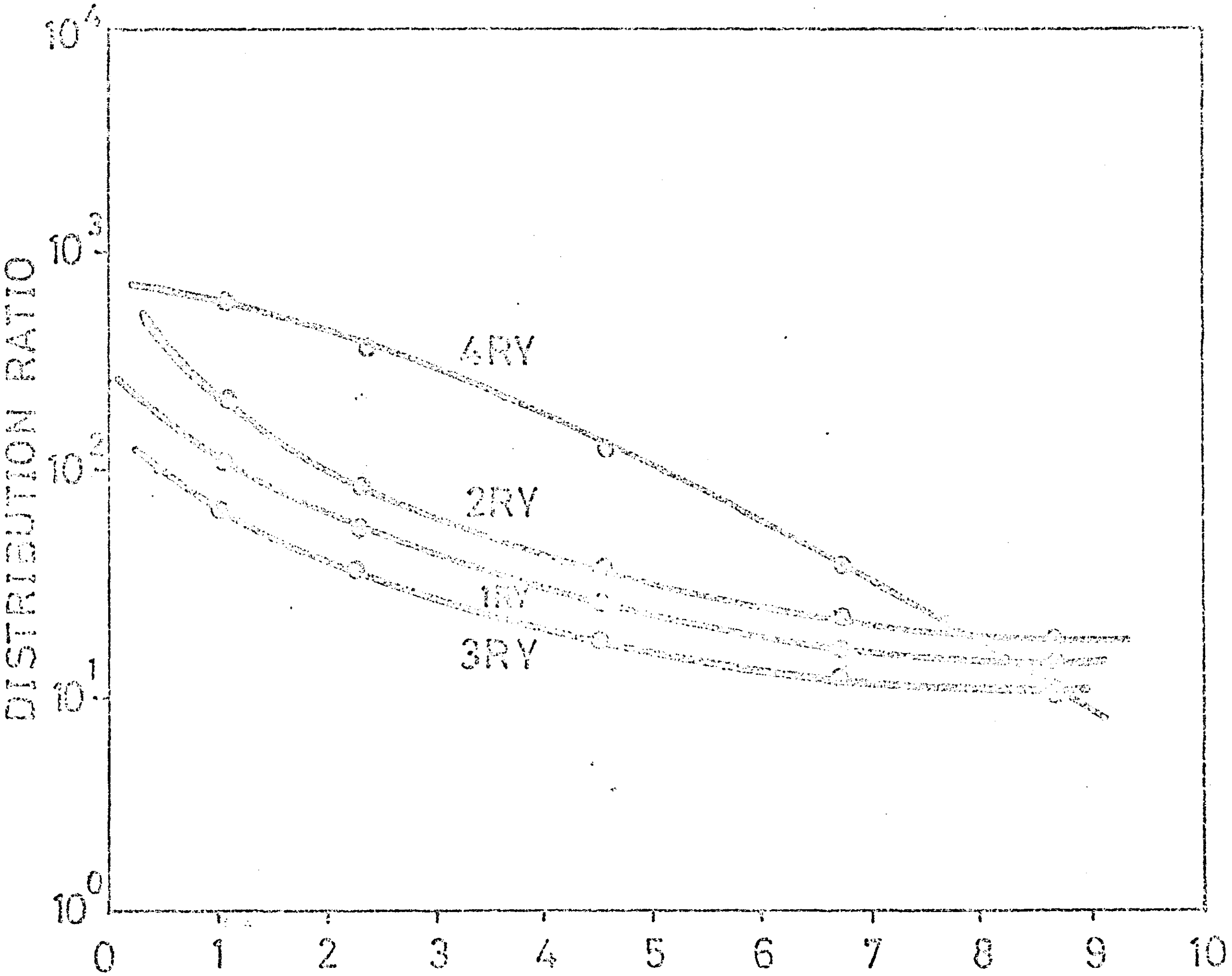
Extraction of $RhCl_6^{3-}$ (0·05M) by primary, secondary, tertiary octylamines, and quaternary heptyl ammonium chloride (10% v/v) in benzene.

FIG.6



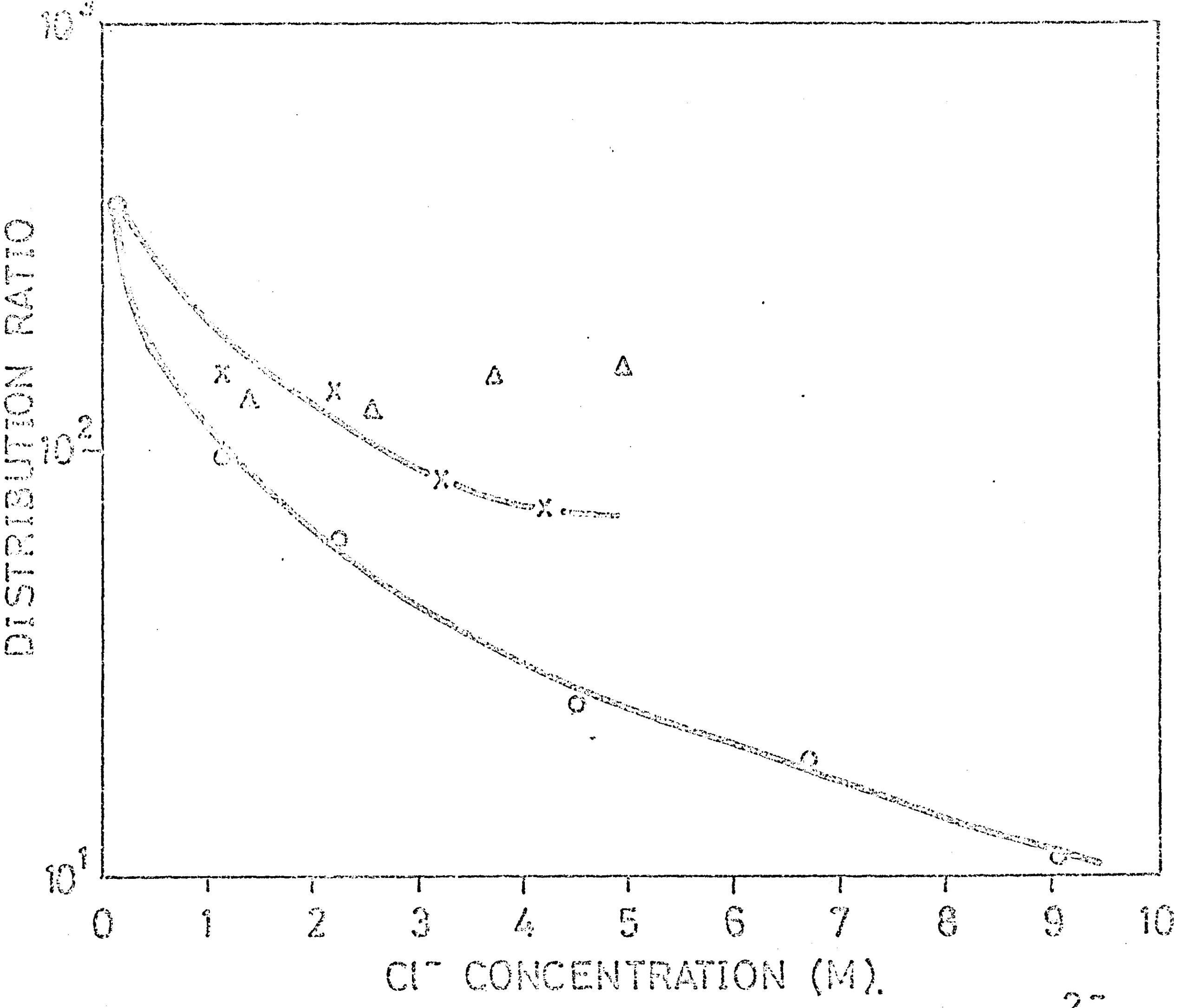
Extraction of $PdCl_4^{2-}$ (0·05M) by primary, secondary, tertiary octylamines, and quaternary heptyl ammonium chloride (10% v/v) in benzene.

FIG.7



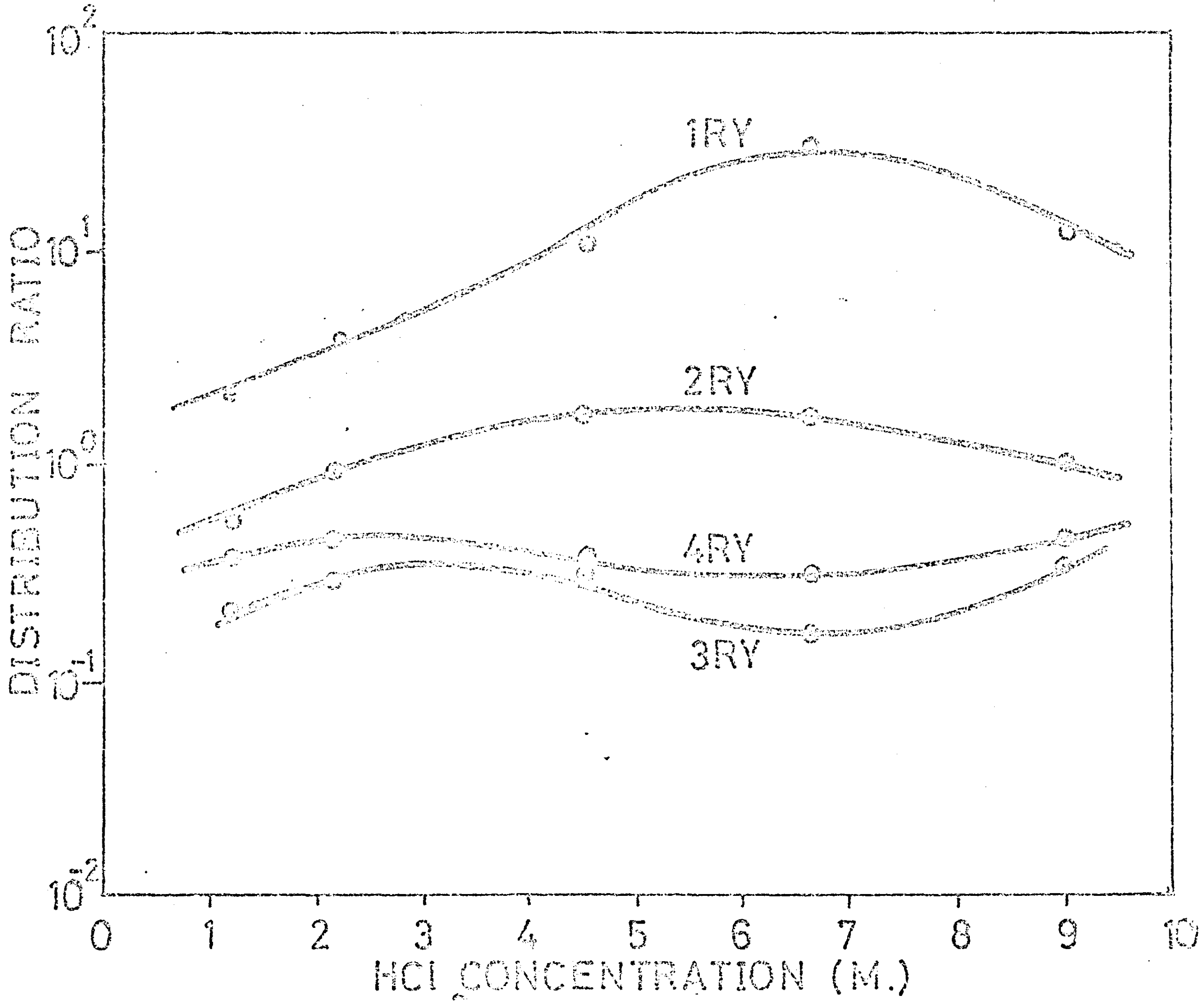
Extraction of $PtCl_6^{2-}$ (0·05M) by primary, secondary, tertiary octylamines, and quaternary heptyl ammonium chloride (10% v/v) in benzene.

FIG. 7a



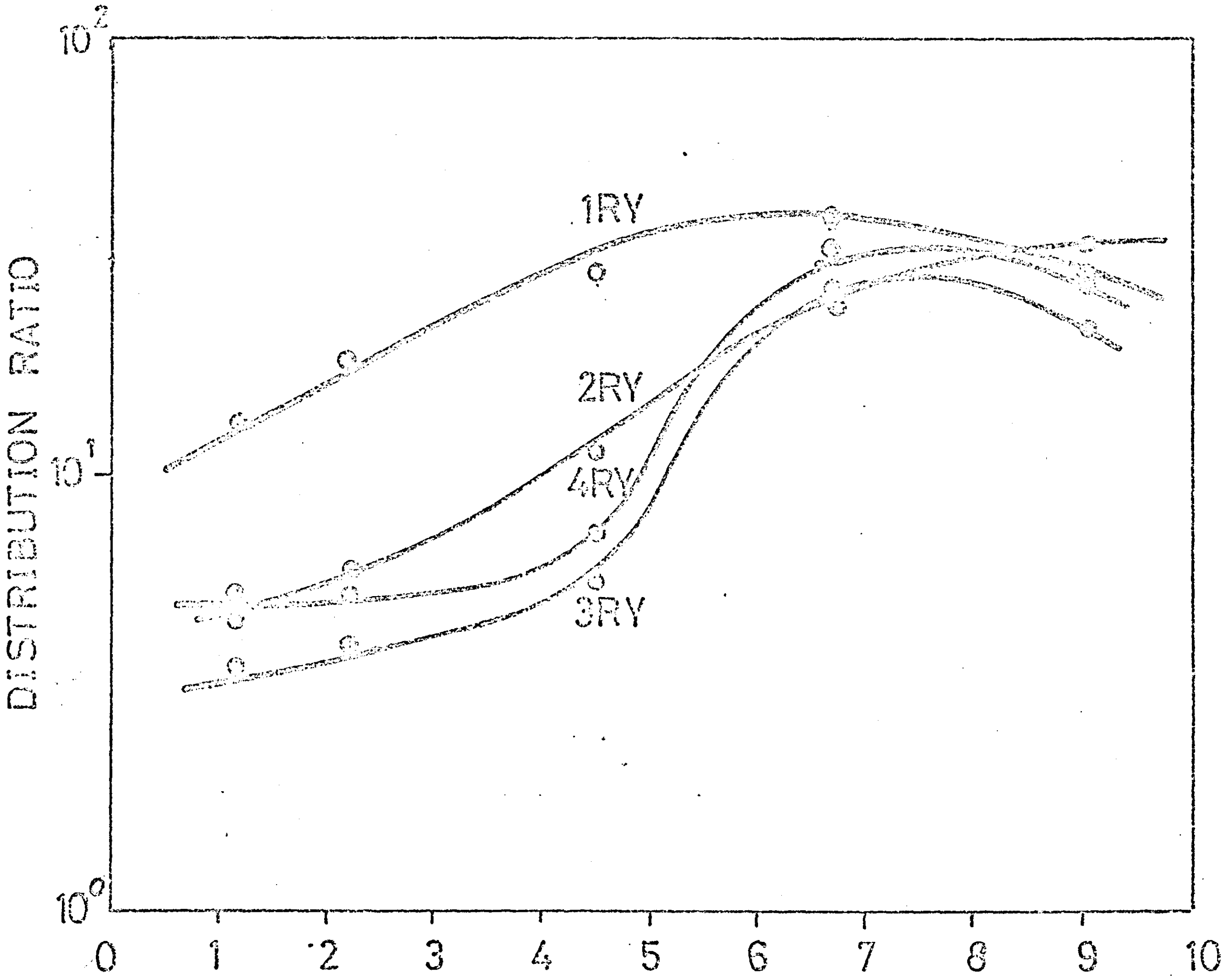
Effect of Cl⁻ concentration on extraction of $PtCl_6^{2-}$ by 10% trioctylamine in benzene independant of pH. o - HCl ; x - NaCl ; Δ - $AlCl_3$.

FIG.8

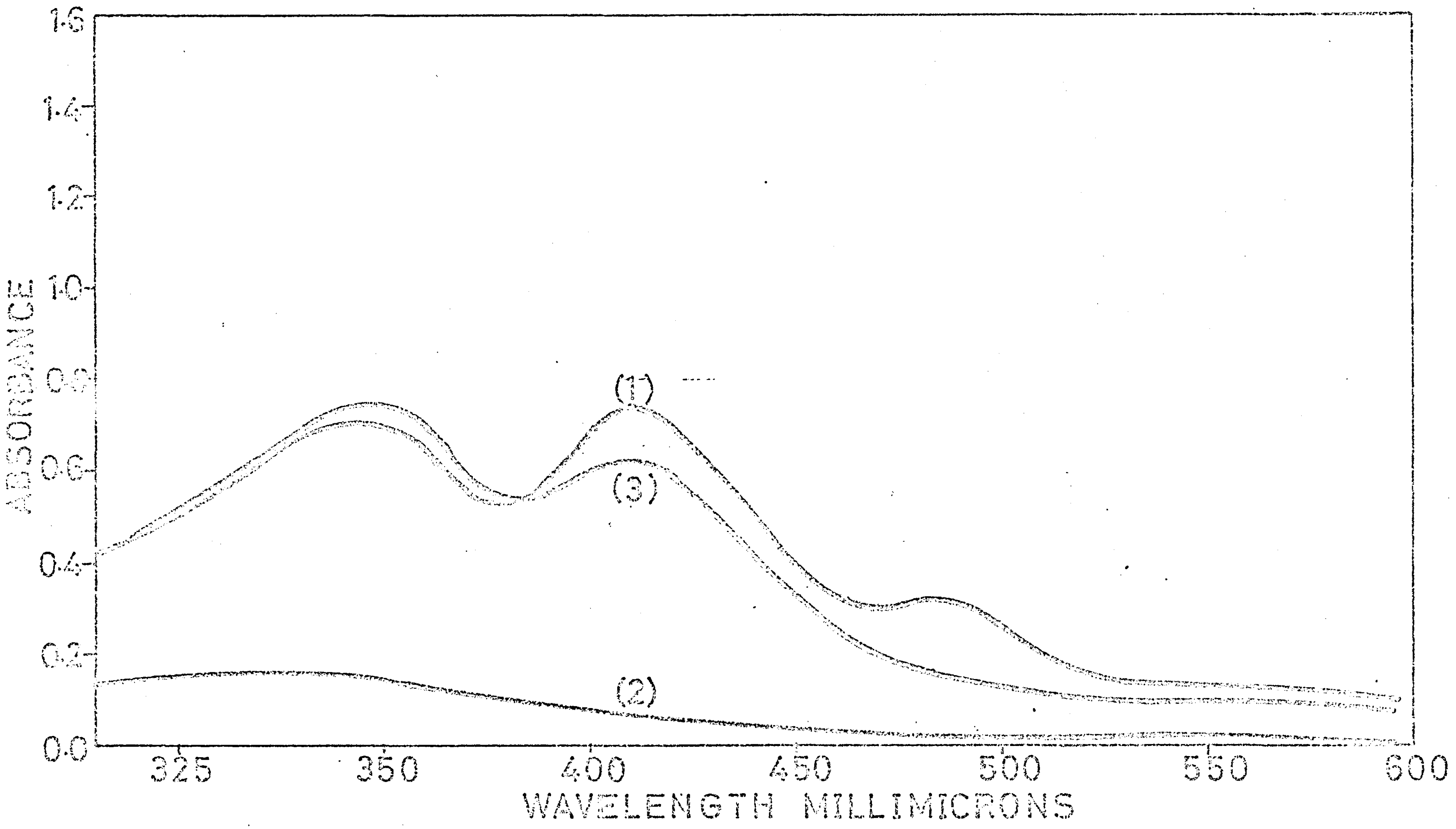


Extraction of $RuCl_6^{3-}$ (0·025M) by primary, secondary, tertiary octylamines, and quaternary heptyl ammonium chloride (10% v/v) in benzene.

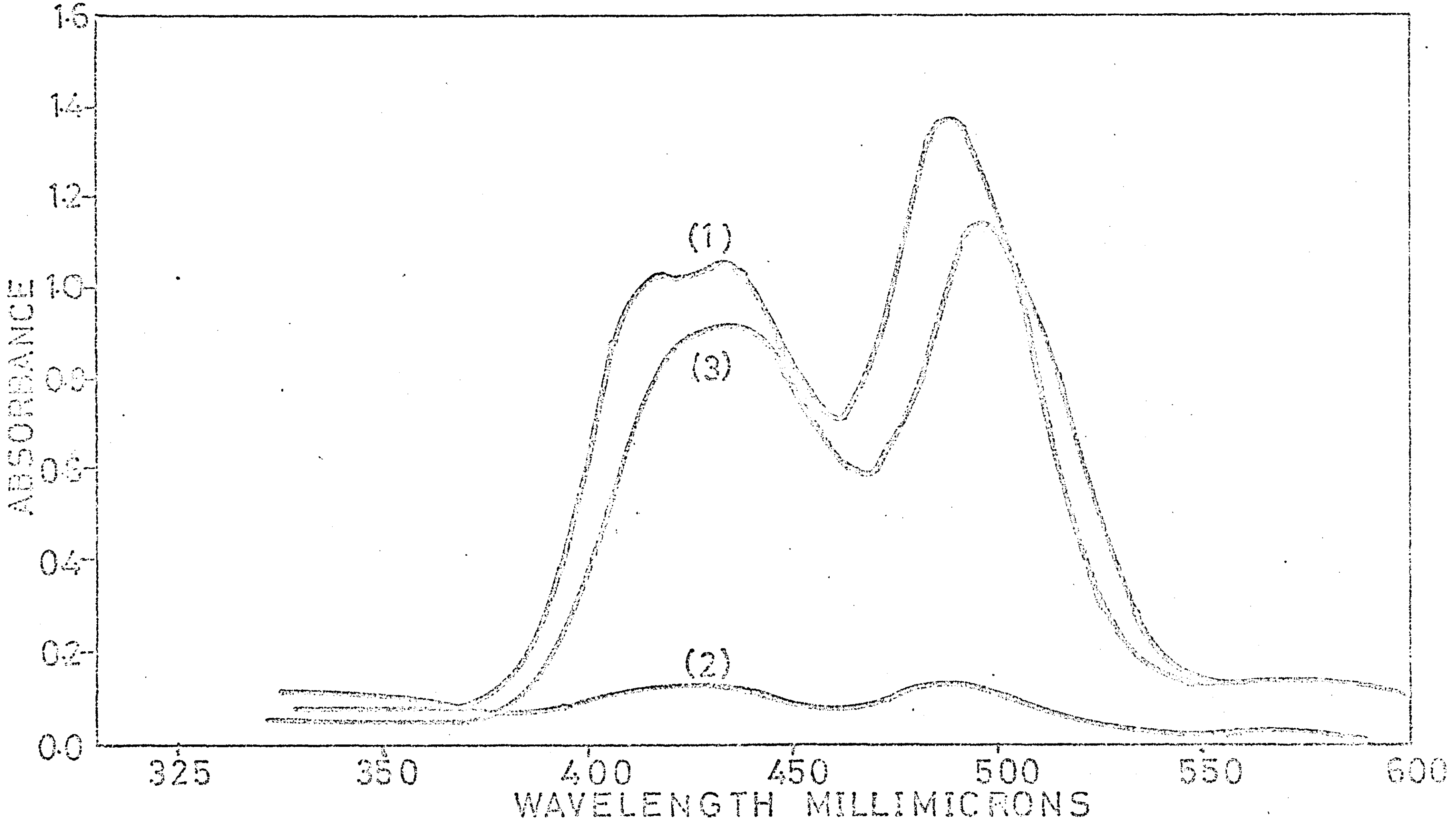
FIG. 9



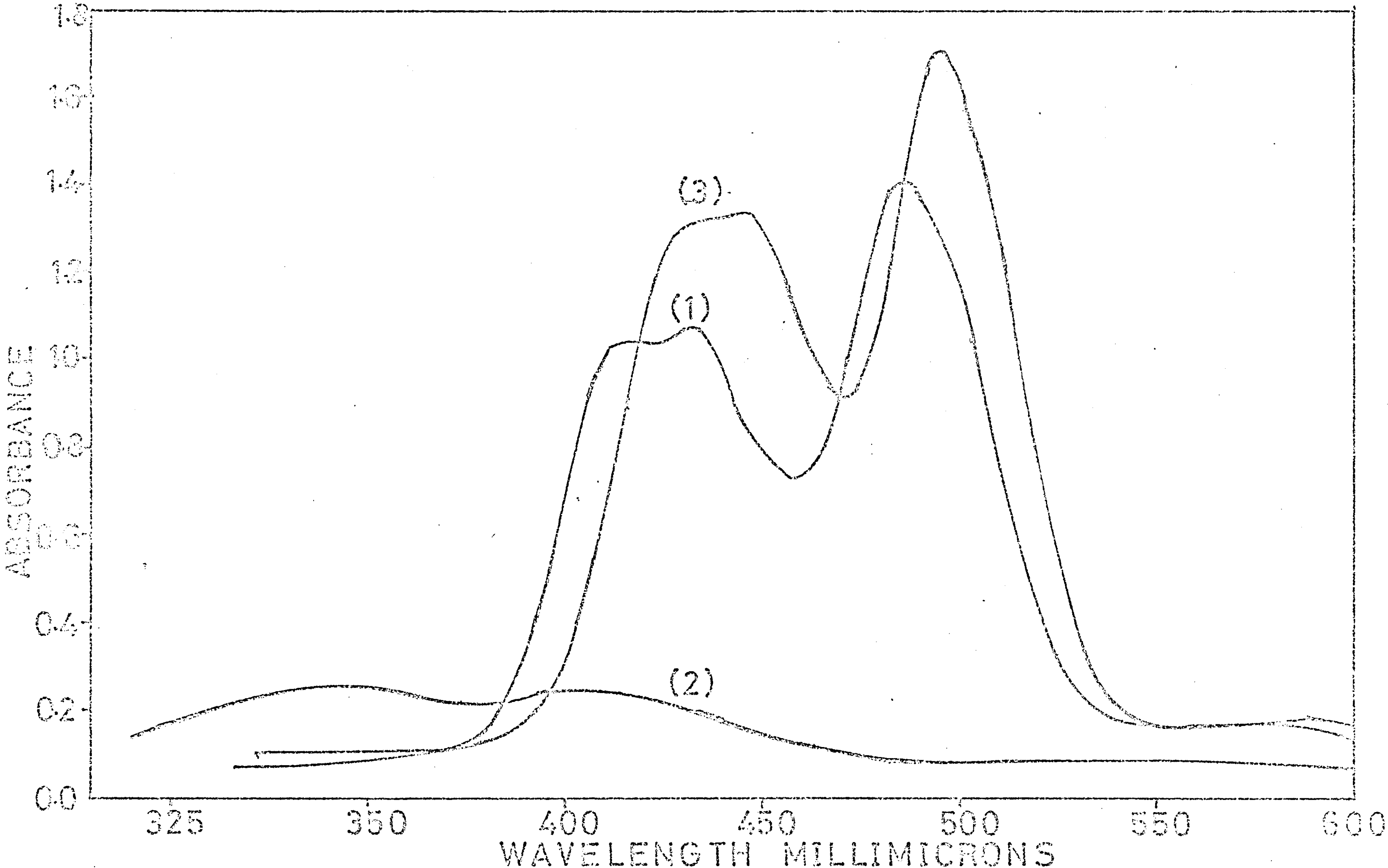
Extraction of $OsCl_6^{2-}$ (0·05M) by primary, secondary, tertiary octylamines, and quaternary heptyl ammonium chloride (10% v/v) in benzene.



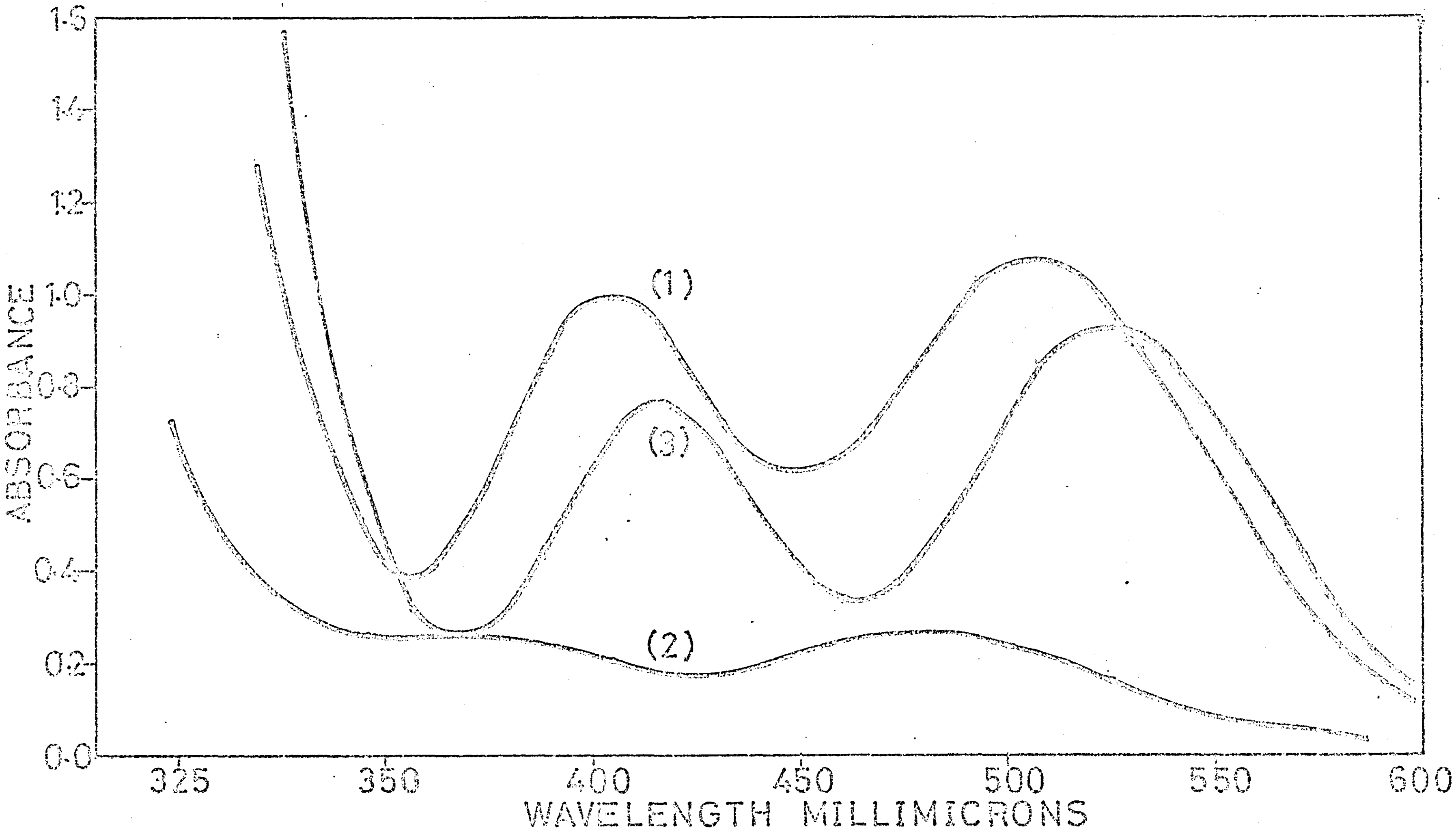
Absorption specta of $IrCl_6^{3-}$ during extraction by 10% v/v 2 amino-dodecane in benzene. (1) Aqueous feed solution. (2) Aqueous raffinate. (3) Organic extract.



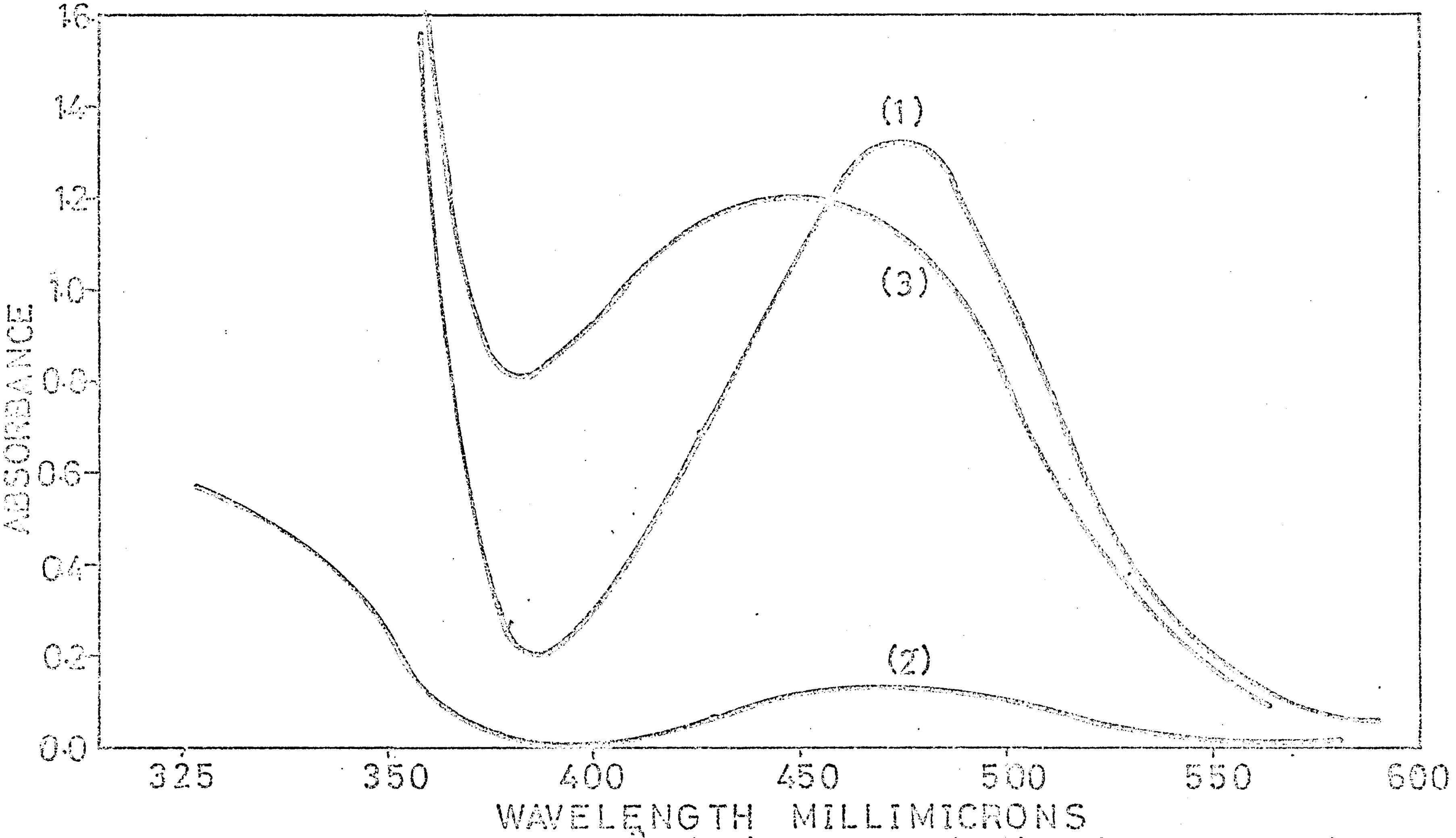
Absorption spectra of $IrCl_6^{2-}$ during extraction by 10%v/v 2-amino dodecane in benzene.(1)Aqueous feed solution.(2)Aqueous raffinate.(3) Organic extract.



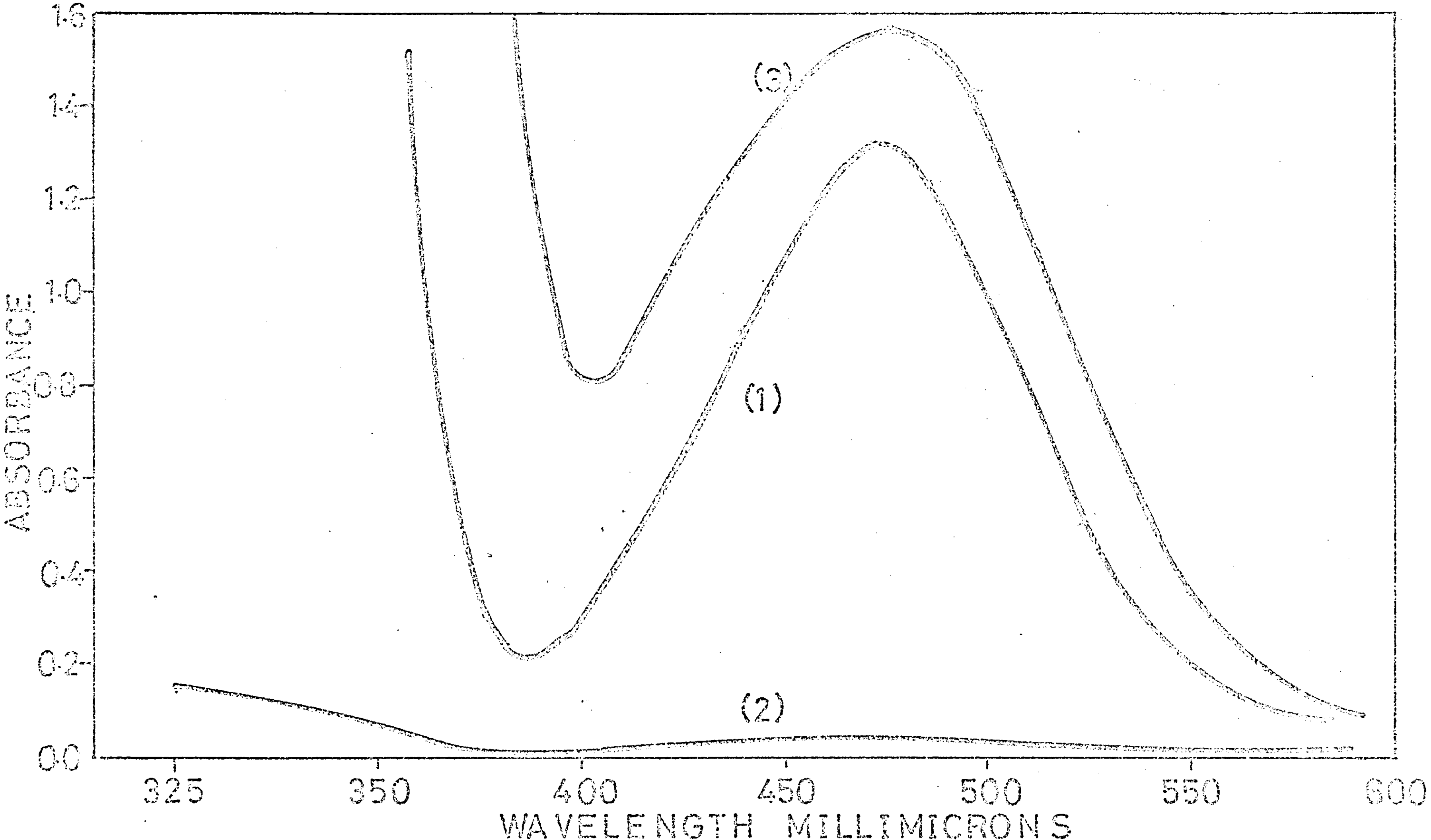
Absorption spectra of $IrCl_6^{2-}$ during extraction by 10% v/v tetraheptylammonium chloride in benzene. (1) Aqueous feed solution (2) Aqueous raffinate. (3) Organic extract.



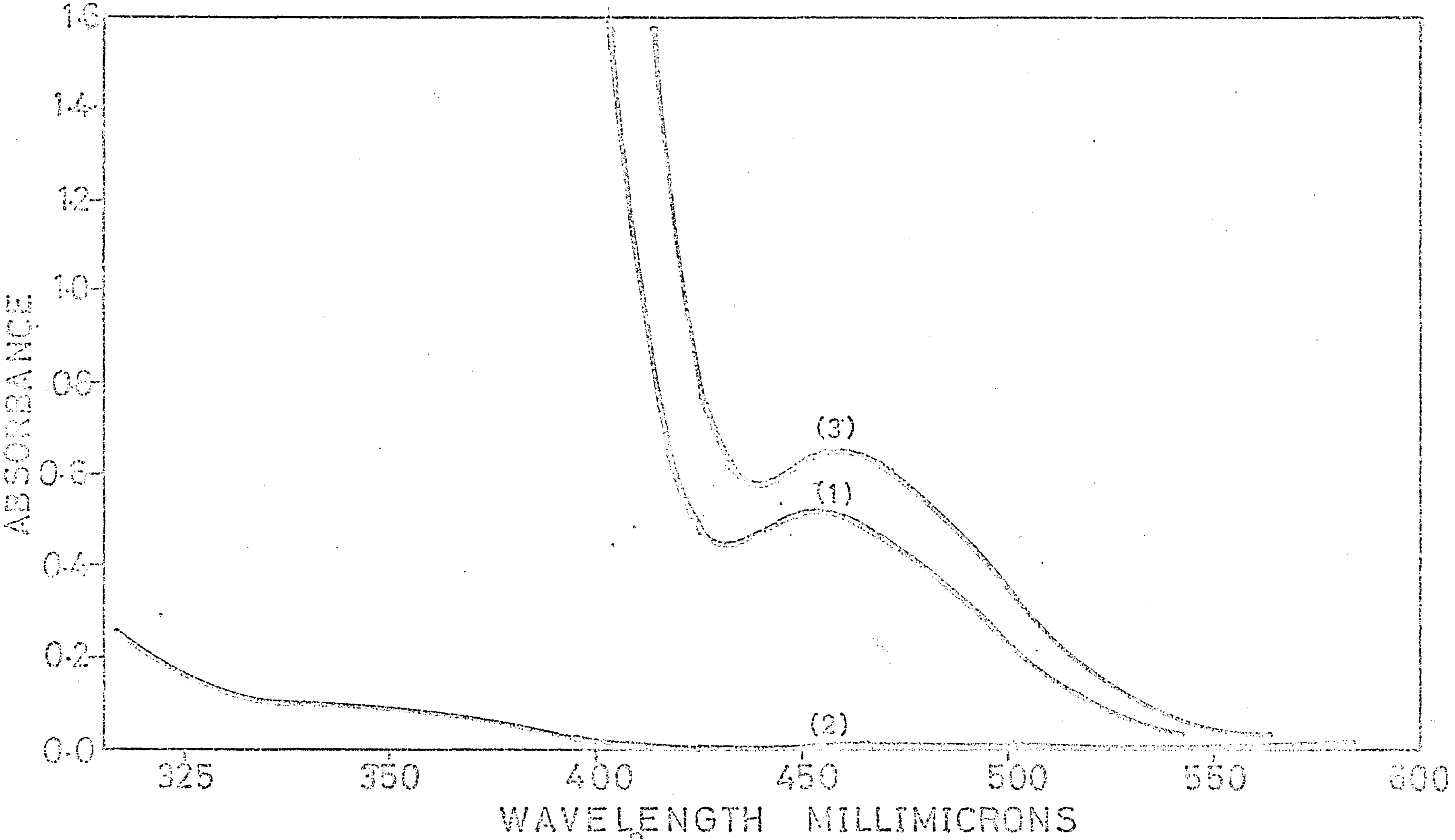
Absorption spectra of $RhCl_6^{3-}$ during extraction by 10% v/v 2 amino-dodecane in benzene. (1) Aqueous feed solution. (2) Aqueous raffinate. (3) Organic extract.



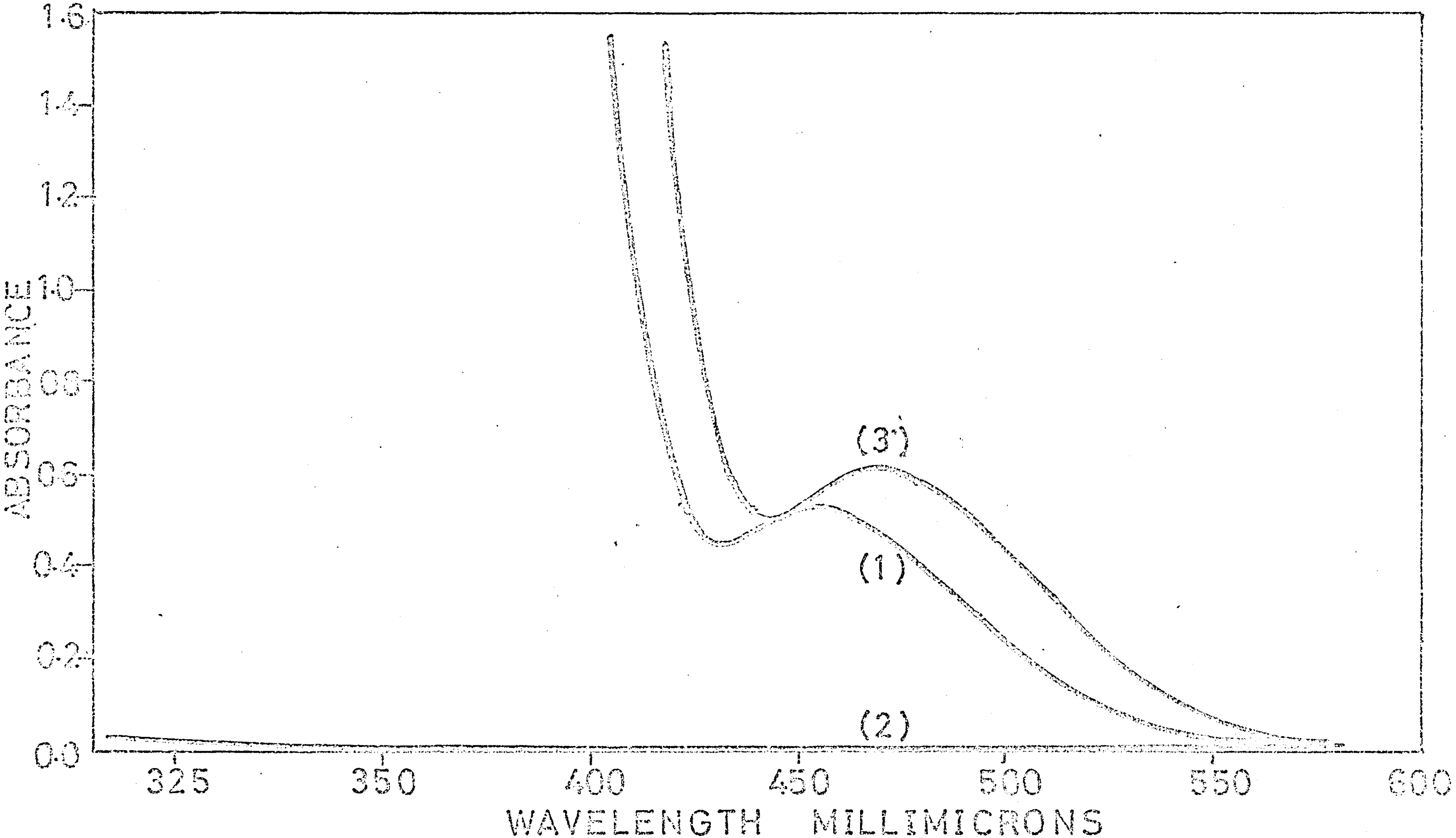
Absorption spectra of $PdCl_4^{2-}$ during extraction by 10% v/v 2 amino-dodecane in benzene. (1) Aqueous feed solution. (2) Aqueous raffinate. (3) Organic extract.



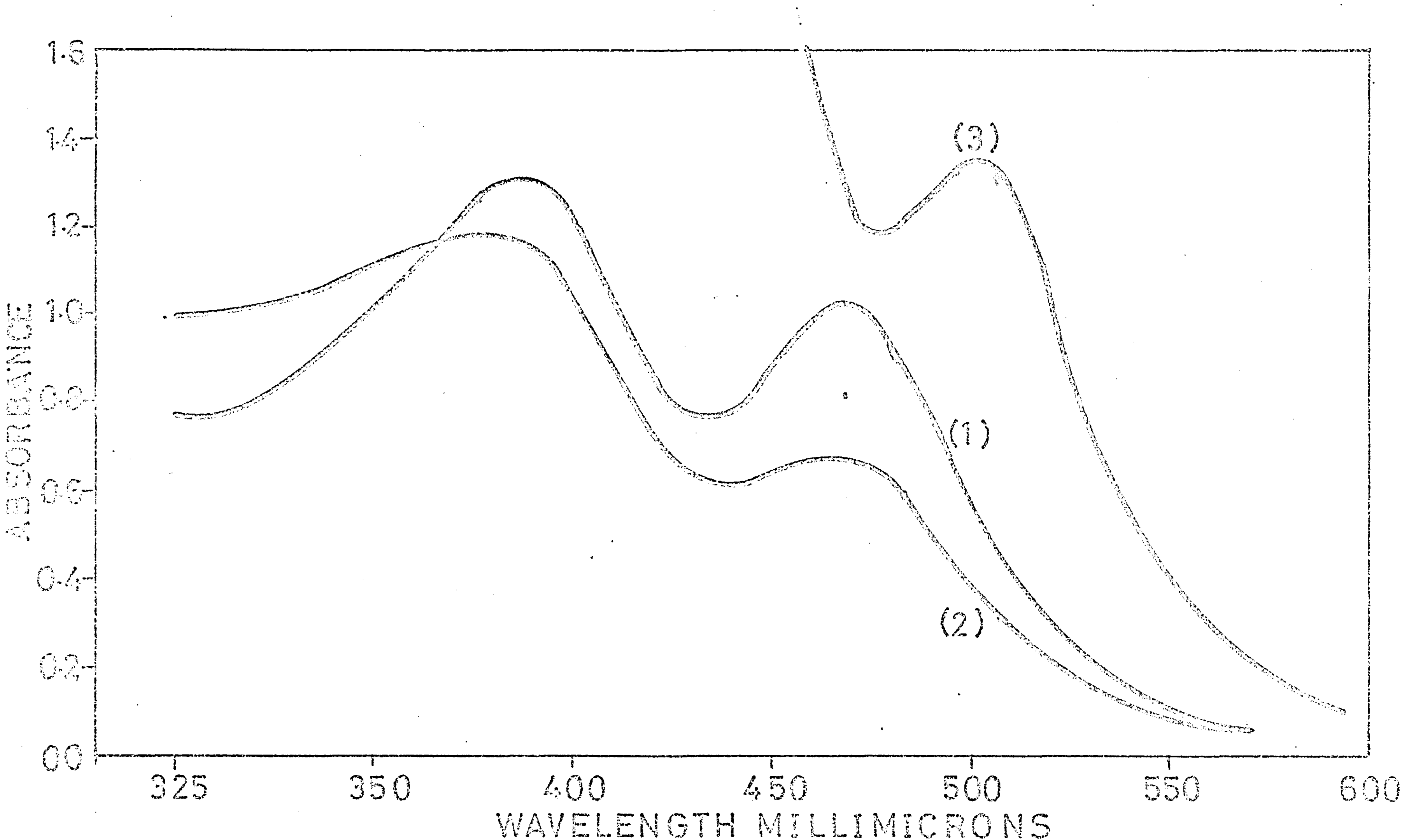
Absorption spectra of $PdCl_4^{2-}$ during extraction by 10% v/v tetraheptylammonium chloride in benzene. (1) Aqueous feed solution. (2) Aqueous raffinate. (3) Organic extract.



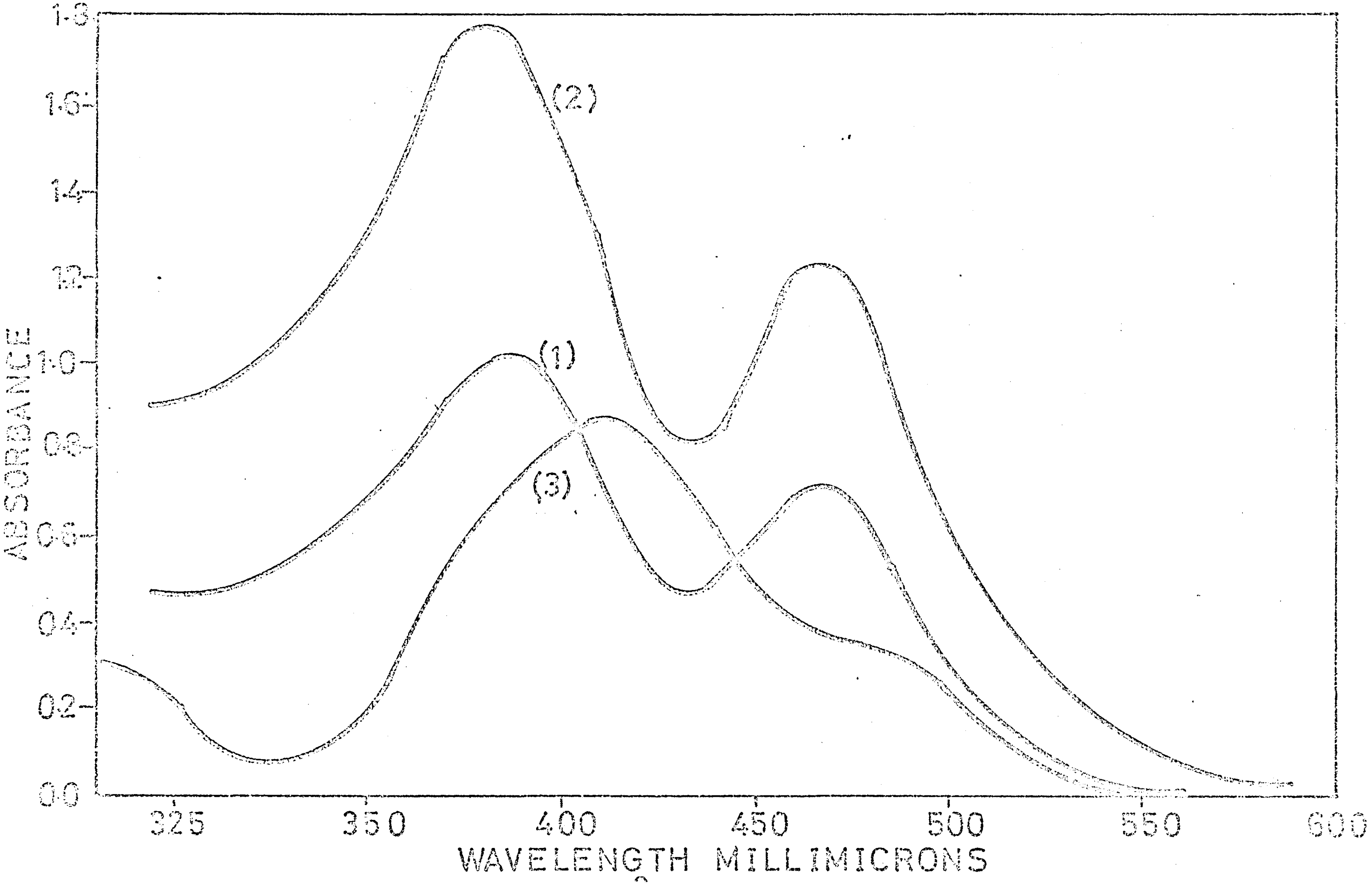
Absorption spectra of $PtCl_6^{2-}$ during extraction by 10% v/v 2 amino-dodecane in benzene. (1) Aqueous feed solution. (2) Aqueous raffinate. (3) Organic extract.



Absorption spectra of $PtCl_6^{2-}$ during extraction by 10% v/v tetraheptylammonium chloride in benzene. (1) Aqueous feed solution. (2) Aqueous raffinate. (3) Organic extract.

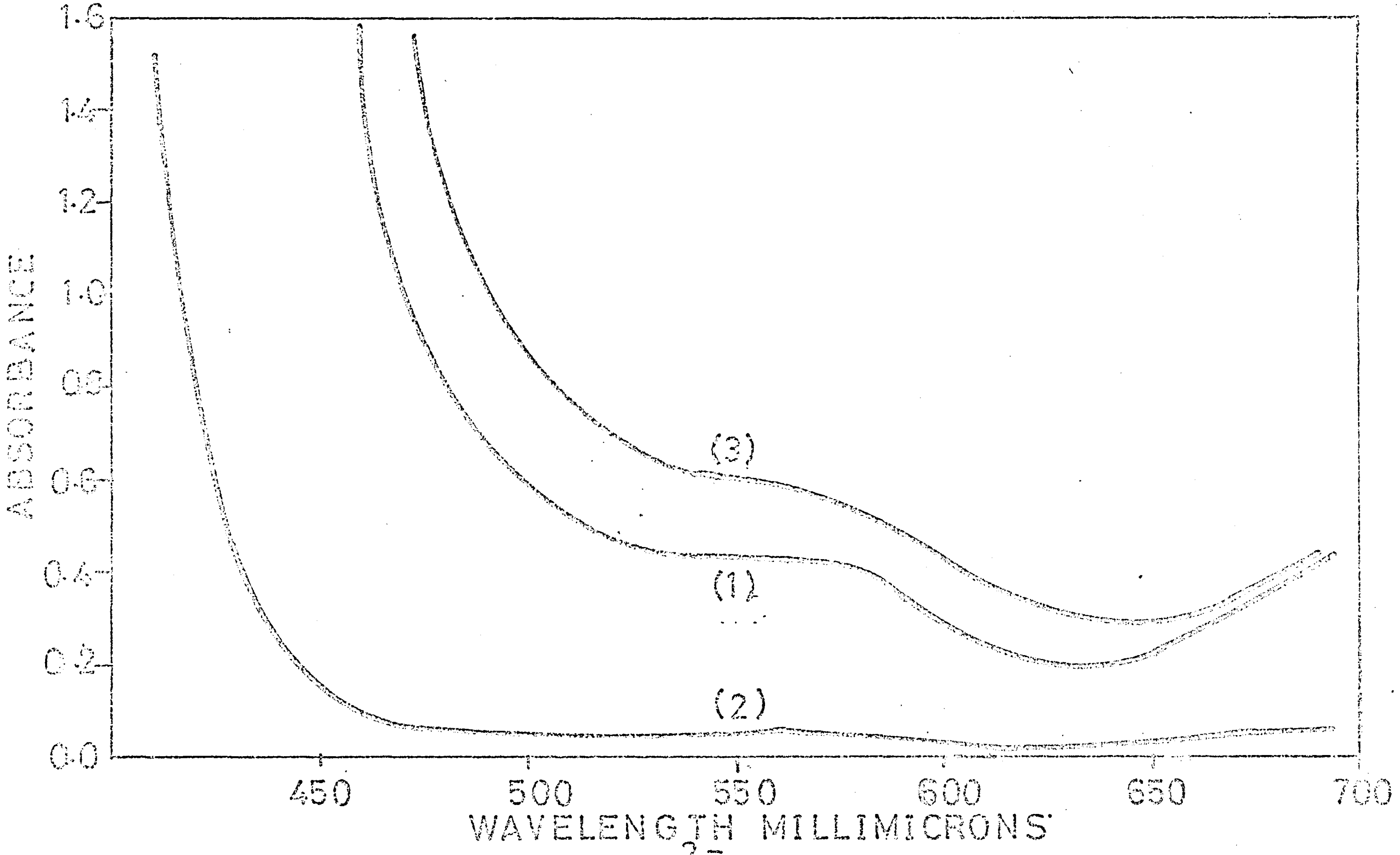


Absorption spectra of $RuCl_6^{3-}$ during extraction by 10% 2 amino-dodecane in benzene. (1) Aqueous feed solution. (2) Aqueous raffinate. (3) Organic extract.



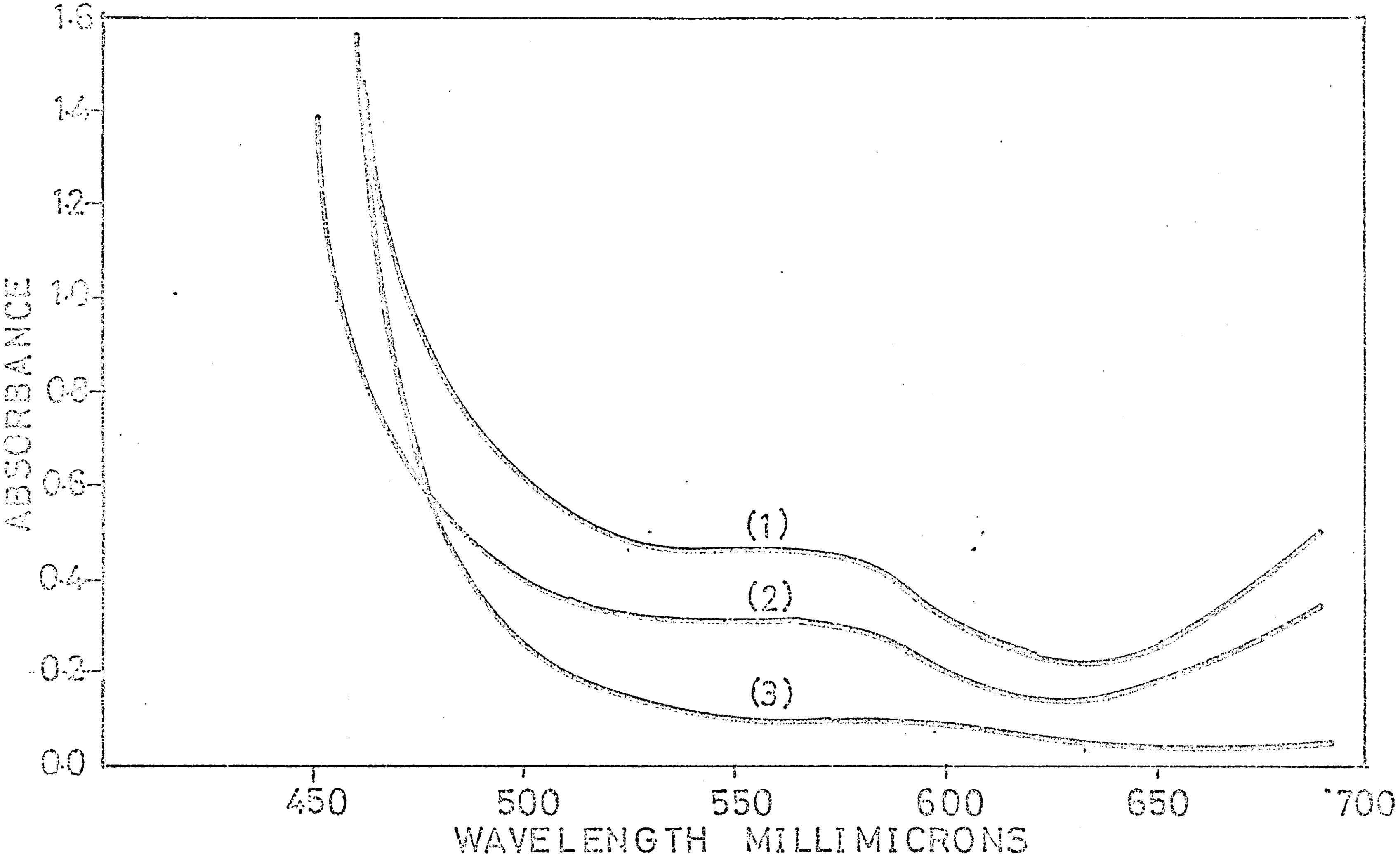
Absorption spectra of $RuCl_6^{3-}$ during extraction by 10% v/v tetraheptylammonium chloride in benzene. (1) Aqueous feed solution (2) Aqueous raffinate. (3) Organic extract.

FIG. 20



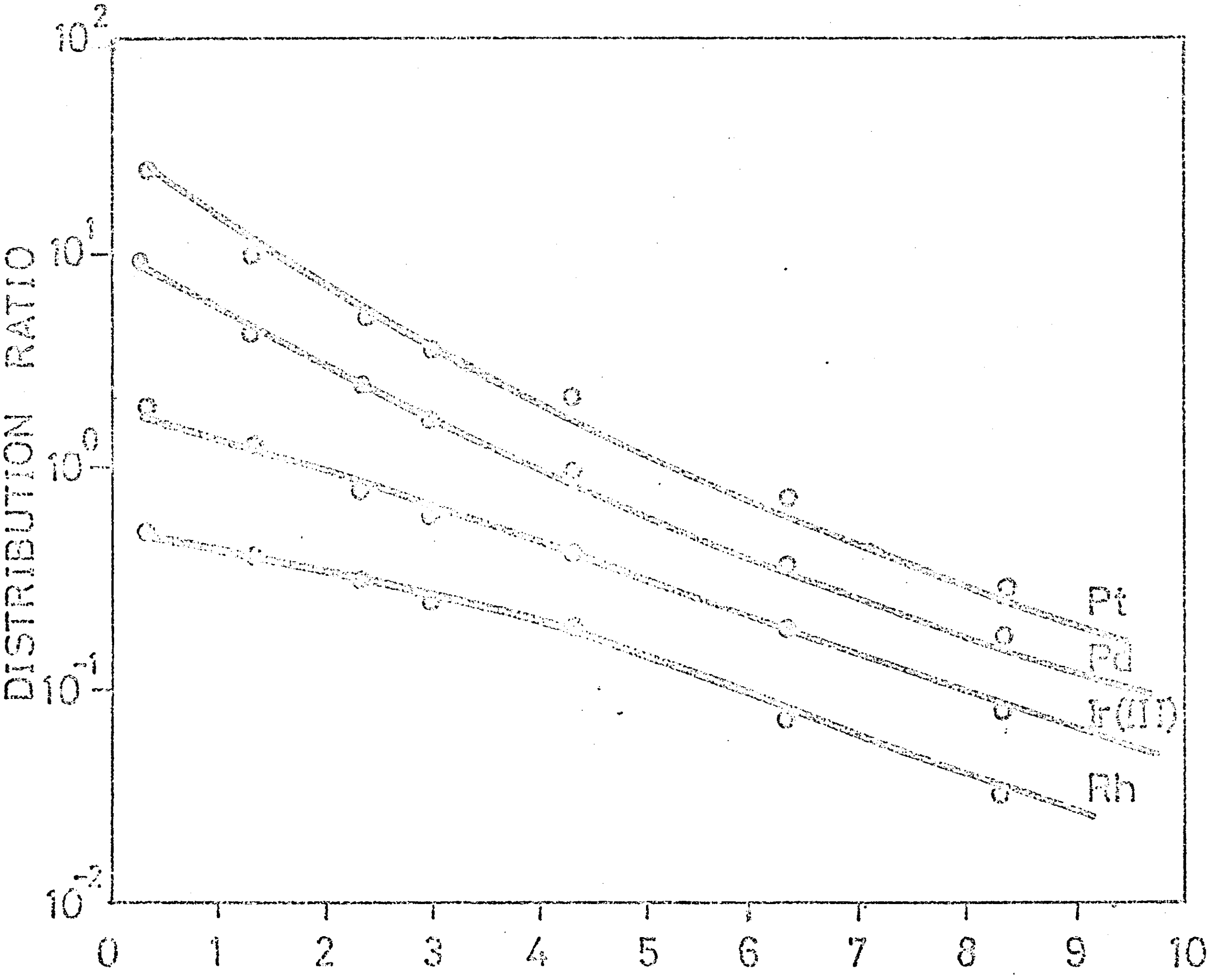
Absorption spectra of $OsCl_6^{2-}$ during extraction by 10% v/v 2 amino-dodecane in benzene. (1) Aqueous feed solution. (2) Aqueous raffinate. (3) Organic extract.

FIG. 21



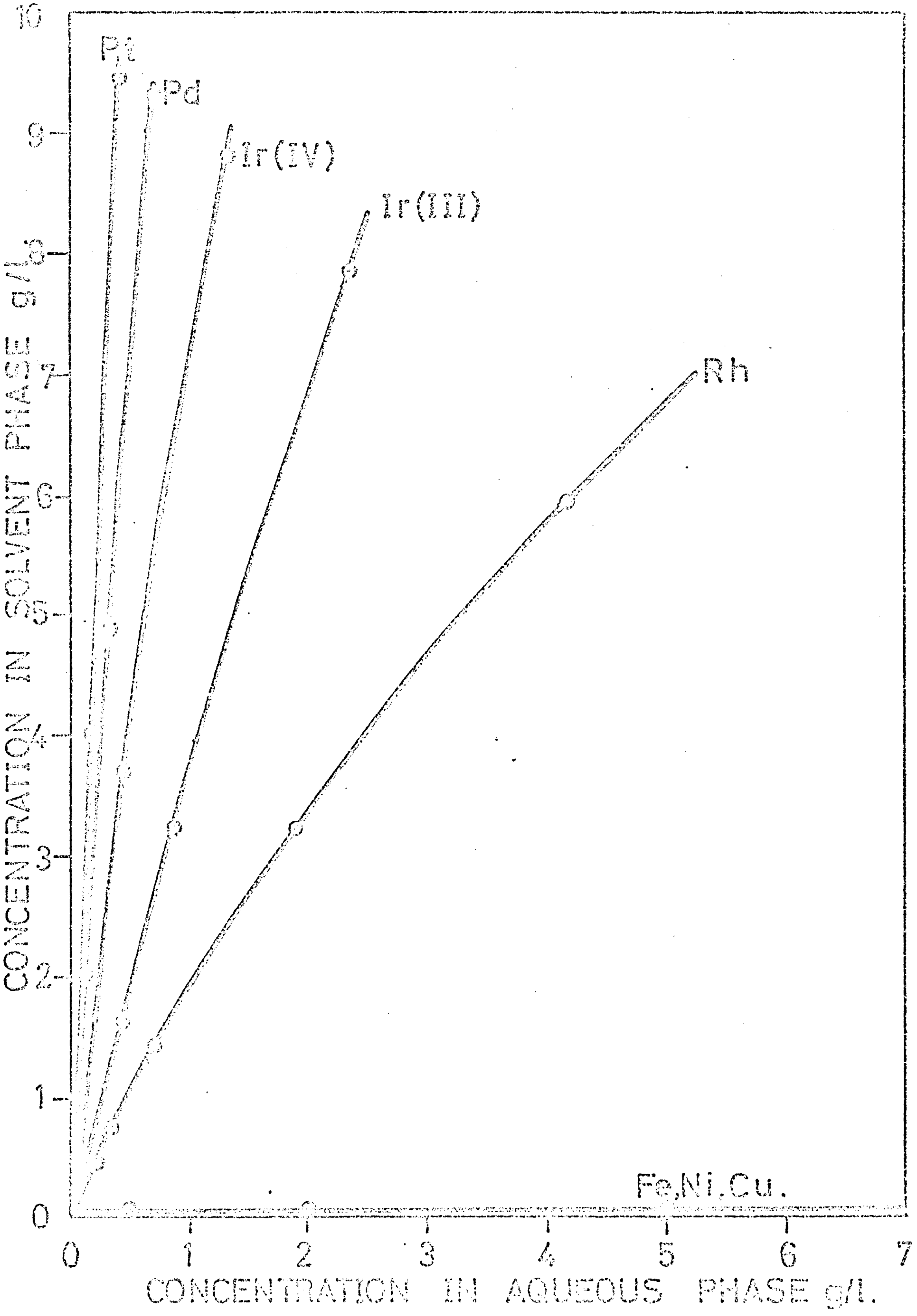
Absorption spectra of $OsCl_6^{2-}$ during extaction by 10% v/v tetraheptylammonium chloride. (1) Aqueous feed solution. (2) Aqueous raffinate. (3) Organic extract.

FIG.22



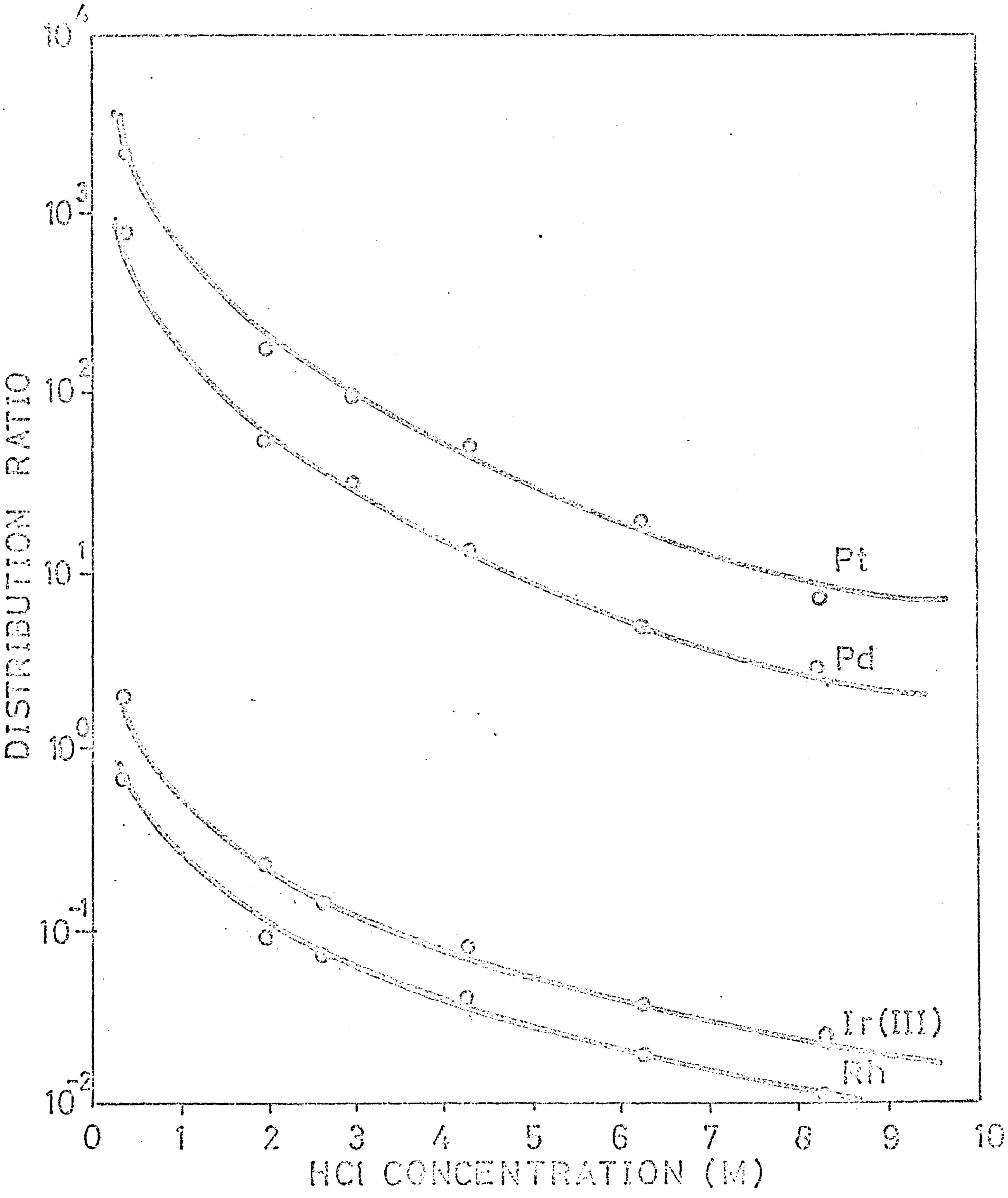
Extraction of platinum metals by Primene 81-R (10% v/v) in Solvesso 150. Metal concentration 0·01M.

FIG. 23



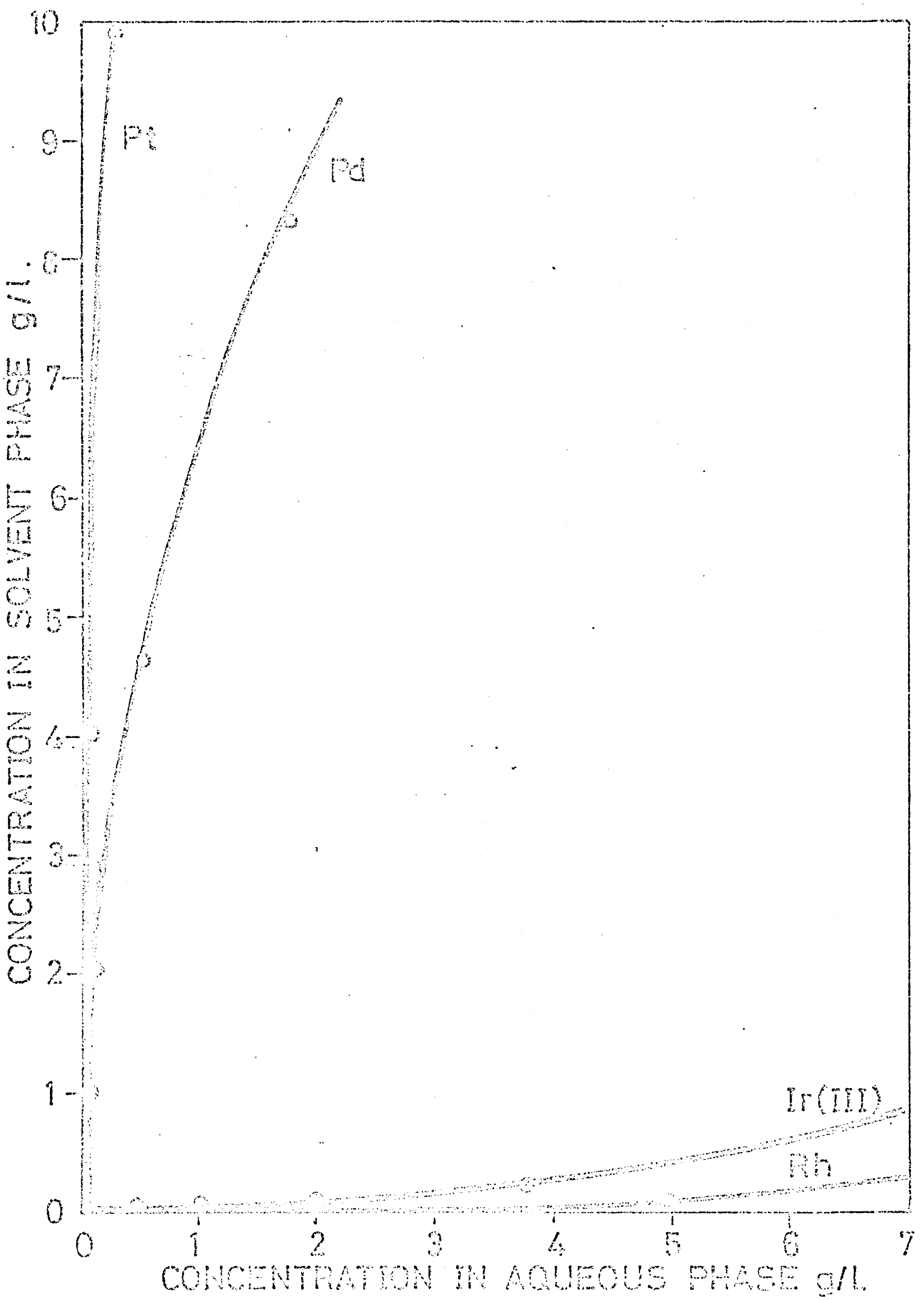
Distribution of platinum and base metals between 1M HCl and 20% v/v Primene 81-R in Solvesso 150.

FIG.24



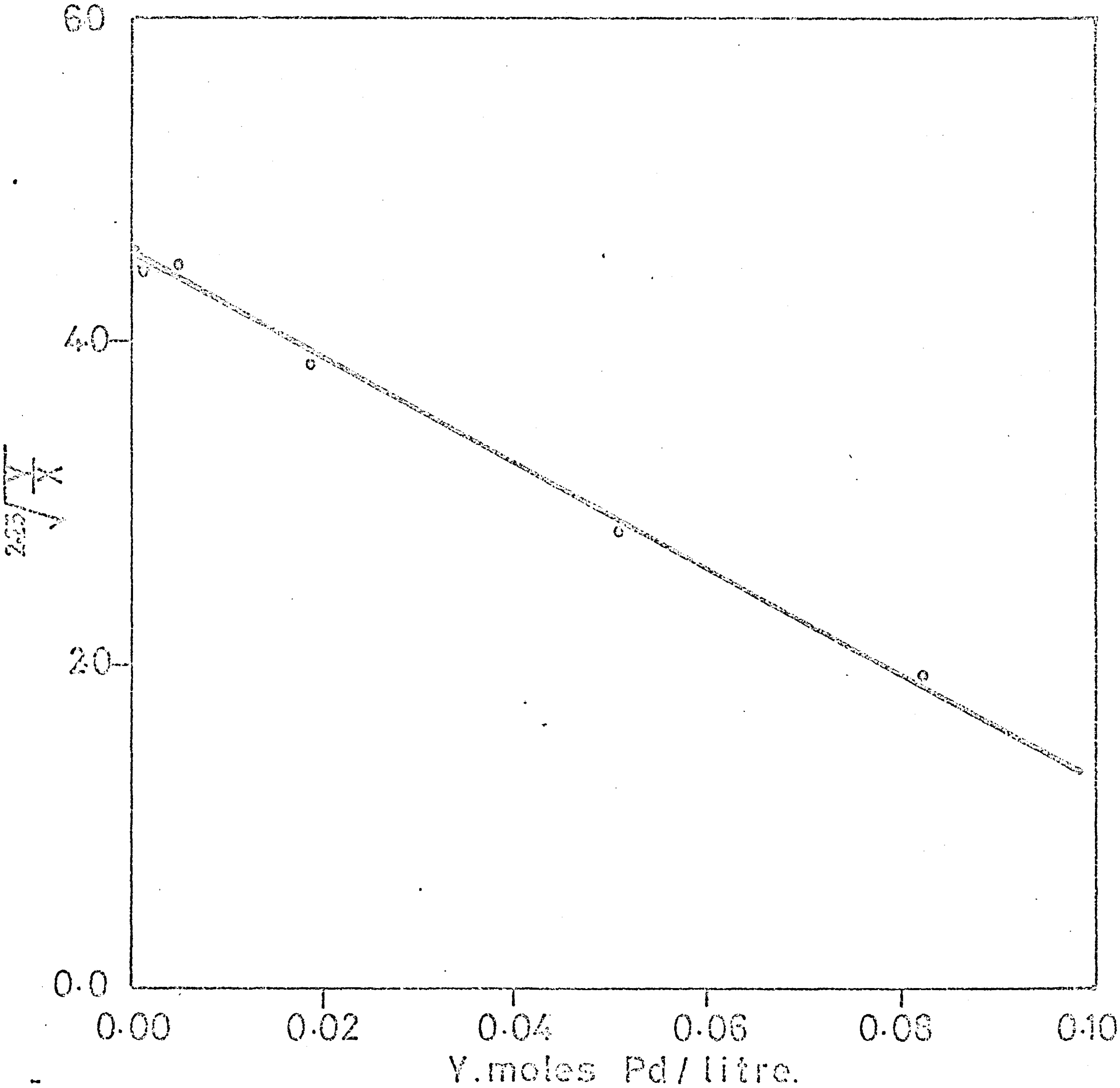
Extraction of platinum metals by Alamine 336 (10% v/v) in Solvesso 150. Metal concentration 0·01M.

FIG.25



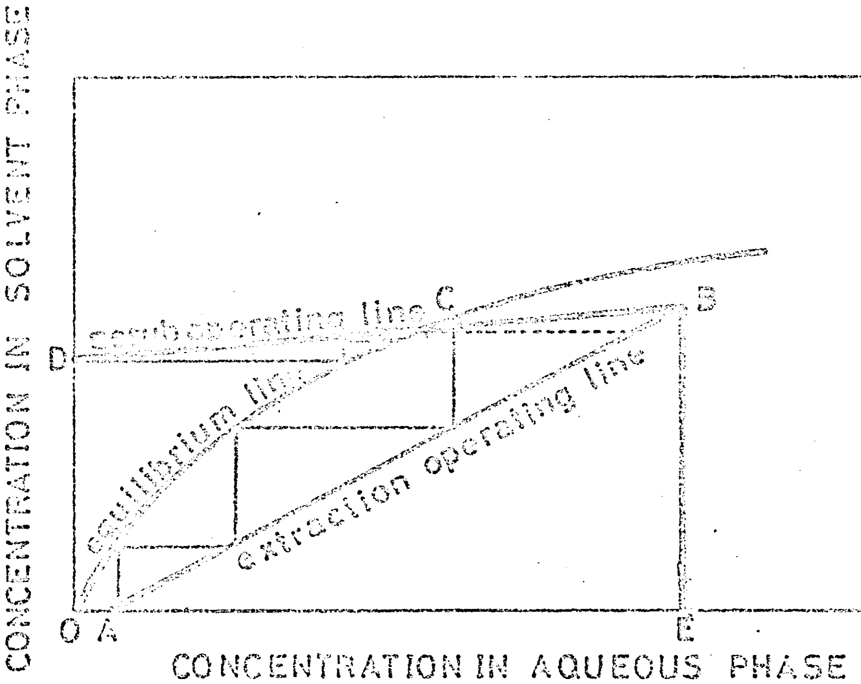
Distribution of platinum metals between 3M HCl and 10% v/v Alamine 336 in Solvesso 150.

FIG.26



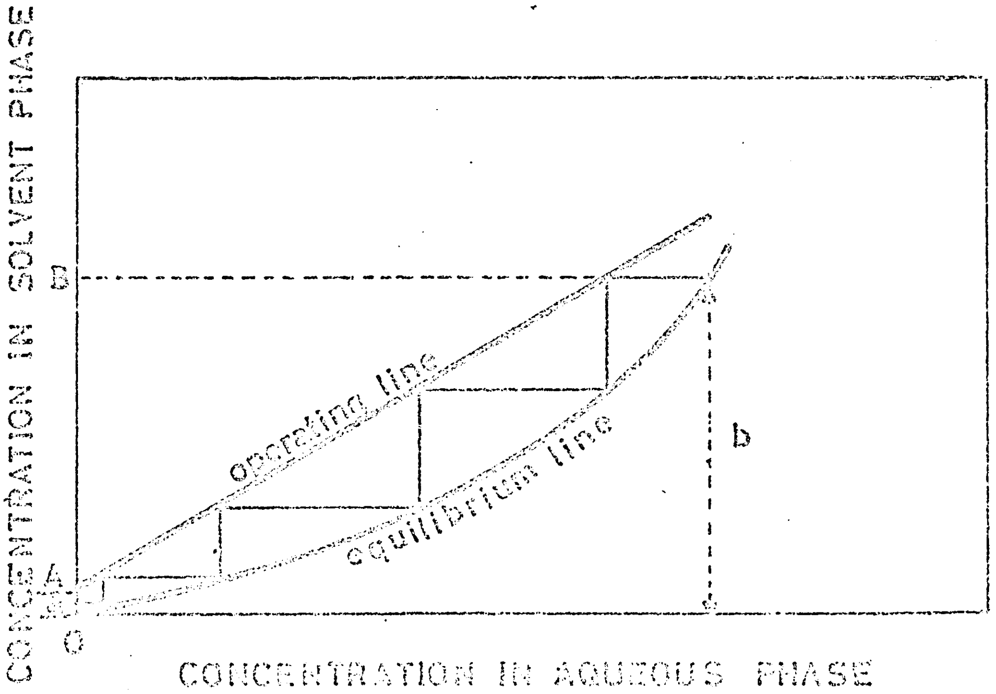
Extraction isotherm of palladium by Alamine 336 plotted as $\left[\frac{Y}{X}\right]^{1/n}$ vs. Y according to the analysis of Lloyd and Oertel.

FIG. 27

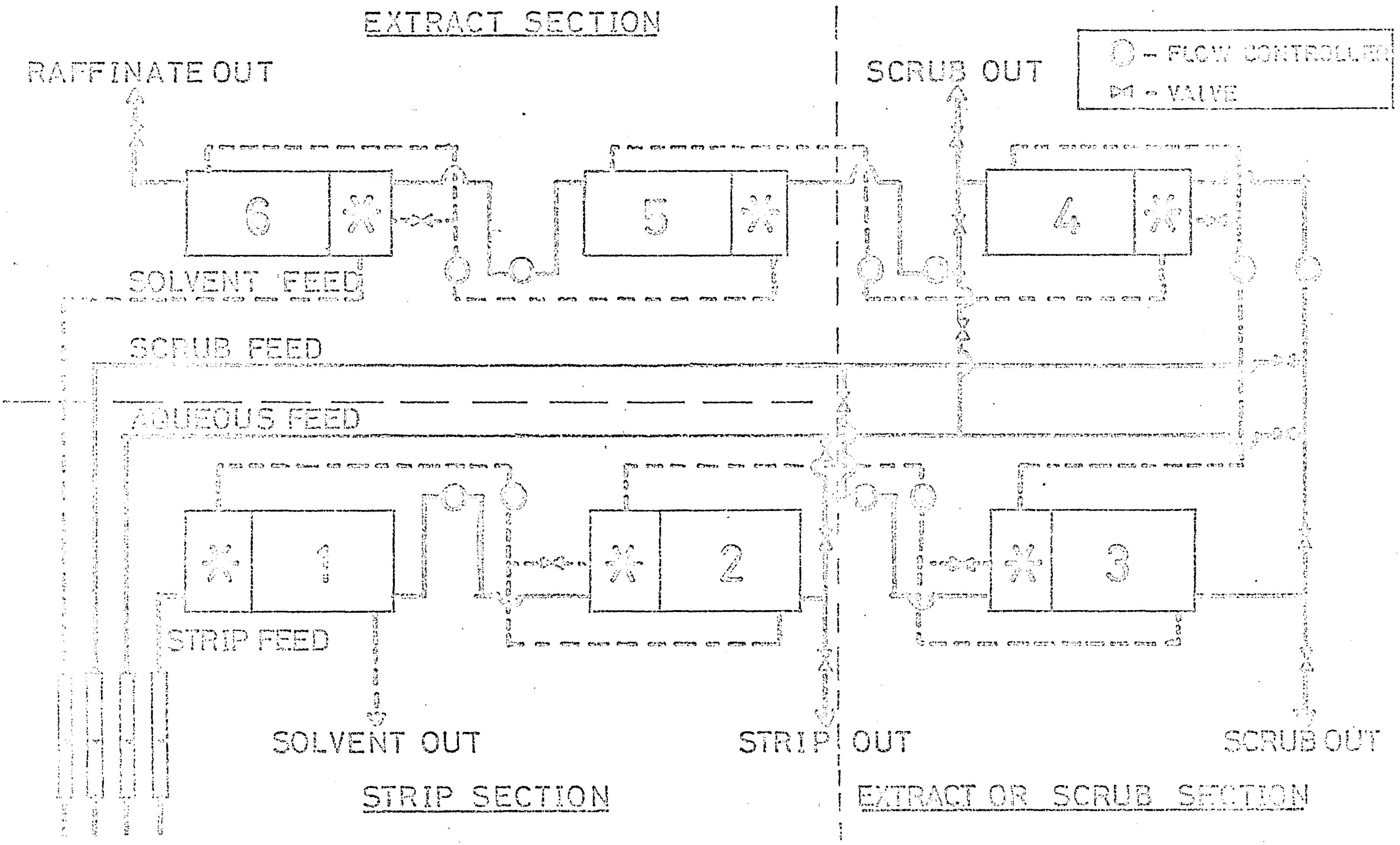


Equilibrium diagram for extraction and scrubbing of solute with curved equilibrium line.

FIG. 28

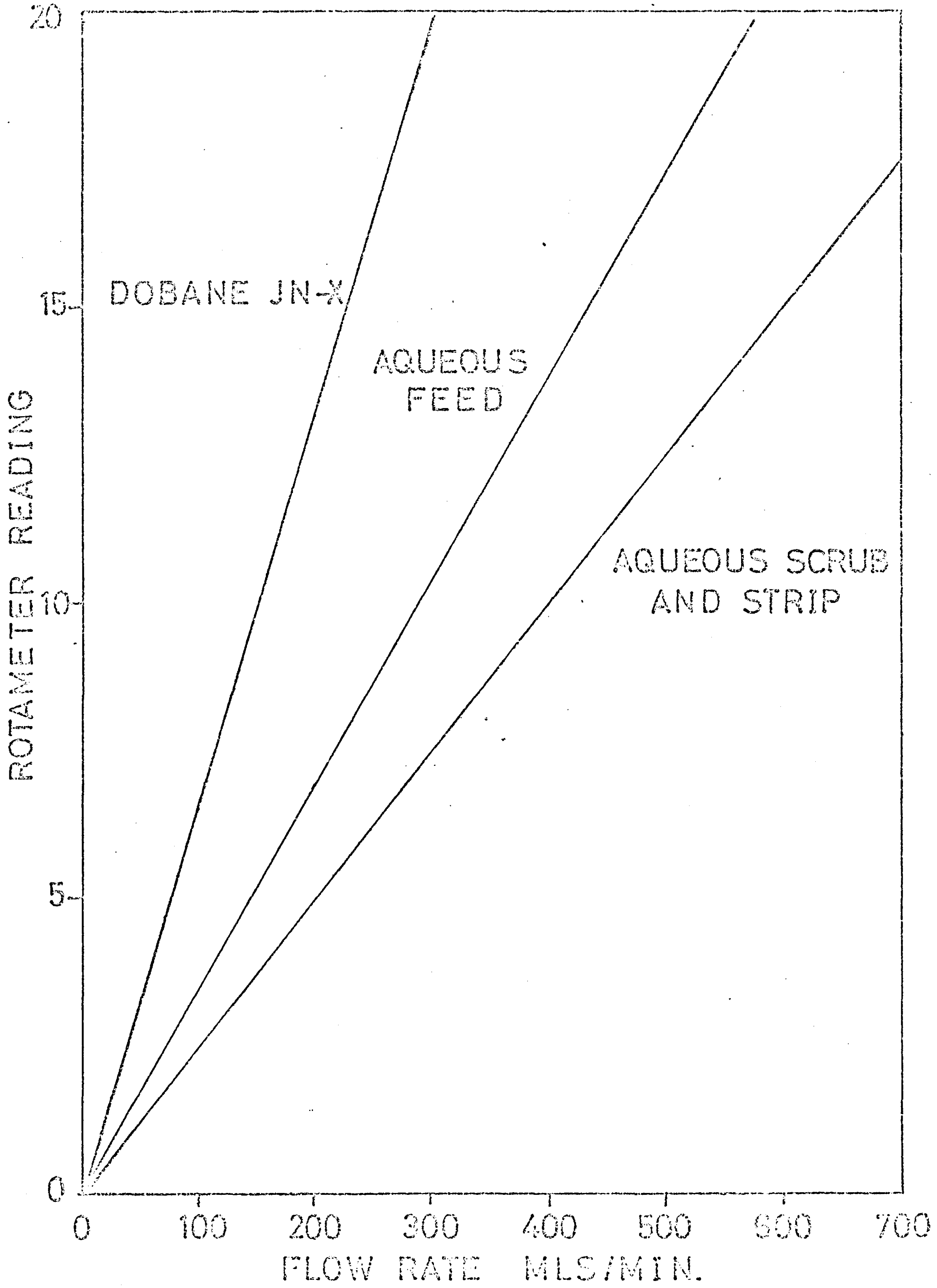


Equilibrium diagram for stripping of solute.

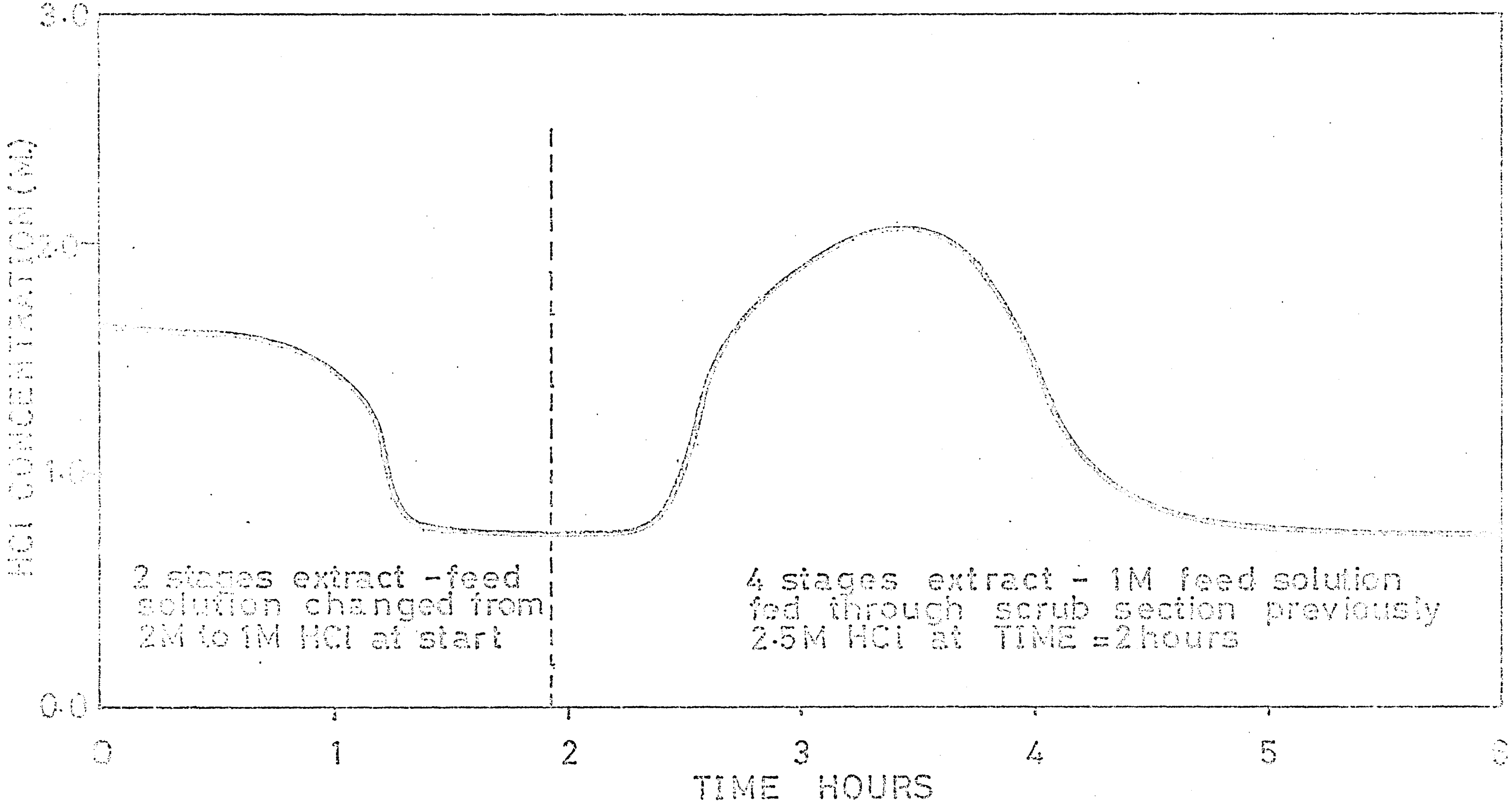


Diagramatic view of six stage mixer-settler unit.

FIG.30

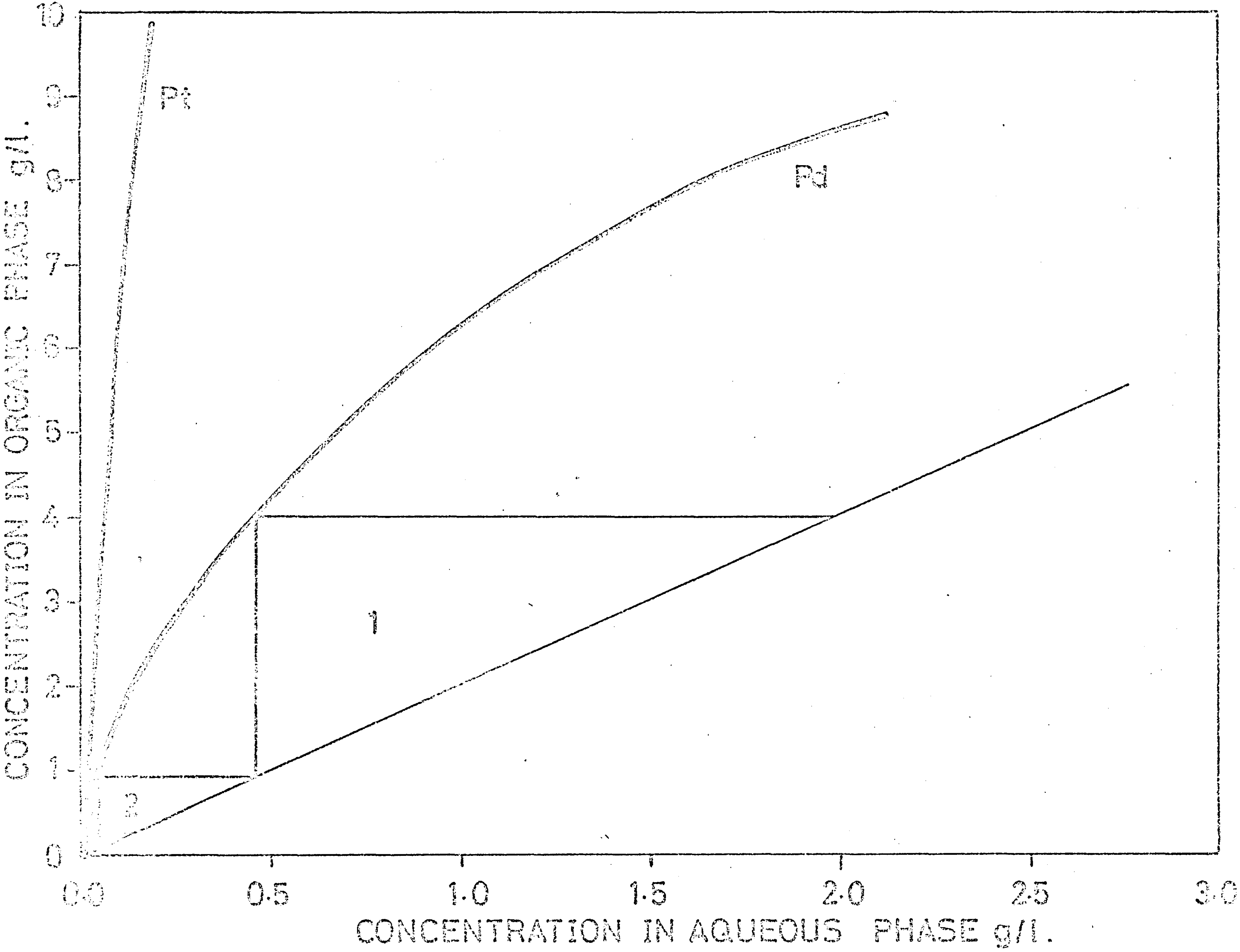


Rotameter calibration chart.



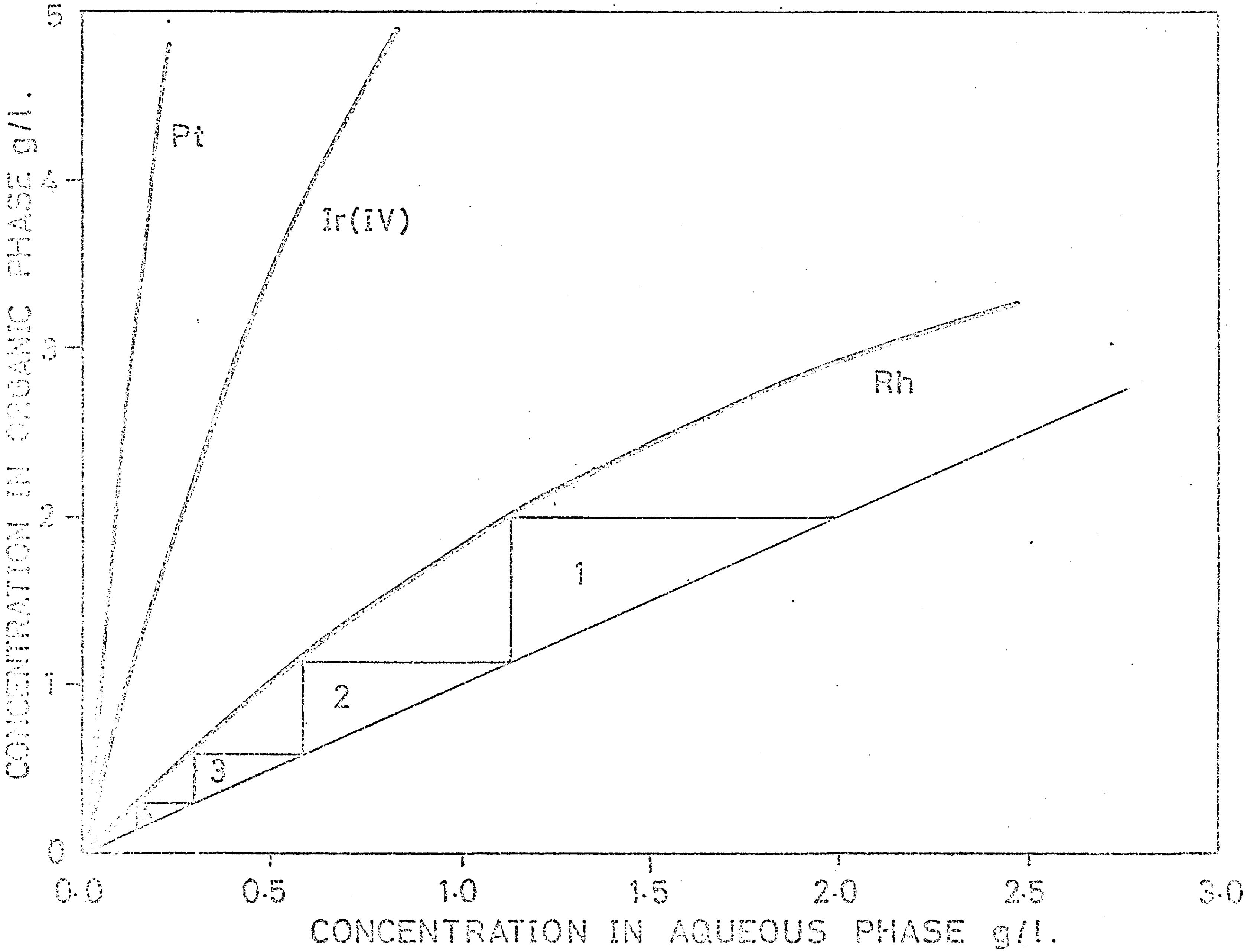
Response characteristics of 6 stage mixer-settler unit. Response of raffinate HCl concentration to stepwise changes in input conditions.

FIG. 37

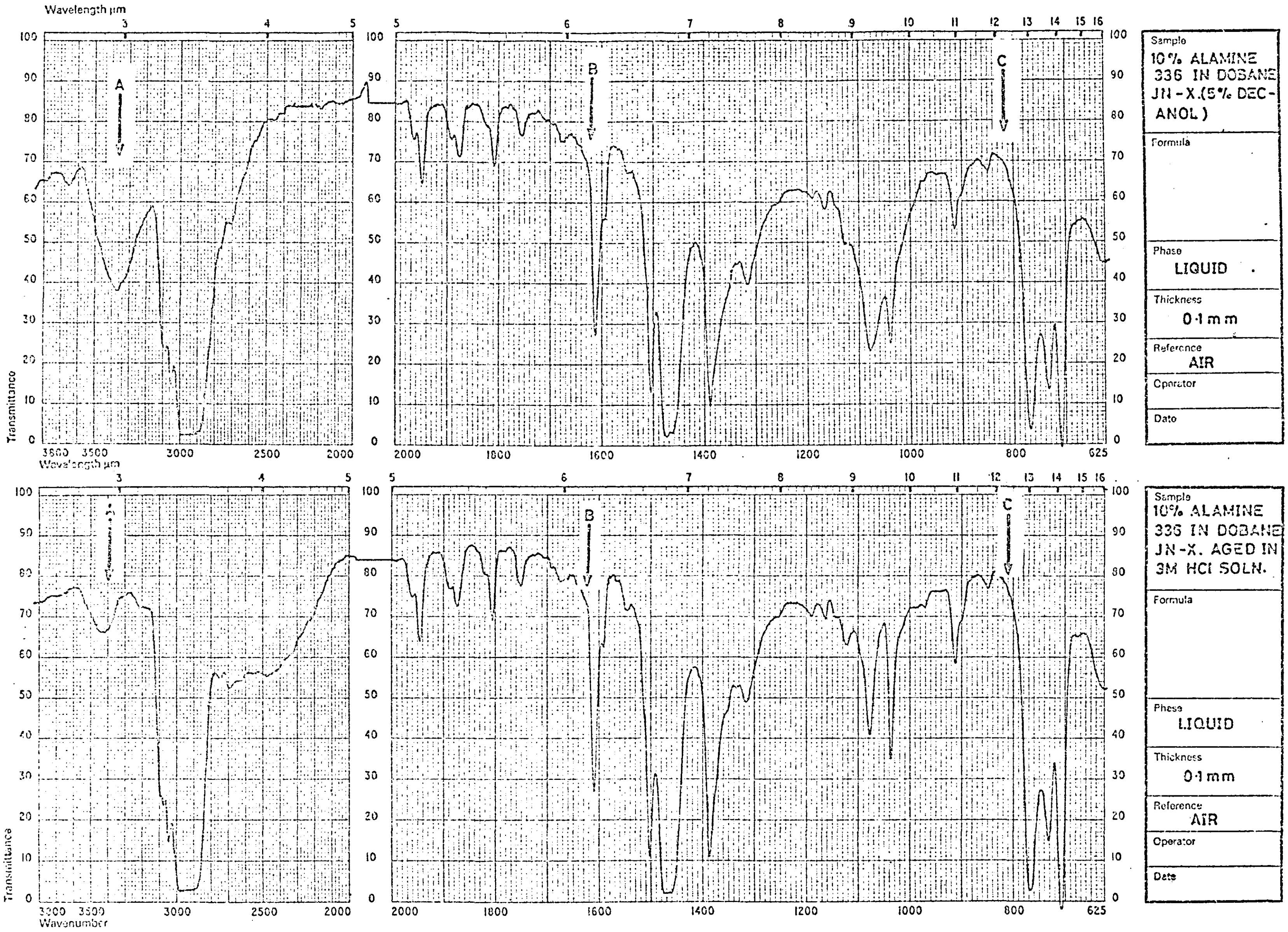


McCabe – Thiele equilibrium isotherm for extraction of palladium by Alamine 336 showing 2 stages. Phase flow ratio 1:2.

FIG. 33



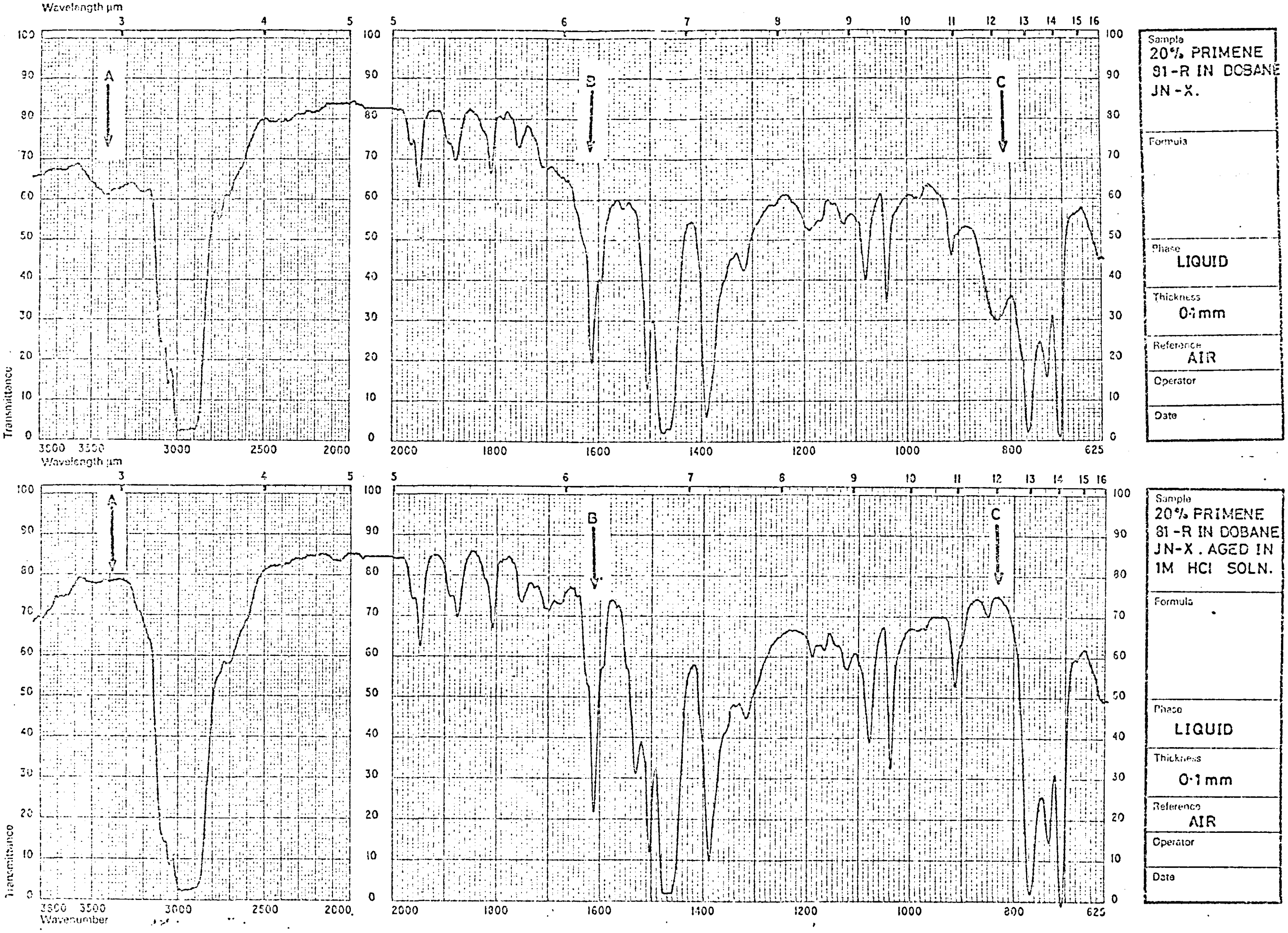
McCabe–Thiele equilibrium isotherm for extraction of rhodium by Primene 81-R showing 4 stages. Phase flow ratio 1:1.



Sample
10% ALAMINE 336 IN DOBANE JN-X.(5% DECANOL)
Formula
Phase
LIQUID
Thickness
0·1 mm
Reference
AIR
Operator
Date

Sample
10% ALAMINE 336 IN DOBANE JN-X. AGED IN 3M HCl SOLN.
Formula
Phase
LIQUID
Thickness
0·1 mm
Reference
AIR
Operator
Date

I.R. spectra for fresh and aged Alamine 336 solutions.



Sample
20% PRIMENE
81-R IN DOBANE
JN-X.

Formula

Phase
LIQUID

Thickness
0·1 mm

Reference
AIR

Operator

Date

Sample
20% PRIMENE
81-R IN DOBANE
JN-X. AGED IN
1M HCl SOLN.

Formula

Phase
LIQUID

Thickness
0·1 mm

Reference
AIR

Operator

Date

I.R. spectra for fresh and aged Primene 81-R solutions

PLATE 1.

Mixer-Settler Unit showing glass float flow-controllers, mixed-phase inlet baffle and adjustable outlet wier.

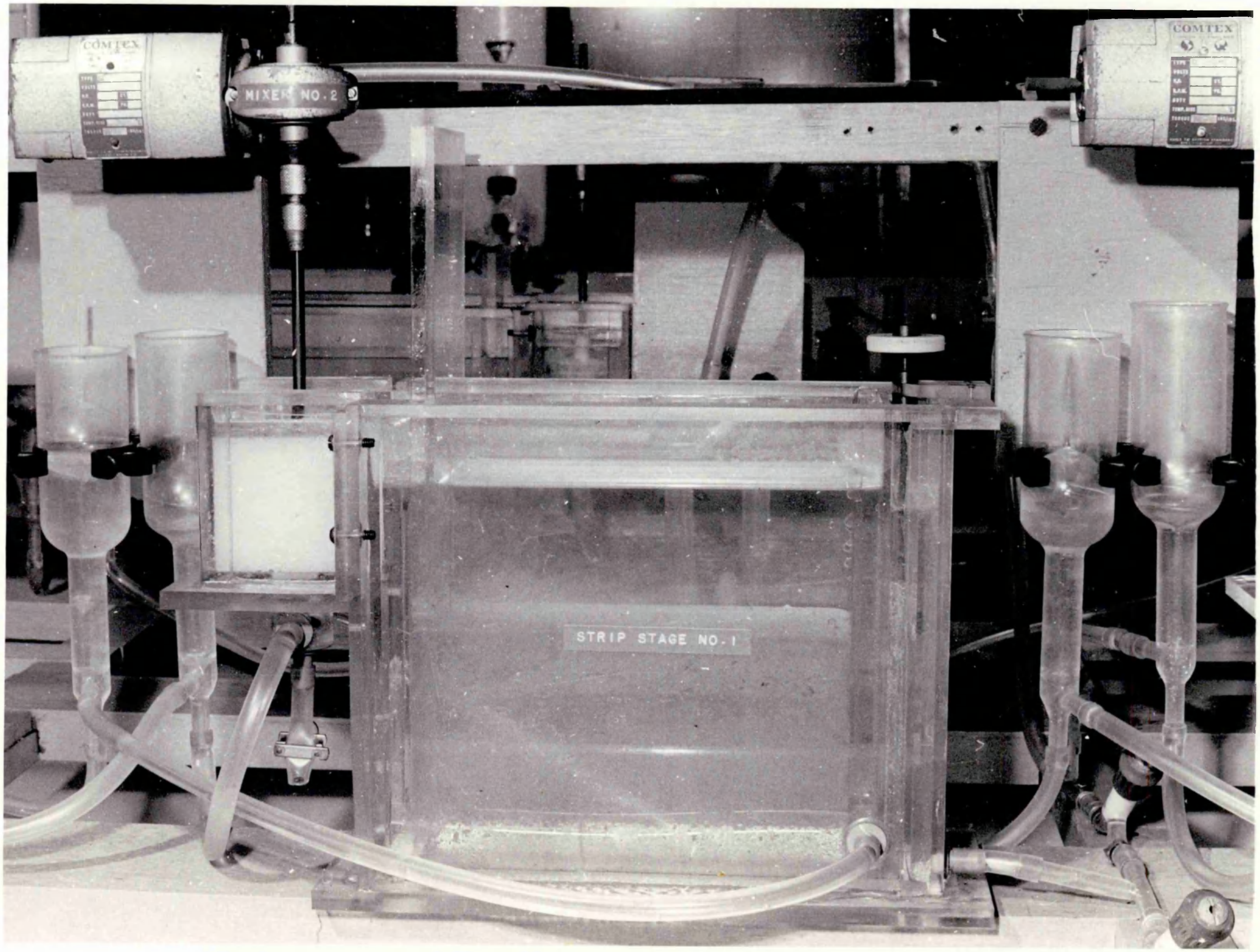

COMTEX
MIXER NO. 2
COMTEX
STRIP STAGE NO. 1

PLATE 2

General view of multistage mixer-settler test rig showing bed, motor gantries and control board.

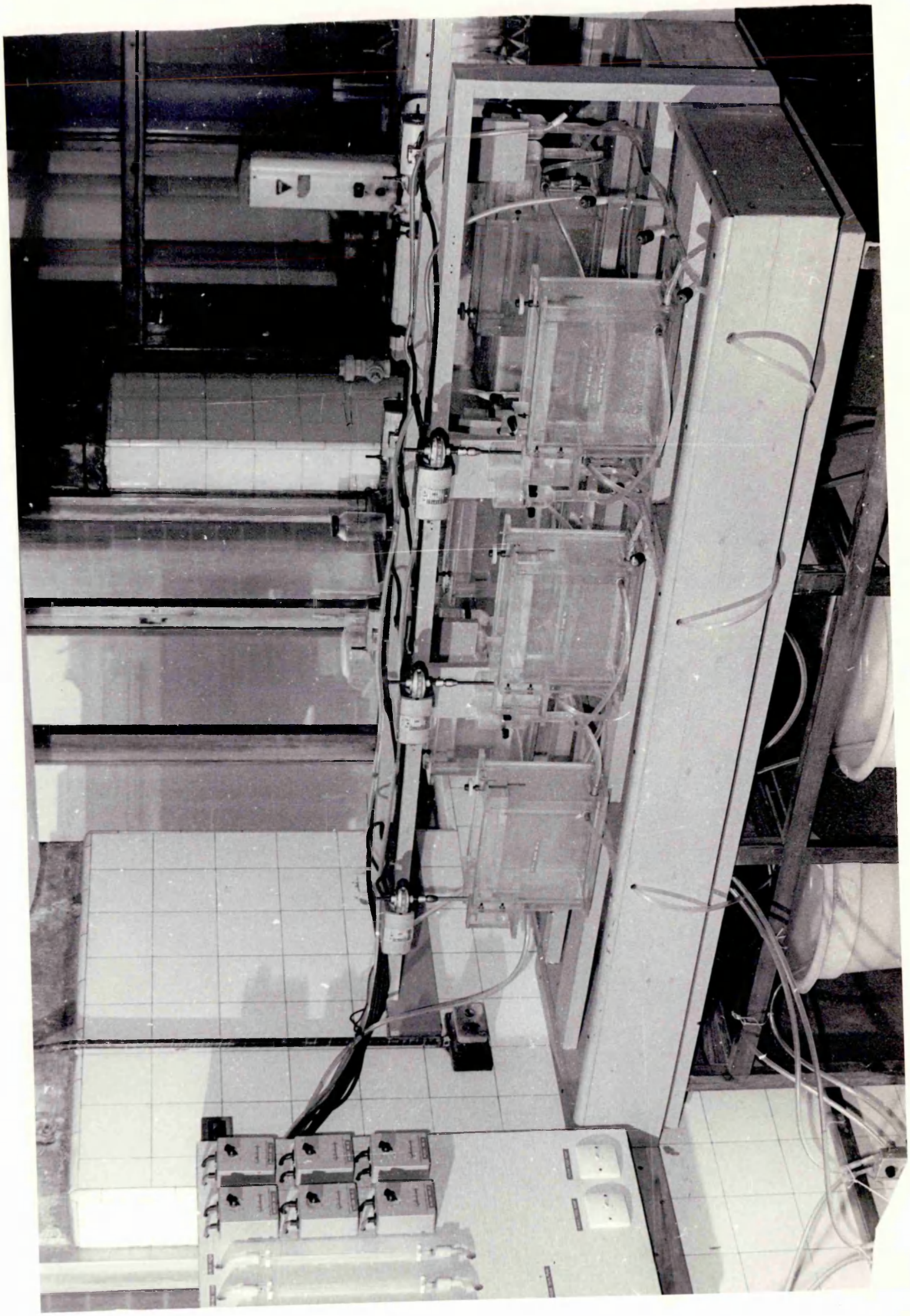
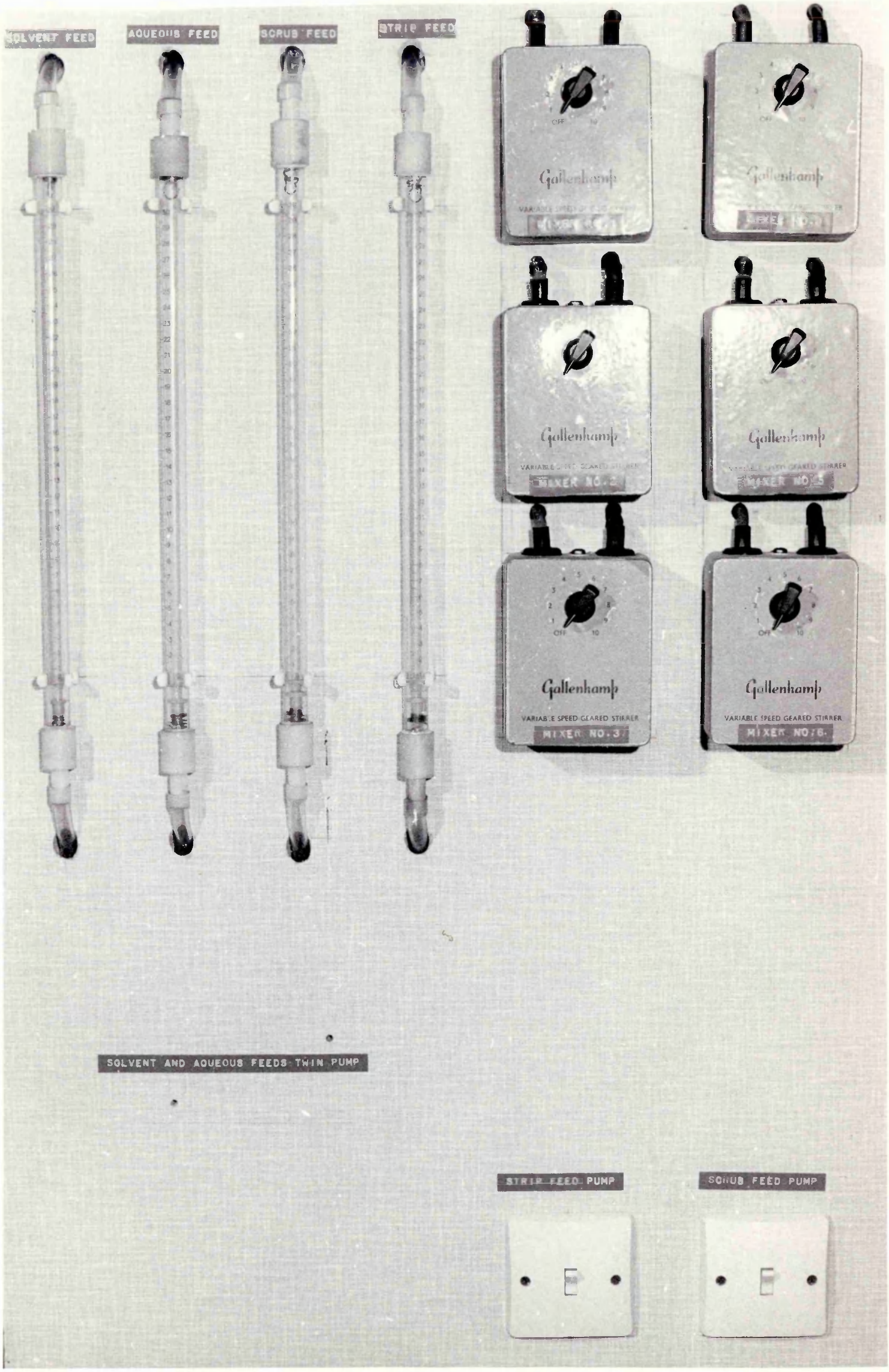


PLATE 3

Layout of control board showing rotameters and stirrer motor speed controllers.


SOLVENT FEED
AQUEOUS FEED
SCRUB FEED
STRIP FEED
Gallenkamp
MIXER NO. 2
MIXER NO. 5
VARIABLE SPEED GEARED STIRRER
MIXER NO. 3
MIXER NO. 6
SOLVENT AND AQUEOUS FEEDS TWIN PUMP
STRIP FEED PUMP
SCRUB FEED PUMP

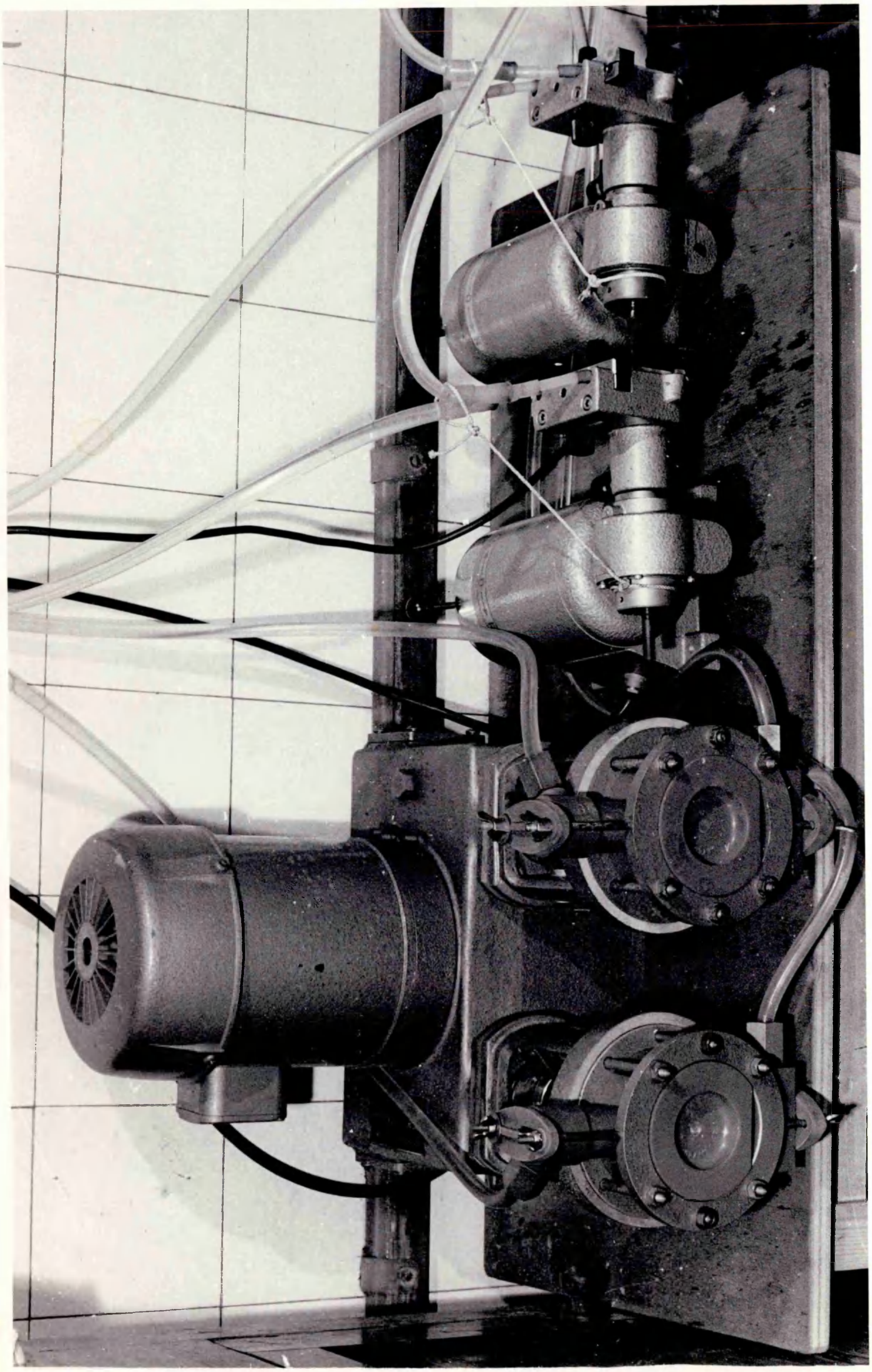
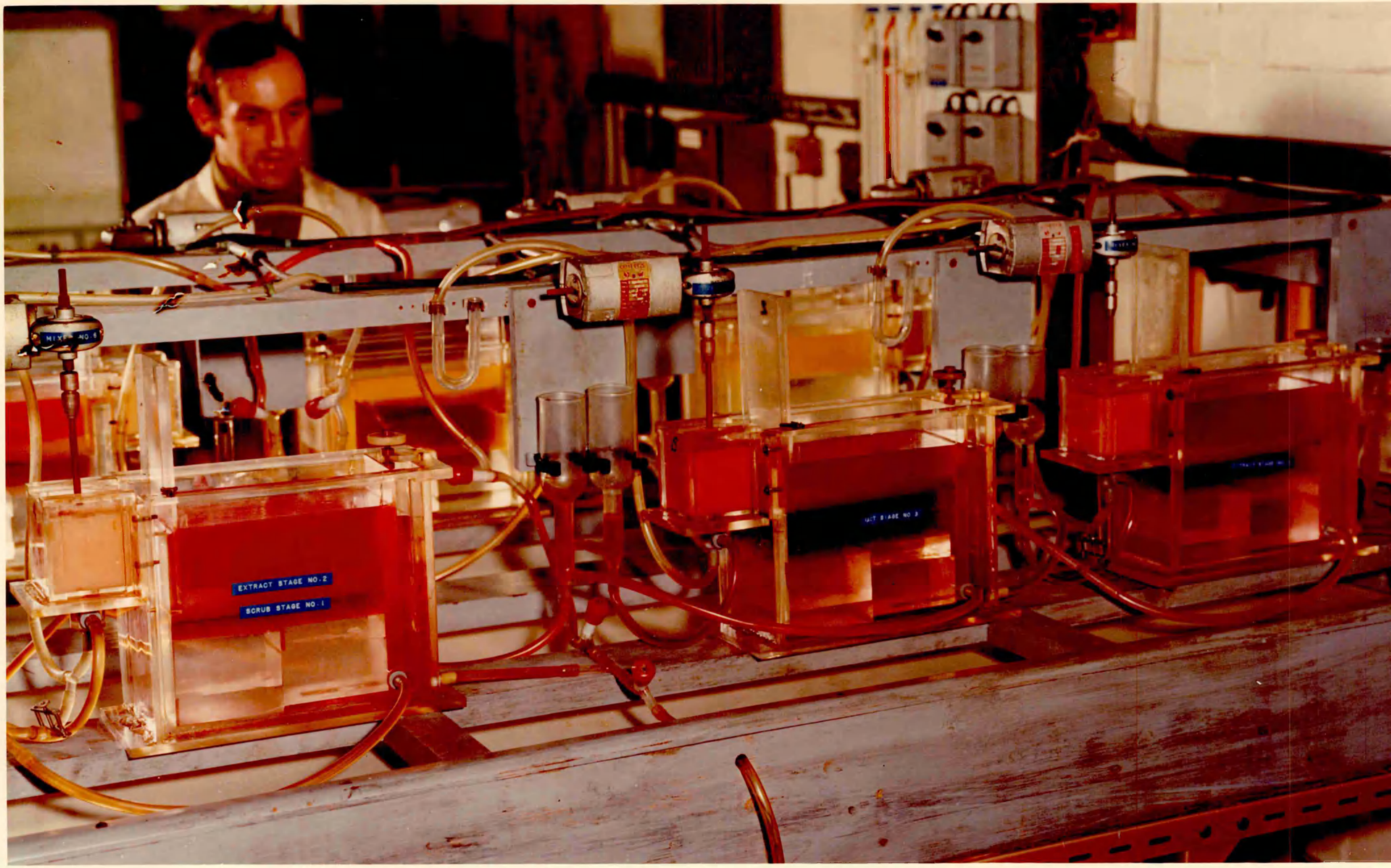


PLATE 5

General view of mixer-settler rig during continuous testing of Alamine 336 for separation of platinum and rhodium. (Extract section, centre and right foreground; scrub section left foreground; strip section background).


MIXER NO. 6
EXTRACT STAGE NO. 2
SCRUB STAGE NO. 1
ACT STAGE NO. 3

Appendix A

Statistical Considerations

Due to the very large number of experiments involved and the relatively short half-lives of some radiotracers it was considered impractical to determine the statistical errors of every single distribution ratio measured which would have required triplicate determinations. Instead periodic statistical tests were made on both the errors in radiometric measurements and in the experimental procedure.

1. Errors in Radioactivity Measurements: Radioactive disintegration is an essentially statistical phenomenon in which it can be shown [98] that when two conditions are obeyed, the binomial distribution law gives the standard deviation, σ, of any count rate, M from its square root:

$$\sigma = \sqrt{M}$$

The two conditions are that the measurement time is short in relation to the half-life and that the number of radio-active atoms being observed is large, which is normally the case in practice.

Hence if 10^4 counts are recorded, the standard deviation is $\pm\ 10^2$ or about 1%. However, where a function such as a distribution ratio is involved while there may be a very large difference between the relative concentrations in the two phases there may be a standard deviation difference between them of upto $\pm$ 10%. Since the standard deviation propagated by the division of one error by another is given by:

$$\frac{\sigma^2_{\bar{x}/\bar{y}}}{\bar{x}^2/\bar{y}^2} = \frac{\sigma^2_{\bar{x}}}{\bar{x}^2} + \frac{\sigma^2_{\bar{y}}}{\bar{y}^2}$$

where $\bar{x}$ and $\bar{y}$ are the arithmetic means,

the error in the low concentration phase becomes dominant

2. Experimental Error: Random experimental errors may be measured

by determining the standard deviation of a set of otherwise identical extractions from

$$\sigma_{\bar{x}}^{\,2} = \frac{1}{N_o - 1} \sum_{i=1}^{No} (x_i - \bar{x})^2$$

where No is number of experiments of average count rate $\bar{x}$.

In the table below is shown a typical statistical test on extraction of Ir(III) chlorocomplex by 2-aminododecane. Each count is an average of three counts of 100 seconds duration on each phase. σ_{DR} values were computed using an Olivetti 101 desk computer.

No	$\overline{Org}$	$\overline{Aq}$	$\overline{B.G.}$	$\sigma_{\overline{Org}}$	$\sigma_{\overline{Aq}}$	$\sigma_{\overline{B.G.}}$	$\bar{x}$	$\bar{y}$	$\sigma_{\bar{x}}$	$\sigma_{\bar{y}}$	DR	σ_{DR}
1	42992	4396	2782	208	67	53	40244	1614	214	85	24.9	1.32
2	42510	4361	2782	206	66	53	39728	1569	213	84	25.3	1.36
3	46813	4592	2782	216	68	53	44031	1807	223	86	20.7	1.17

$\bar{x}$ = organic phase activity - Background

$\bar{y}$ = aqueous phase activity - Background

The standard deviation in experimental error was calculated to be ± 0.31 which was significantly less than the intrinsic error in the analytical procedure. Thus with distribution ratios significantly larger or smaller than one, the radiometric error predominated.

Appendix B

Linear Regression Analysis

Using an Olivetti 101 desk computer a computer programme was used to calculate the "n" values in equation (31) and their standard errors. This programme computed the parameters a and b of the "least squares" regression line

$$Y = a + bX$$

through a set of N points, and their errors.

Formula Used

$$\text{Let } Sx^2 = \sum X^2 - \frac{1}{N}\left(\sum X\right)^2$$

$$Sy^2 = \sum Y^2 - \frac{1}{N}\left(\sum Y\right)^2$$

$$Sxy = \sum XY - \frac{1}{N}\sum X \sum Y.$$

$$\bar{X} = \frac{1}{N}\sum X \qquad \bar{Y} = \frac{1}{N}\sum Y$$

Then $$b = \frac{Sxy}{Sx^2}$$

$$a = \bar{Y} - b\bar{X}$$

Standard of error of b, $$\sigma_b = \sqrt{\frac{1}{N-2}\frac{Sy^2}{Sx^2} - b^2}$$

Standard error of a, $$\sigma_a = \sigma_b\sqrt{\frac{1}{N}\sum X^2}$$