Radiochemical investigations of the separation of chemical elements using N-benzoyl-n-phenylhydroxylamine

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RADIOCHEMICAL INVESTIGATIONS OF THE SEPARATION OF CHEMICAL ELEMENTS USING N-BENZOYL-N-PHENYLHYDROXYLAMINE

THESIS

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DOCTOR OF PHILOSOPHY

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by

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MEMORANDUM

The work described in this thesis was carried out partly in the Londonderry Laboratory for Radiochemistry, Durham University, Durham and partly in the University Chemical Laboratory, Canterbury, Kent, between April 1963 and May 1966 under the supervision of Dr. S.J. Lyle, Lecturer in Radiochemistry.

The thesis contains the results of some original research by the author and no part of the material presented has previously been submitted by the candidate for a degree in this or any other university. Where use has been made of the results and conclusions of other authors in the relevant studies, care has been taken to ensure that the source of the information is always clearly indicated, unless it is of such general nature that indication is impracticable.

A.D. Shendrikar

ABSTRACT

A study has been made of the application of N-benzoyl-N-phenylhydroxylamine (NBPHA) to separations of a number of transition and main group elements by liquid-liquid extraction methods. In general the partition of each element from aqueous hydrochloric or perchloric acid has been examined as a function of acidity, reagent concentration in chloroform (the second phase), rate of extraction and range of metal ion concentration. Where extraction occurred only at low hydrogen ion concentrations an aqueous acetate buffer was employed. Back-extraction into aqueous phases of various compositions was also investigated. Niobium is thus separated from zirconium; niobium, tantalum, protactinium from each other; protactinium from uranium, thorium and its fission products and gallium, indium, thallium, germanium, tin and lead from each other.

A comparative study of NBPHA and the ammonium salt of N-nitroso-phenylhydroxylamine (cupferron) in the extraction of tin, antimony, arsenic and bismuth has also been carried out and potential separations with NBPHA noted. Depending on the valency state of tin, cupferron gives two distinct products, while NBPHA gives only a

single product in which the valency state of the tin has previously been in some doubt. Partition studies have been devised to examine the dependence of extraction on reagent, chloride ion (a constituent of the product precipitated from hydrochloric acid) and hydrogen ion concentrations. The results in combination with those from infra-red and nuclear magnetic resonance examinations of the product of precipitation show that the substance extracted from 1 M hydrochloric acid is the same as that obtained by precipitation under similar conditions. It is $Sn(C_{13}H_{10}O_2N)_2Cl_2$ which contains tin-(IV).

Decomposition products of cupferron were examined using vapour phase chromatographic methods.

Some polarographic work on the behaviour of tin and antimony in the presence of NBPHA has been carried out. Methods for the determination of these two elements in mixtures are presented using NBPHA.

CONTENTS

CHAPTER 1

Page

1. Introduction

CHAPTER 2

1. General theory, method and equipment used in the experimental work

Page

CHAPTER 3

1. Separation of some transition elements with particular reference to protactinium using liquid-liquid extraction methods

CHAPTER 4

1. The application of N-benzoyl-N-phenylhydroxylamine to the separation of gallium, indium, thallium, germanium, tin and lead by solvent extraction

Page

CHAPTER 5

1. Some properties of N-benzoyl-N-phenylhydroxylamine and cupferron systems containing tin, antimony and other elements

CHAPTER 6

1. General discussion and suggestions for further work

CHAPTER 1

Introduction

Organic Reagents in Chemical Analysis

Although applications of organic reagents to problems in inorganic analysis were occasionally reported in the nineteenth century, it is only during the present century that such substances have been used extensively.[1-6] The sensitivity, versatility and sometimes specificity which they exhibit by comparison with inorganic reagents essentially explains their applications.

In 1905 Tschugaeff reported the use of dimethylglyoxime as a specific reagent for testing nickel and Brunck[7] used the same substance for the determination of nickel in stainless steel. With the knowledge that dimethylglyoxime is a highly selective precipitant for nickel, as well as a sensitive reactant, chemists later instituted a search for organic substances superior in specificity and sensitivity to those then currently in use. The search was essentially a rather haphazard one, since relationships between structure and analytical function had not previously received much attention. The investigation of organic substances as analytical reagents is by no means complete, but in the intervening years many careful investigations coupled with a better understanding of the nature of chemical bonding and valency have revealed certain underlying principles which may be used in the search for new reagents and for the improvement of old ones.

Any organic substance used in chemical analysis may be regarded as an organic reagent[1] but those capable of forming chelates - a term first used by Morgan[8] - by reaction with metal ions in solution are of particular importance in analytical chemistry. A chelate may be defined as a molecule possessing a ring structure one member of which is a metal. To form a chelate, the substance must be capable of attaching itself at two or more co-ordinating positions around a metal ion. The group attaching itself to the metal ion is commonly known as a ligand; attachment at two co-ordination positions makes it a bidentate, and at three a tridentate ligand and so on. Ligands may be anions such as chloride, acetate or neutral molecules like ammonia and 1,10-phenanthroline, so that complexes may be cations, neutral molecules or anions. For a substance to act as a ligand, it must have at least one lone pair of electrons which it can donate to a metal ion. Five or six membered rings are favoured in chelate formation; stability is further enhanced if the ligand is multidentate.[9] Qualitatively, the latter can be explained on the grounds that the more points of attachment there are between a ligand and a metal ion, the more difficult it would be for the metal ion to break its bonds and move away. However, the majority of organic chelating substances which have been used in chemical analysis are bidentate.

To achieve adequate selectivity in analytical work, it is frequently necessary to exploit differences in physical or chemical properties among reaction products. Some of the more common properties and their applications are as follows:-

1. The production of characteristic colour. This may be used,

   (a) for a direct spectrophotometric determination of the species giving rise to the colour.

   (b) as indicators in the detection of end points in titrimetric methods of analysis.

   (c) in qualitative testing as for example in spot tests.

2. Differences in solubility. These may be made the basis for gravimetric methods of analysis. Trace constituents may be concentrated by co-precipitation or alternatively by partitioning into a water immiscible solvent by following the practice known as solvent extraction.

Since a large number of organic compounds are available, they offer many possibilities for research. Consequently it would be of value to set out the general considerations which are applicable to an initial selection of substances for analytical work. Frequently, ligands giving rise to bi-dentate chelates possess groups containing a dissociable hydrogen atom and a complementary group having a lone pair of electrons suitable for the formation of a co-ordination bond with a metal ion. Such a chelate forming substance is often capable of neutralising the charge on the metal ion in addition to satisfying its co-ordination requirements. It is probable that in many reactions N-benzoyl-N-Phenyl-hydroxylamine, hereafter referred to as NBPHA, the substance on which most of the work described in this thesis has been carried out behaves in this way. A list of acidic radicals which are responsible for salt formation in organic compounds is given below;

1.-COOH	(Carboxyl)	6. = NOH	(oxime).
2.-SO_2H	(sulphinic)	7. -NO-OH	(nitroxyl)
3.-SO_3H	(sulphonic)	8. =NH	(imine)
4.-OH	(hydroxyl)	9. -$As(OH)_2$	(arsenic)
5.-SH	(mecapto)	10. -$AsO(OH)_2$	(arsonic)

Because of the predominant role of the chelate functional groups, in many cases it is possible to prepare, as reagents, a series of organic compounds containing the same reactive grouping but in which the remainder of the molecule is different. It may thus be possible through structural changes to improve the properties of organic reagents e.g. by increasing or decreasing the water solubility of the reagent and the product formed in analytical reaction. A historical survey of the development of organic reagents would show very many attempts to alter the properties of organic compounds by substituting various groups in them[4]. Such substitution may have one or more of three effects:-

1. it may alter the solubility of the complex.
2. it may, by increasing the size of the reagent, lead to steric interference of the groups around the metal ion,
3. it may, alter the availability of electrons for bond formation at the reacting groups.

In liquid-solid or liquid-liquid systems where solvent-solute interaction or lack of it is of importance, the classical rule of "like dissolves like" is normally applicable. In other words substances are most soluble in those solvents with which they show structural resemblances. Thus any change in the composition or structure of a molecule which tends to increase its similarity to water is expected to increase its solubility in water and so also any change in the structure which will decrease its similarity to and hence affinity for water will decrease its solubility in that medium. However, it should be noted that other factors such as the relative positions and sizes of different groups, also have an effect on the solubility.[10] The influence of molecular weight on the solubility is an important factor in the selection of a substance for analytical purposes. An increase in molecular weight achieved by increasing the hydrocarbon content of the molecule while retaining the functional groups unchanged may be expected to lead to reaction products of reduced solubility in aqueous systems, with a consequent increase in the sensitivity of the reaction. At the same time the 'loading' of the reaction product with hydrocarbon may well enhance the partition of the metal into water immiscible solvent.

Solvent extraction in inorganic-analytical chemistry

Solvent extraction systems may be divided into two classes depending on the nature of the reaction leading to extraction.

(a) ion-association systems.
(b) chelate systems.

While it is thought that much of the work to be described subsequently concerns chelate systems, ion-association undoubtedly plays a part in certain reactions. For ion-association it is necessary that complete dissociation of the essentially ionic substance does not occur in the aqueous phase. It is then possible to arrange conditions so that ion aggregation is enhanced and thus favourable solvation by water immiscible solvents can take place.

The solubility of metal chelates in water immiscible solvents is often utilised for the removal of metal ions from the aqueous phase. It is thus possible to separate, and also concentrate, many substances which are soluble in commonly available organic solvents such as alcohols, esters, ethers, ketones, and hydrocarbons and their halogen substituted products such as chlorobenzene and chloroform.

The term solvent extraction includes both liquid-liquid and solid-liquid extraction, but normally when used without qualification the former is intended. In liquid-liquid extraction the process of equilibrating a solution containing one or more solutes (inorganic or organic) leads to the distribution of the partitioning material between the two phases. It is a useful technique because of the simplicity, wide scope and the ease with which it may be carried out.[11-13] Although solvent extraction has been practised by chemists for a considerable time, it is only in the last two to three decades that it has been used extensively in inorganic analysis.[14-18]

Solvent extraction, in its simplest form in the laboratory is performed using a separating funnel and under favourable circumstances need take only a few minutes. Distribution ratios are obtained by determining the amount of substance in each phase; this may be done by using radioactive tracers as in much of the work to be described. Radiotracers are particularly well suited to solvent extraction studies. According to Irving[19] the first reported use of a radiotracer in solvent extraction is that of Seaborg and Grahame.[20] Since then ready availability of radioisotopes of many elements have extended the scope of such measurements.[21-25] Alternatively, distribution ratios are obtained by absorptiometric, polarographic, titrimetric or other applicable analytical methods. Recoveries of the extracted solutes are effected from the organic phase either by back extracting into an aqueous phase of suitable composition or by evaporation of the organic solvent.

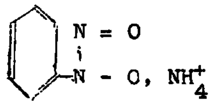
Cupferron and N-Benzoyl-N-Phenylhydroxylamine in solvent extraction

A substance which has received considerable attention because of its versatility in reaction with metal ions is the ammonium salt of nitrosophenylhydroxylamine otherwise known as cupferron. It was first proposed as an analytical reagent by Baudisch.[26] The name cupferron was suggested since it precipitates copper (II) and iron (III) quantitatively. The reagent is freely soluble in water and also in many organic solvents, such as ethanol, ethyl acetate and chloroform. The fact that it can react with certain metal ions even in the presence of masking agents such as oxalic and tartaric acids, further contributes towards the versatility of the reagent in analytical procedures. Unfortunately, solutions of cupferron are unstable and are decomposed on heating. Among other defects of this reagent are instability to visible and ultra violet light and to air. To minimise these defects it is usual to store it in an amber coloured bottle together with a few lumps of ammonium carbonate.

Metal derivatives of cupferron are frequently soluble in solvents immiscible with water. As early as 1896, Bamberger and Ekecrantz[27] noted the solubility of the iron (III) complex of cupferron in diethyl ether; later it was found[28,29] that many of these cupferron complexes are soluble in chloroform and could be extracted into it from an aqueous solution. While cupferron is not as selective in its reaction with metal ions, as might be desired, it has nevertheless proved of value in

TABLE 1

A survey of extraction data for metal deravatives of Cupferron



H																	He
Li	Be II 3.8											B	C	N	O	F	Ne
Na	Mg											Al III 3.5	Si	P	S	Cl	A
K	Ca	Sc III 3	Ti IV 4	V IV,V 0-1,2.5	Cr III 3	Mn II* 7	Fe III 0	Co II 4.5	Ni II* 9	Cu II 2	Zn II 9	Ga III 4.5	Ge	As	Se	Br	Kr
Rb	Sr	Y III 5	Zr IV 3	Nb V 3.5	Mo VI 1.5	Tc	Ru	Rh	Pd II 0	Ag I 3.5	Cd II 4.5	In III 3	Sn II,IV 0-1,0-1	Sb III 0-1	Te	I	Xe
Cs	Ba	La III 4	Hf IV 0-1	Ta V 3	W VI* 0.3	Re	Os	Ir	Pt	Au	Hg II 5	Tl III* 1.5	Pb II 3	Bi III 2	Po	At	Rn
Fa	Ra	Ac															

Ce III,IV 5,0-1	Pr	Nd	Pm III 5	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th IV 2.5	Pa V 0-1	U IV,VI* 0-1,3	Np	Pu IV 2	Am	Cm	Bk	Cf	E	Fm	Mv	102	[illegible]

The number under each element shows the pH required for complete extraction. Where two numbers occur they refer to the two valency states of the element taken in the same order.

* = Partial extraction.

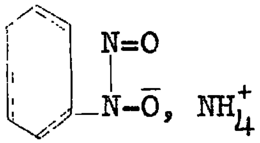
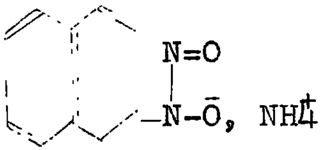
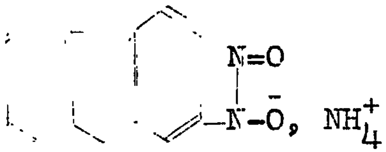
many analytical procedures.[30] The pH required for the extraction of metal derivatives of cupferron is given in table 1.

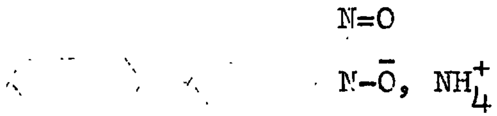
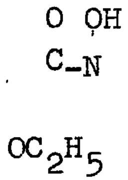
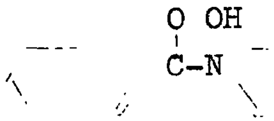
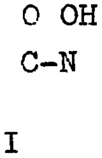
Meunier[31] was one of the first to use extraction of cupferron complexes as a means of separating metals ions and found that iron-III, titanium-IV and copper-II could be partitioned from 1 M hydrochloric acid by extracting them into chloroform. This observation led to the application of cupferron to the separation of several chemically similar elements. Mathers and Prichard[32] used this substance for separating iron from indium in an acid medium and noted the interference of tin. Mack and Hecht[33] separated tin from antimony using cupferron also in an acid medium. A carrier-free separation of tin-113 from deuteron bombarded indium (also containing indium-114) was achieved by Bhakti and Radhakishna.[34] Tin has been determined gravimetrically by precipitation with this substance followed by careful ignition to the oxide.[35-37]

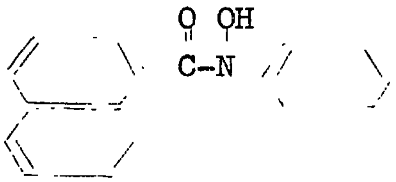
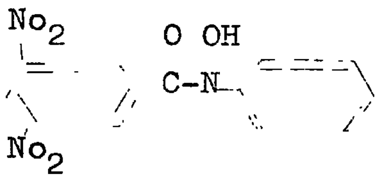
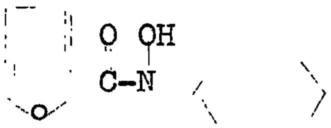
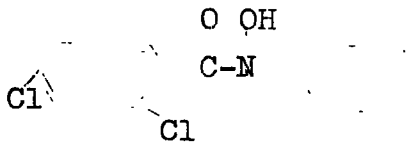
While the versatility of cupferron has been amply verified it is not without its disadvantages which in addition to those already mentioned include instability to mineral acids and the non-stoichiometric nature of its metal derivatives. It is not entirely surprising therefore that from time to time efforts have been directed to the examination of related substances with the hope of finding

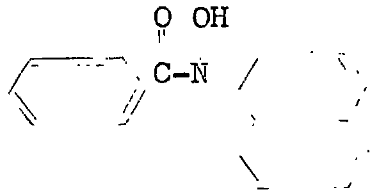
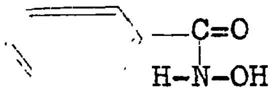
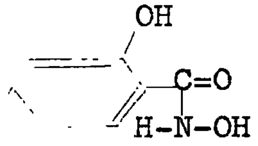
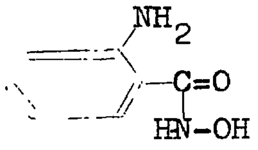
TABLE 2

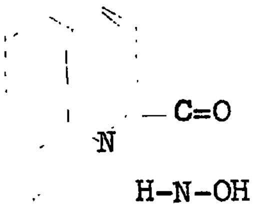
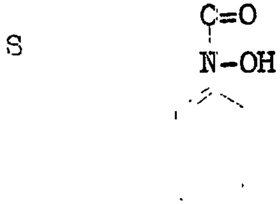
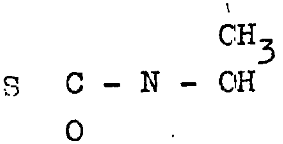
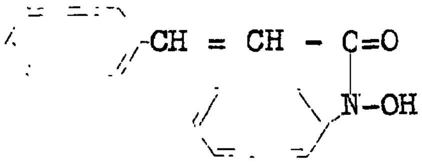
Hydroxylamine derivatives and their properties

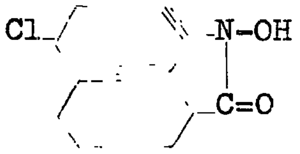
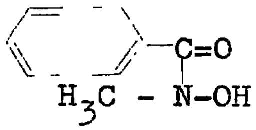
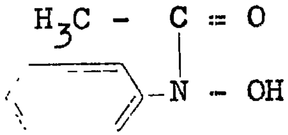
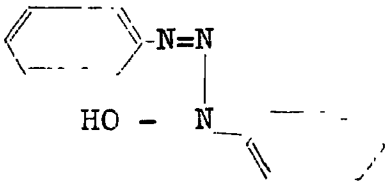
Compound	Structural formula	M.P. °C	Solubility in water g/100ml (at room temperature
Cupferron		-	12
Neocupferron		-	6·0
Fluorenyl analog of cupferron		-	-

Compound	Structural formula	M.P. °C	Solubility in water g/100ml (at room temperature
p-Phenyl Cupferron		-	-
N-(o-Ethoxybenzoyl)-phenylhydroxlamine		103	0·011
N-Benzoyl-N-phenylhydroxylamine		120-121	0·04
N-(o-Iodobenzoyl)-phenylhydroxylamine		128	0·01

Compound	Structural formula	M.P. °C	Solubility in water g/100ml (at room temperature
N-(1-Naphthoyl)phenylhydroxylamine		129	0·003
N-(3,5 Dinitrobenzoyl)-phenylhydroxylamine		133	0·007
N-(2-Furoyl)phenylhydroxylamine		134	0·013
N-(2,4-Dichlorobenzoyl) phenylhydroxylamine		137	0·006

Compound	Structural formula	M.P. °C	Solubility in water g/100ml (at room temperature.
N-Benzoyl-1-naphthyl hydroxylamine		164	0·013
Benzoylhydroxamic acid		131-132	2·25
Salicoylhydroxamic acid		168-170	0·5
Anthranilohydroxamic acid		149	4·0

Compound	Structural formula	M.P. °C	Solubility in water g/100ml (at room temperature
Quinaldinohydroxamic acid		205-206	0·5
N-2-Thiophenecarbonyl)-N-(p-tolyl) hydroxylamine		123	-
N(2-Thiophenecarbonyl)-N-phenylhydroxylamine		98	-
N-Cinnamoyl-N-phenyl-hydroxylamine		162-163	-

Compound	Structural formula	M.P. °C	Solubility in water g/100ml (at room temperature
N-Benzoyl-p-Chlorophenylhydroxylamine		155	-
N-Benzoyl-N-methylhydroxylamine		No sharp M.P.	40·5
N-Phenyl-N-Acetylhydroxylamine		-	-
3-hydroxyl-1:3-diphenyltriazene		119·5-120	-

alternatives, retaining the advantages but free from the defects, of cupferron.[38] The benzene ring has been replaced by the naphthalene and fluorene ring systems but the products show marginal superiority to cupferron.[39] Elving and Olson[40] have made a study of the solubility, spectrophotometric and polarographic behaviour of cupferron and some related substances in their reactions with metal ions. In Table 2 the properties of some hydroxylamine derivatives are summarised.

Most of the substances in the table have been recommended as analytical reagents. They all show solubility in common organic solvents but with a few exceptions all are just slightly soluble in water. The melting points are usually accompanied by decomposition, the melt first appearing coloured e.g. red and then turning black as decomposition proceeds. For example the N-methyl derivative of hydroxylamine is reported[41] to have no sharp melting point but it is highly soluble in water. It is claimed[42] that most of these hydroxylamine derivatives can be stored for a considerable time without any preservative.

Apart from NBPHA Ryan and Lutwick[42] have prepared O-ethoxybenzoyl, α-naphthoyl, 3,5 dinitrobenzoyl and benzene sulphonyl derivatives of phenylhydroxylamine, as well as N-benzoylnaphthoyl hydroxylamine. With the exception of the benzene sulphonyl derivative all precipitate manganese-(II), lead-(II), aluminium-(III), uranium-(VI), copper-(II) and iron-(III) in neutral solutions. The furoyl derivative is also fairly soluble in water but not much relevant work has been done with it.[42] Many hydroxamic acids react with transition elements to give highly coloured solutions. Oxalohydroxamic acid[43] has been used for the colorimetric determination of uranium-(VI). Salicylhydroxamic acid reacts with uranium-(VI) and molybdenum-(VI) producing colours suitable for absorptiometric measurement within the pH ranges 8.5 to 9.5 and 6.3 to 6.7 respectively.[44] Benzoylhydroxamic acid has been suggested for the colorimetric determination of vanadium-(V) with which a red colour is obtained in dilute acid and blue in concentrated acid.[45] N-phenylacetylhydroxamic[46] acid gives incomplete precipitation of niobium and tantalum. N-cinnamoylphenylhydroxylamine[47] quantitatively precipitates these two elements but both precipitates have to be ignited to their oxides before weighing. 3-hydroxyl-1:3-diphenyltriazene was first suggested for the gravimetric determination of palladium at pH 1.6 to 8. Sogani and Bhattachari[48] extended the use of this reagent, which is prepared at little cost for the determination of copper, nickel and titanium.

It would appear that very few of the organic reagents mentioned above have advantages over the earlier reagents they were intended to supersede. Of the substances related to cupferron only NBPHA shows promise of advancing into the small group of useful reagents.[42] NBPHA was first synthesised by Bamberger[49] who noted that it gave coloured precipitates with certain transition elements like copper, iron and nickel. However, Shome[50] was the first to demonstrate that this reagent has definite advantages over cupferron in chemical analysis and he extended knowledge of its behaviour to many metal ions in precipitation reactions.[51]

NBPHA has the following general characteristics:-

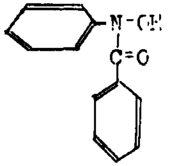
1. A good stability to air, light and moderate temperatures (C.f. cupferron).
2. Although only slightly soluble in water, it is readily soluble in organic solvents like alcohols, benzene, chloroform, ethers etc.
3. Precipitates formed with many metal ions have a granular form facilitating filtration or centrifugation as a means of separation from mother liquor.
4. The precipitates are not usually contaminated with the reagent when formed from hot solutions and therefore being stoichiometric they can be weighed directly.[51]
5. Solubility of metal derivatives in organic solvents, opens up possibilities for separation of metal ions by solvent extraction.

NBPHA is a white chrystalline solid, melting point 120 to 121°. The solubility in water is about 0.04 g.

TABLE 3

A comparative account of the elements extracted by N-benzoyl-N-phenylhydroxylamine.

N-Benzoyl-N-Phenylhydroxylamine



H																	He
Li	Be II 6.5											B	C	N	O	F	Ne
Na	Mg											Al III 3.6	Si	P	S	Cl	A
K	Ca	Sc III 5.2	Ti IV 0-1	V V 6.5	Cr III 3	Mn II 10	Fe II,III 5,0-1	Co II 10	Ni II 9	Cu II 3.6	Zn II 9	Ga III 3.1	Ge	As	Se	Br	Kr
Rb	Sr	Y III 3	Zr IV 0-1	Nb V 3.5	Mo VI 1	Tc	Ru	Rh	Pd II 3	Ag I 1	Cd II 10	In III 5.3	Sn II,IV 0-1	Sb III,V* 0-1	Te	I	Xe
Cs	Ba	La III 8	Hf IV*	Ta V [illegible]	W VI 3	Re	Os	Ir	Pt	Au	Hg II 8	Tl I 10.5	Pb II [illegible]	Bi III 4	Po		Rn
Fa	Ra	Ac															

Ce III.IV 7.0-1	Pr III 6	Nd III 6	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th IV 4.5	Pa V*	U VI 3.5	Np	Pu IV*	Am	Cm	Bk	Cf	E	Fm	Mv	102	103

The number under each element indicates the pH at which the element can be extracted quantatively. Where two numbers occur they refer to the two valency states of the element taken in the same order.

* = Extracted almost completely from high acid concentration.

per 100 ml at room temperature. The low solubility in water necessitates close control of the use of excess of reagent while the weakness of its acidic function (pK = 8.15)[52] prevents the effective use of its salts. Shome[53] in 1951 used this compound for the colorimetric determination of vanadium-V and in the following years NBPHA has been used as a precipitant for many metal ions.[54] In certain circumstances its non-selectivity might be considered a disadvantage, but several effective gravimetric separations have been described.[55-57] Recent reviews[58,59] of NBPHA served to indicate the scope of its applications to chemical analysis and over the last five years or so, many papers have appeared describing its use as a precipitant,[60] colorimetric and absorptiometric reagent[61,62] and as an extractant.[63,64] Extraction data for NBPHA metal derivatives have been summarised in table 3.

Outline of the present work.

As already pointed out, NBPHA has been shown to provide stoichiometric precipitates containing metals and to permit separation from other elements in the process. Occasionally in the description of these gravimetric methods of analysis reference has been made to the solubility of the metal derivatives in water immiscible solvents. In addition, preliminary tests showed that other metals containing precipitates with NBPHA were also soluble in such solvents. The accumulated data suggested that convenient separations of metal ions should be possible by solvent extraction methods.

Of particular interest to the laboratory were some main group and also transition group elements mainly centred around groups III, IV and V in the periodic table (short form). Because of interest in certain nuclear reactions of protactinium its separation from the chemically similar elements, tantalum, niobium and zirconium and from neighbouring elements, thorium and uranium were also of interest.

The elements indium, tin and antimony are produced by nuclear transformation processes and may thus occur together as also do thallium and bismuth although they are of less direct interest to us. Efficient, simple and rapid separations of these elements are frequently called for, particularly when dealing with short-lived isotopes.

A survey of the accounts of the substance formed by interaction of tin with NBPHA in chloride solution shows that agreement has not been obtained as to the valency state of the tin in the substance - both tin-II and tin-IV give identical products. Some work has therefore been carried out to resolve this uncertainty. It appears that cupferron readily gives identifiable reaction products with tin-II and tin-IV. A comparative liquid-liquid distribution study has therefore been made for tin and also for antimony and arsenic. Since much of this work was performed in moderate to strong mineral acid, conditions where cupferron exhibits appreciable instability, some attempt has been made to identify decomposition products of the reagent.

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CHAPTER 2

General Theory, Method and Equipment used in the Experimental Work

This chapter deals with theoretical aspects of solvent extraction for systems in chemical equilibrium containing a monobasic acid (e.g. NBPHA) and an extractable metal ion. The general experimental procedure used for the chemical separation of elements employing NBPHA is outlined. Equipment used in the course of the work on chemical separations, in the study of structural aspects of the products and in trying to ascertain the nature of certain reactions is also described.

A. General theory of solvent extraction.

(a) The Distribution law.

Solvent extraction is based on the distribution of a solute between two immiscible phases; the phase rule of Gibbs may therefore be applied. viz.

$$P + F = C + 2 \qquad (1)$$

Where P is the number of phases, F the number of degrees of freedom and C the number of components in the systems. Then a system consisting of two immiscible solvents with one solute distributed between them has one degree of freedom at constant temperature and pressure. Therefore, if the concentration of the solute in one phase is constant, its concentration in the other phase is also fixed. The relationship between concentration of solute in each of the solvent phases led to the formulation of the distribution law first stated in 1872 by Berthelot and Jungfleisch[1] and modified by Nernst in 1891.[2] The Berthelot version of the law states that if the dissolved substance distributes itself between two liquids of small mutual solubility, then at a given temperature and under equilibrium conditions, the ratio of the concentration of the solute in the two phases is independent of the total amount of solute i.e. for a given solute A, distribution between the two immiscible phases a and b is given by

$$\frac{[A]a}{[A]b} = P^o_A \qquad (2)$$

P^o_A is called the distribution or partition coefficient. The law thus stated is a useful approximation but two types of defects have come to light.

(i) The law is not thermodynamically rigorous, but one can define a thermodynamic partition constant P^T_A such that

$$P^T_A = \frac{[A]_a \cdot t_a}{[A]_b \cdot t_b} \qquad (3)$$

$$= P^o_A \cdot \frac{t_a}{t_b}$$

where t is the activity coefficient.

(ii) When the solute or partitioning component is involved in association or dissociation reactions in either phase, the partition law no longer applies to concentration of gross solute species but (according to Nernst) only to the individual, discrete species present in both the phases. However at low solute concentrations, and sometimes over wide concentration ranges, the simple Berthelot relationship is valid.

(b) The distribution ratio and its dependence on the chemical equilibria.

The aqueous phase contains hydrated metal ions, M^{n+}, a ligand also in the aqueous phase, L, and the chelating agent which is a monobasic acid (e.g. NBPHA) largely in the chloroform phase, HR.

The following equilibria exist in this system:

(i) The ionisation of HR in the aqueous phase

$$HR \rightleftharpoons H^{+} + R^{-} \qquad (5)$$

(ii) Distribution of the chelating agent between water and the chloroform phase

$$(HR)_{w} \rightleftharpoons (HR)_{o} \qquad (6)$$

where subscripts o and w refer to the organic and aqueous phases respectively.

(iii) The reaction of active R^- of the chelating agent (HR) with hydrated metal ion

$$MRn \rightleftarrows M^{n+} + nR^- \quad \text{(aqueous phase)} \qquad (7)$$

(iv) Assuming that only one metal chelate extracts into chloroform, its distribution in the two phases may be expressed as:

$$(MR_n)_w \rightleftarrows (MR_n)_o \qquad (8)$$

Then respective equilibrium constants are:

$$K_{HR} = \frac{[H^+]\ [R^-]}{[HR]} \qquad (9)$$

$$\frac{[HR]_o}{[HR]_w} = P_{HR} \qquad (10)$$

where P_{HR} is the partition of the chelating agent between the two phases.

$$\frac{[M^{n+}]\ [R^-]^n}{[MRn]} = K_m \qquad (11)$$

$$\frac{[MRn]_o}{[MRn]_w} = P_m \qquad (12)$$

Combination of these expression gives:

$$\frac{[MR_n]_o}{[M^{n+}]} = \frac{P_m}{K_m}\left(\frac{K_{HR}}{P_{HR}}\right)^n \left\{\frac{[HR]_o}{[H^+]}\right\}^n = K\left\{\frac{[HR]}{[H+]}\right\}^n \qquad (13)$$

A value for the equilibrium constant K may be calculated if the following data is known.

$$\frac{P_m}{K_m} = \frac{[MR_n]_o}{[M^{n+}][R^-]^n} \qquad (14)$$

$$\frac{K_{HR}}{P_{HR}} = \frac{[H^+][R^-]}{[HR]_o} \qquad (15)$$

The value of Pm/Km is obtained by dividing the molar solubility of the metal chelates in the organic solvents by the solubility product in water saturated organic solvent; the value of $\frac{K_{HR}}{P_{HR}}$ is found similarly.

The pK value for NBPHAis 8.15 $\pm$ $0.0\overset{3}{1}$. The value of the parition coefficient for NBPHA is log P_{HR} = 2.33 $\pm$ $0.0\overset{3}{1}$. This means the amount of undissociated NBPHA remaining in the aqueous phase after shaking with chloroform is very small. Where the distribution of metal into chloroform is large the amount of undissociated metal derivative MR_n in the aqueous phase is probably no larger than P_{HR}.

We are interested in the distribution of metal in all its forms between the two phases. This means that account must be taken of metal species other than the simple ions i.e. the presence of ligand (L) if present in the aqueous phase. If the equilibrium constants of all the reactions involved and the concentration of the complex forming agent L are known, M^{n+} in the equation can be replaced by an expression involving these and the total metal concentration in the aqueous phase. If the concentration of the ligand, L, in the aqueous phase is large compared to that of the metal, it can be taken to remain approximately constant as the total concentration of metal varies, and a simple expression is obtained for the ratio of the metal forms in the two phases under specified conditions.

For example, let us suppose that M^{n+} forms a series of complexes with ligand L. The aqueous phase will contain the species M^{n+}, $ML^{(n-1)+}$, $ML_2{}^{(n-2)+}$ .....ML_n. Then neglecting the metal hydrolysis, the sum of the concentration of the metal in all its forms in the aqueous phase is given by

$$\Sigma[M]_w = [M^{n+}]_w \left\{ 1 + \frac{[L^-]}{K_1} + \frac{[L^-]^2}{K_2} + \cdots\cdots \right\} \qquad (16)$$

Therefore, for a constant concentration of L, we have the relation:

$$[M^{n+}]_w = \Sigma[M]_w \text{ x } \quad \text{constant.}$$

From equation 13, it follows that

$$\frac{[MR_n]_o}{[M]_w} = K^1 \left\{ \frac{[HR]}{[H^+]} \right\}^n \qquad (17)$$

K^1 is a constant for a specified concentration of L, in the absence of other complexing agents. As long as there is no association of the metal in either phase i.e. if the species in the aqueous phase contains only one atom of M - the fraction of the total M in the organic phase will be independent of the total amount of metal present.

Taking logarithms of equation (17)

$$\log E = \log K^1 + npH + n \log [HR]_o \qquad (18)$$

Therefore under these conditions an n fold change in the concentration of the reagent in the organic phase $[HR]_o$ can be exactly offset by an n fold change in pH.

Let us suppose

V_w = volume of the aqueous phase

V_o = volume of the organic phase

X = Percentage of the metal extracted into the organic phase

then (100-x) metal remains in the aqueous phase.

$$E = \frac{[M]_o}{[M]_w} \qquad (19)$$

$$= \frac{x}{v} \Big/ \left(\frac{100-x}{vw}\right) \qquad (20)$$

From equation (17) If $V_o = V_w$ then,

$$E = \frac{x}{(100 - x)} = K^1 \; [H^+]^n \qquad (21)$$

This assumes $[HR]_o$ is constant.

B. Outline of the general method of investigation of possible chemical separations by solvent extraction.

The following experiments were performed to obtain the desired information on the partitioning of a metal ion and hence to point the way to possible separations.

(a) Extraction into the chloroform phase.

(i) Initially if ligand (L) is present (e.g. fluoride ion) in the aqueous phase, the effect of its concentration on the percentage extraction of the metal transferred into the organic phase was examined. During this study, other conditions, namely NBPHA (HR), total acidity, a metal ion concentrations. and the time of equilibration. were kept constant.

(ii) After establishing maximum ligand concentration consistent with maximum efficiency of extraction, under conditions imposed in (i) the effect of other variables such as hydrogen ion concentration was investigated.

In the experiments described in (i) and (ii) a 1% solution of NBPHA was used and although the metal ion concentration varied from one metal to another, a 20 fold (molar) excess of the former was maintained. The time of equilibration was 15 minutes; this was known to be longer than that required for the equilibrium to be established.

(iii) Keeping the ligand L, the metal ion ,equilibration time, and acidity constant the effect of varying the NBPHA concentration in the chloroform phase as a function of metal ion partitioned between the two phases was then examined.

(iv) With the optimum (minimum) reagent concentration the partition of the metal between the two phases was investigated as a function of time keeping the other variables constant.

(v) Using the data thus obtained, the maximum metal ion concentration which could be transferred to the organic phase without impairing the extraction efficiency of the system was determined.

(b) Back-extraction into the aqueous phase.

(i) Following the above mentioned experiments, back-extraction of each element into aqueous phases of different compositions was studied. The investigation was then extended to a study of back-extraction as a function of the concentration of extracting component for promising systems.

(ii) Under the conditions chosen as a result of experiments referred to in (i) extraction from the organic phase into the aqueous phase was investigated as a function of time in order to set a lower limit on the time required.

(c) Apparatus for solvent extraction experiments:

In each of the operations described in (a) and (b), mixing of the two phases was performed in polyethelene bottles, using a mechanical shaker of the vibrator type (this was found to give mixing of comparable efficiency to manual shaking). The phases were separated in a separating funnel. The aqueous phase was washed twice with 10 ml. portions of chloroform before withdrawing samples for counting, titrating or for spectrophotometric measurements. Data recorded in the figures and tables in the following chapters has been obtained in this way unless it is otherwise stated as for example in determining separation factors. A check on the material balance was frequently performed by counting the activity transferred to the organic phase as well as that remaining in the aqueous phase.

(d) Separations.

From the data thus collected it was readily apparent what separation of metal ions were possible and separations of pairs of the elements could then be examined. For these tests a synthetic mixture of the two elements in question were prepared and a radioactive tracer was added to one member of each pair. The acidity and other conditions were adjusted to the previously determined values and the extraction was performed. The inactive component thus separated was examined for radioactivity. The experiments were then repeated with the other member of the pair made the labelled component. From the results, separation factors were calculated. (See the footnote to table 9 for a definition of separation factor).

C. Apparatus

This section deals with aspects of the instruments, which have been used in the experimental work. It includes the apparatus employed for the measurement of the radioactive tracer in solution. Apart from radiochemical equipment, with the aid of which most of the work has been carried out, where suitable radiotracers were not available, spectrophotometric measurements have been carried out. (c.f. chapter 3). Further in connection with the studies of the nature of the tin-NBPHA complex Nuclear Magnetic Resonance (NMR) and Infra-red work has been performed. The comparative study of the chemical behaviour of cupferron and NBPHA with tin and antimony led to a study of the decomposition products of cupferron with vapour phase chromatography (VPC). In connection with the tin work a polarographic study has been carried out.

(a) Radiochemical measurements

(i) Geiger-Muller Counter.

Radioisotopes, emitting β particles of end-point energy more than about 1 Mev were counted in the liquid form in a Twentieth Century Electronics, Annular Geiger-Muller counter of the type M6H. The counter, having a capacity of 10 ml, consists of a spiral cathode $1\frac{1}{2}$ cm. in diameter, along the central axis of which is a wire anode. The intervening space is filled with argon containing a small portion of a halogen to act as a quenching agent. A source of stabilised and variable voltage is applied across the electrodes and pulses from the counter on passing through a probe unit are fed to a scaling device which records the number of pulses over required time intervals.

In order to reduce the back-ground counting rate, the counter is mounted in a lead shield. The working voltage selected is in the plateau region i.e. the region in which the counting rate is nearly independent of the applied voltage. The counting efficiency of the counter was often checked before actual measurements using a standard radioactive source. A standard deviation of 1% in the counting rate was allowed as a statistical variation; this requires accumulated counts of at least 10^4 each time. Solutions with low activities were counted for a sufficiently long time to minimise statistical errors.

(ii) γ-Scintillation Counter

For the nuclides emitting γ-rays, scintillation counting equipment was used; this consists of a well-type sodium-iodide (thallium activated) scintillator, a photomultiplier tube, amplifier, analyser and scaling unit, connected in that order. The solutions (2 ml.) containing the activity were placed in small snap-top polythylene capsules (1.2 cm. diameter and 5.5 cm. in height) and counted by placing them in the well of the crystal. Details of the equipment associated with the working of the scintillation counter are as follows:

A well-type crystal, diameter $1\frac{3}{4}$", height 2" and depth $1\frac{1}{3}$" (type 7F8, manufactured by Nuclear Enterprises Ltd. G.B.) was used. From the crystal, scintillations were detected by a photomultiplier tube which converts them into electrical pulses which are fed into a 'non-over loading' linear amplifier (type NE 8202) from which they pass to a single channel pulse height analyser (NE 101, manufactured by Dynatron Radio Ltd. Maidenhead G.B.). The pulses in the analyser are analysed or sorted according to their sizes which are related to the energy of the original photons. The single channel analyser incorporates a variable bias voltage by means of which the discrimination level could be set. This allows the selection of photopeaks corresponding to a particular γ-ray energy. After selection, the pulses are fed into a scaling unit.

Before counting the isotope of interest, the γ-ray spectra of two standard sources e.g. cobalt-60 and caesium-137 were obtained. A plot of γ-ray energy for photopeaks from these isotopes verses bias voltage thus obtained was useful in determining the required bias voltage and other instrumental settings for the isotope of interest. In the course of the actual measurements a source containing the isotope under investigation was always prepared and kept as a standard which can be counted before measurements.

(iii) Multi-channel analyser

γ-ray spectra of various nuclides were obtained by using a Hutchinson-scarret pulse height analyser (100 channels) of type 1363 D made by Clifford and Snell, Sutton, Surrey, U.K. This instrument was used with a 3" flat sodium iodide (thallium activated) crystal (12/DM - 2/12) and a 'non-over loading' linear amplifier of the same specification as that used with the scintillation counter.

(b) For spectrophotometric measurements a Unicam SP 500 was used. Silica cells of 1 cm. path length were used.

(c) The infra-red (IR) spectra were obtained in the range

2.5 to 15 μ using a Unicam SP 200 spectrometer which is a double beam pen-recording arrangement. Sodium chloride cells and prisms were used. Far-intra red spectra were obtained using a Grubb-Parson DM"/DB-3 double beam grating spectrometer - range 22 - 50 μ.

(d) The Nuclear Magnetic Resonance studies were performed on a Varian A-60 Analytical NMR spectrometer operating at 60 mc/sec. at a temperature of 35°. It is manufactured by Varian Associates, polo, atto, California, U.S.A. Tetra methyl silane (TMS) was used as the internal reference substance.

(e) pH measurements were made on a Doran 'Universal pH meter'. Doran Instrument Co. Ltd., Stroud, Glos. U.K. This was standarised at pH 4 with 0.05 M potassium hydrogen phthal ate.

(f) A Pye series 104 chromatograph was used for VPC measurements. The column packing was SE-30 (methyl silicone gum) with a flame ionisation detector and nitrogen as carrier gas (flow rate 40 c.c. per min.). The column temperature was 150 ± 5°.

(g) <u>A general description of polarograph</u>

A Cambridge 'General Purpose Polarograph' was used. This can be operated manually as has been done in the work to be described (Chapter 5) in which case the potential applied can be chosen and varied at will or used automatically, when the applied potential is varied continuously sweeping from the positive to negative potentials for the mercury drop.

The potentiometer dial is graduated from +0.4 to -1.4 volts at 10 milli volt intervals. It is possible to vary the sensitivity of the polarograph by means of a sensitivity range switch which has a number of fixed positions. A damping device which enables the operator to smooth out the oscillations on the polarogram if the mean current during the drop time is required to be measured. A 6 volt accumulator was used as voltage supply. The polarograph was coupled to a Cambridge spot galvanometer which has a response time of about 3 seconds for full deflection.

The cathode consists of droplets of mercury emerging regularly from the end of a fine capillary tube.

The anode is a large pool of mercury. The reaction cell having a capacity of 2 ml. has a side tube which allows nitrogen to be passed through the solution for the removal of dissolved oxygen.

The reaction cell has a platinum wire sealed through the base of the cell making contact with the anode by means of a mercury contact. The upper portion of the cell is in the form of an annulus into which fits a glass bell attached to the capillary. The annulus is partially filled with water to form a valve allowing nitrogen to pass out but preventing entry of air.

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CHAPTER 3

Separations of Some Transition Elements with Particular Reference to Protactinium Using Liquid-Liquid Extraction Methods

Introduction

In this chapter the extraction of zirconium, niobium, tantalum and protactinium is examined in hydrochloric acid media employing fluoride (where useful) as a masking agent. The behaviour of uranium and thorium in acetic acid - acetate buffer systems is also investigated. Forward extractions were performed into chloroform solutions of NBPHA by experiments carried out according to the scheme in chapter 2, section B',a. The results are examined for potentially useful separations. Work has also been done on the back-extraction of these elements into various aqueous phases and the additional separations thus revealed are discussed.

All of the elements quoted are either related through radiochemical transformations, occur together naturally or have been used in the past as carriers for isotopes of protactinium. For example, protactinium-231 occurs as a decay product of the naturally occurring long-lived uranium isotope, uranium-235. The protactinium content of natural uranium is, however, very small[1] (about 0.34 parts of protactinium per million parts of uranium) and its separation from natural sources is therefore rendered difficult.

27.4 day protactinium-233 is obtained by slow neutron irradiation of thorium-232 according to the reaction

$$^{232}\mathrm{Th}\ (n,\gamma)\ ^{233}\mathrm{Th}\ \xrightarrow[23.5\ \mathrm{min}]{\beta^-}\ ^{233}\mathrm{Pa}\ \xrightarrow[27.4\ \mathrm{day}]{\beta^-}\ ^{233}\mathrm{U}$$

From this reaction it is clear that protactinium obtained from such a source is likely to be contaminated with uranium and thorium and its daughter products. It is therefore desirable to separate protactinium from such elements.

Many separation procedures have been put forward based on co-precipitation, ion-exchange and solvent extraction techniques[1-3] for the separation of these two isotopes of protactinium. While others are known, they have not assumed the same importance since they are difficult to obtain, are short-lived or do not decay by emitting radiation readily measured - a criterion of a satisfactory isotope for the tracer work. Protactinium-233 is the most convenient isotope for tracer work while for macro chemical investigations, protactinium-231 is undoubtedly the most satisfactory because of its relatively long half-life (3.43×10^4 years).

The earliest attempts to isolate protactinium were made by Hahn amd Meitner[4] and, independently, by Soddy and Cranston[5]; they used co-precipitation methods. Elements like zirconium, niobium, tantalum, titanium, thorium and manganese have been found to concentrate protactinium from uranium ores and ore residues[6]. The separation of protactinium from some of these elements, especially the first three mentioned, is difficult[6], particularly if only a small quantity is present. The first attempted isolation was based on the assumed similarity in chemical behaviour of protactinium to tantalum[7,8], but this gives rise to cumbersome and time consuming procedures and, in addition, the final products do not have a high purity[6]. Titanium was also found to be an unsatisfactory carrier for protactinium[9] as it tended to co-precipitate with tin, lead and bismuth during their elimination as sulphides[10,11]. With the availability of more information on the ion-exchange and solvent extraction behaviour of protactinium, the usefulness of such methods became apparent, particularly for the isolation of chemically pure protactinium.

Kraus and Moore[12] have described the separation of protactinium from iron-(III) using a mixture of hydrochloric and hydrofluoric acids as eluent with an anion-exchange column. These authors[13] have used the same type of resin to separate protactinium from uranium and thorium. Thorium is not absorbed on an anion-exchange resin from 8 M hydrochloric acid while protactinium and uranium are absorbed. Protactinium is then eluted from the column using 3.8 M hydrochloric acid. Protactinium is poorly absorbed on anion-exchange resin in the presence of fluoride; the addition of even small amounts of hydrofluoric acid to the hydrochloric acid eluting solution, causes protactinium to be rapidly desorbed from an anion exchanger and this behaviour of protactinium has been used for separating it from niobium and tantalum which remain on the resin[14]. Ion-exchange methods, while capable of giving very good separations are usually slower than solvent extraction procedures.

Using di-isobutyl carbinol, Moore[15] has extracted niobium from dilute hydrofluoric-sulphuric acid solutions and thus separated protactinium which does not extract with niobium. However, in the course of the present work, it was found that about 30% of tantalum is extracted under the same conditions in a single extraction. The same solvent has been used to separate protactinium from thorium and its fission products[16] but separation from niobium is not good and to minimise emulsification, a problem with this solvent, extractions are performed at 50°. A rapid separation of protactinium-233 from thorium-231 and its daughters using tricaprylmethylammonium chloride has been reported[17]. Maddock and Miles[18], and more recently Spitsyn and Golutvina[19] have used cupferron to separate protactinium from manganese. The first mentioned authors observed losses of protactinium because of the decomposition of cupferron in strong acid (c.f. chapter 1) unless the reagent solution was stabilised (with quinol) and used when freshly prepared. However, a separation from zirconium was not achieved. While the work to be described was in progress, a separation of protactinium using NBPHA was reported from a 3.5 M sulphuric acid solution and separation from iron, niobium, rare earths, thorium and uranium was thus obtained[20].

The work in this chapter has been divided into the following three groups, since the study of each of these groups has been essentially independent of one another.

A. A study of niobium, tantalum and protactinium and separation of protactinium from these and certain other common elements.

B. A study of uranium and thorium and a carrier-free separation of protactinium from neutron irradiated thorium.

C. A separation of niobium-95 carrier-free from zirconium.

A. NIOBIUM, TANTALUM AND PROTACTINIUM

EXPERIMENTAL

(a) Radioisotopes

Zirconium-95/niobium-95 in 0.5% oxalic acid was supplied by The Radiochemical Centre, Amersham, England. Before it was used the niobium-95 had come to equilibrium with the zirconium-95; the mixture was of very high specific activity having been separated from mixed fission products without the addition of a carrier. From the mixture, niobium-95 was separated by the methods outlined in group C of this chapter.

Tantalum-182 was obtained from The Radiochemical Centre, Amersham, England, as tantalum pentoxide dissolved in potassium hydroxide. Protactinium-233 was produced by irradiating thorium oxide with thermal neutrons in BEPO at Harwell, England. It was separated in the carrier-free form by a well-established ion-exchange method[21].

(b) Reagents

All the reagents used were of 'Analytical' reagent grade unless otherwise mentioned.

N-Benzoyl-N-phenylhydroxylamine was supplied either by British Drug Houses (B.D.H.) or L. Light and Company. Samples having a melting point of 120-121° were used directly while those with lower melting points were recrystallised from hot water.

(c) Carrier solutions

Niobium: niobium pentoxide (B.D.H. laboratory reagent grade) was weighed out accurately and fused with twice its weight of potassium hydrogen sulphate in a platinum crucible. The melt was extracted into 1 M tartaric acid, cooled and diluted to give a solution containing 10 mg of niobium per ml[22].

Tantalum: an accurately weighed quantity of tantalum metal was dissolved in a mixture of nitric and hydrofluoric acids by warming to 60°. The solution was cooled and

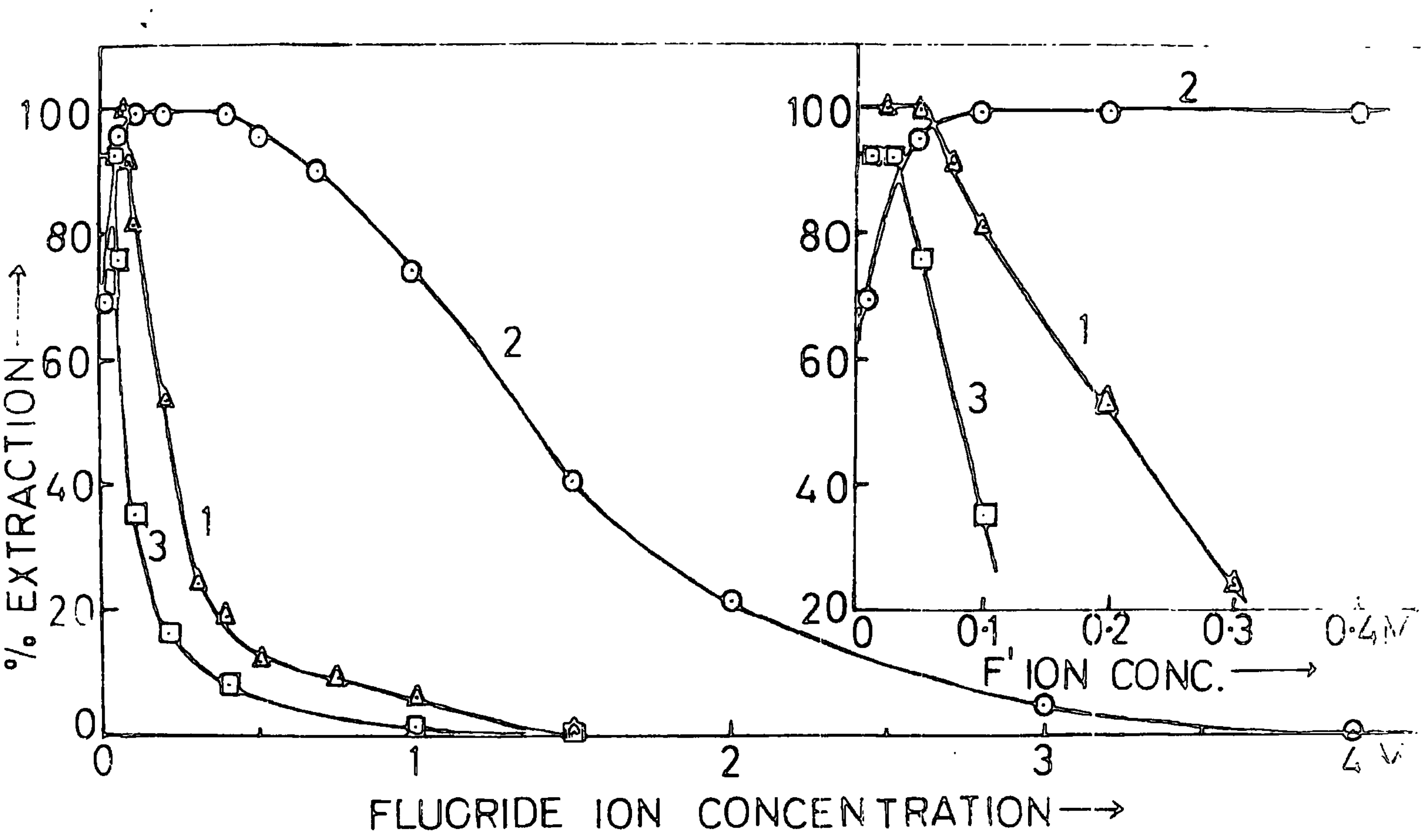

Fig.1. Extraction of niobium (▲), tantalum (⊙) and protactinium (⊡) as a function of fluoride-ion concentration. For conditions see footnotes to Tables 4 and 5. The inset shows curves 1, 2 and 3 drawn to a larger scale at low fluoride-ion concentrations.

diluted to give 10 mg of tantalum per ml[22].

Zirconium: zirconium nitrate was dissolved in 2 N nitric acid to give 5 mg of zirconium per ml.

(d) Measurement of radioactivity

Niobium, tantalum and protactinium samples were counted in the well-type scintillation counter making use of the 776 Kev γ-ray from niobium, the 100 Kev γ-ray from tantalum and the 107 Kev γ-ray from protactinium.

For more information on the radiochemical equipment used see chapter 2, section C. The outline of the general method of investigation is given in section B of the same chapter.

RESULTS AND DISCUSSION

(i) Effect of fluoride ion concentration on the extraction of niobium, tantalum and protactinium

The results of the experiments to demonstrate the effect of fluoride ions on the extraction of niobium, tantalum and protactinium in hydrochloric acid are summarised in Fig. 1. The hydrochloric acid concentration was such that the extraction of these elements was independent of moderate changes in its concentration. The results indicate that the extraction is at a maximum for niobium, tantalum and protactinium up to in the presence of fluoride concentrations of 0.05, 0.4 and 0.025 M in that order. Above these concentrations, the extraction of niobium and protactinium decreases considerably compared

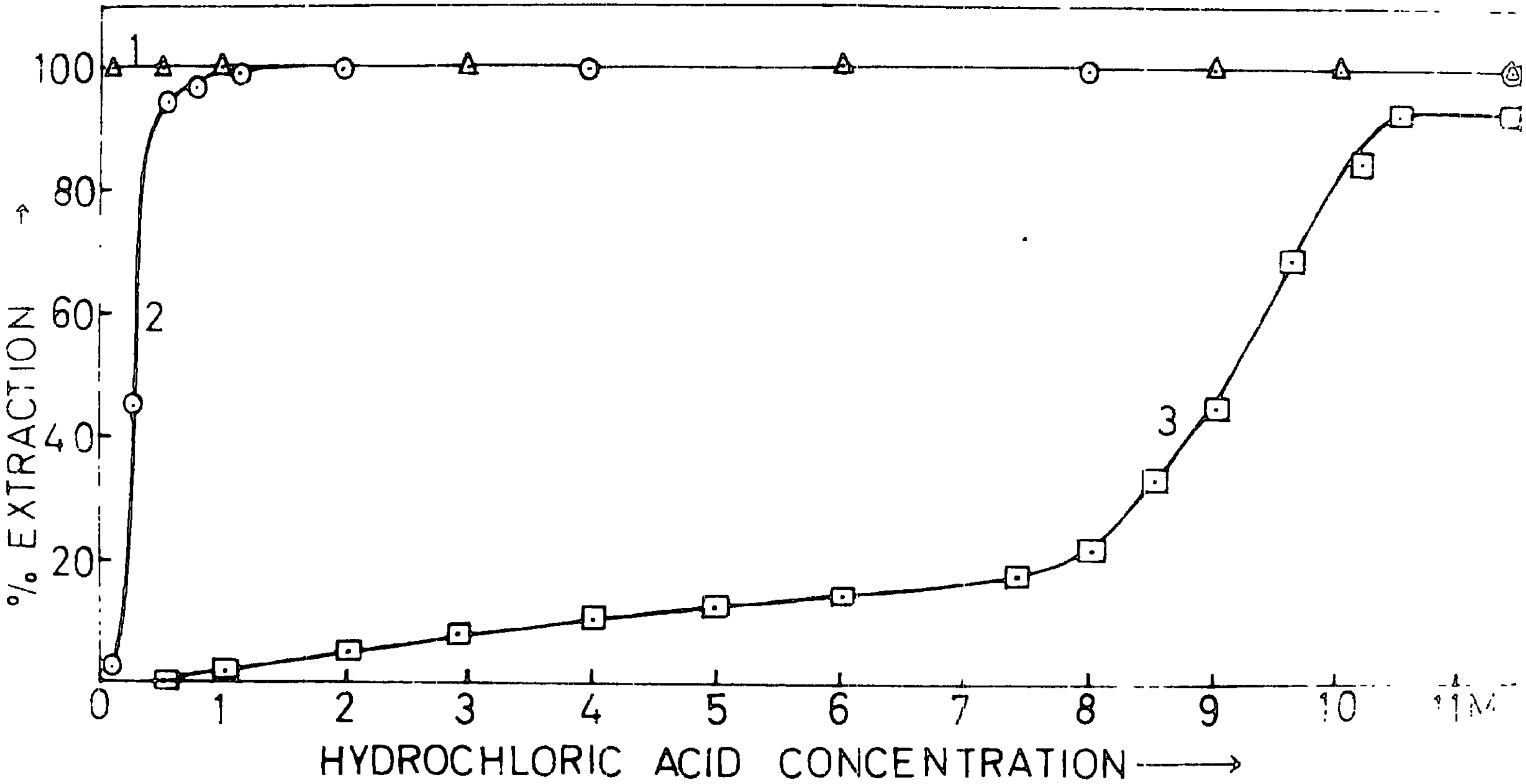

Fig.2. Extraction of niobium (▲), tantalum (◉) and protactinium (▣) as a function of hydrochloric acid concentration. For conditions see footnotes to Tables 4 and 5.

to tantalum. Extraction of tantalum shows a marked dependence on fluoride ion at low concentrations as is apparent from figure I. However, the extraction of tantalum increases rapidly with increase in fluoride ion concentration reaching a maximum at 0.1 M and remaining constant up to 0.4 M with this ligand concentration. With further increase in fluoride ions, the extraction decreases steadily. From the figure, it is clear that the effect of fluoride ions on the extraction of protactinium is greater than that on niobium and less than that on tantalum. It would appear that fluoride ions at high concentration form a strong anionic fluoro complex with protactinium which favours the aqueous rather than the organic phase. At a fluoride concentration of 0.4 M about 19% of the niobium and only 8% of the protactinium are extracted compared to nearly 100% of the tantalum. Further increase in fluoride concentration decreases the extraction of these elements and niobium and protactinium are not extracted at all at 1.5 M fluoride ion concentration into a chloroform solution of NBPHA. An aqueous phase 4.0 with respect to fluoride prevents any partitioning of tantalum into the organic phase.

(ii) The effect of hydrochloric acid on the extraction of niobium, tantalum and protactinium

Fig. 2 records the effect of hydrochloric acid

TABLE 4

Extraction of niobium, tantalum and protactinium as a function of NBPHA concentration.

No.	NBPHA Conc. % w/v.	% EXTRACTION Niobium	% EXTRACTION Tantalum	% EXTRACTION Protactinium
1	0.01	9.0	37.1	3.1
2	0.02	19.0	44.0	-
3	0.025	30.4	49.7	-
4	0.04	46.2	56.8	-
5	0.05	62.6	62.1	7.2
6	0.06	71.0	66.8	10.3
7	0.075	88.3	71.8	12.4
8	0.10	90.3	73.1	15.9
9	0.15	95.6	79.0	21.3
10	0.20	100.0	85.8	27.6
11	0.40	100.0	95.3	53.9
12	0.5	-	99.4	62.8
13	0.8	-	99.4	86.3
14	1.0	-	99.4	92.2
15	2.0	-	99.4	92.2

The composition of the aqueous phases were: 1 M HCl, 0.05 M F^- for Nb; 2 M HCl, 0.4 M F^- for Ta; 10.5 M HCl, 0.025 M F^- for Pa.

Equal volumes of the two phases were equilibrated for 15 min.

Extraction data refer to single extractions. All three elements were present at radio-tracer concentration levels.

concentration on the extraction of niobium, tantalum and protactinium at fluoride concentrations of 0.05, 0.4 and 0.025 M respectively. The extraction of protactinium is markedly dependent on the acid concentration, the maximum only being attained above 10.5 M in hydrochloric acid. At low acidity partial hydrolysis of protactinium in addition to, or rather than, complex formation may account for the low extraction into chloroform phases containing NBPHA. At high hydrochloric acid concentrations, chloride displacement of fluoride in some way may possibly be responsible for higher extraction. In the experiments performed in 1 M hydrochloric acid having 0.025 M fluoride ions, however, hydrolysis is either limited or slow, as losses of protactinium from the aqueous phase were not observed. Niobium is extracted quantitatively even from hydrochloric acid concentrations as low as 0.1 M and varying the acid concentration does not have any effect. With tantalum the extraction increases with increase in acid concentration - it extracts only to the extent of about 2% in 0.1 M hydrochloric acid - the maximum is attained at about 1 M and remains constant above this concentration.

(iii) Effect of NBPHA and time of equilibration

Table 4 shows the effect of reagent concentration on the extraction of niobium, tantalum and protactinium. For maximum efficiency of extraction niobium requires a

TABLE 5

Extraction of niobium, tantalum and protactinium as a function of time.

		% EXTRACTION		
No.	Time(min)	Niobium	Tantalum	Protactinium
1	1	-	31.8	23.1
2	1.5	50.3	-	-
3	3.0	81.6	67.1	80.3
4	4.5	88.0	-	-
5	5.0	-	82.7	84.4
6	6.0	93.0	89.4	92.5
7	9.0	96.0	99.45	92.5
8	12.0	100.0	99.45	92.5

NBPHA concentration in chloroform is 0.2% for niobium, 0.5% for tantalum and 1% for protactinium. The aqueous phases were maintained the same as those described in the footnote to table 4.

TABLE 6

Back-extraction of niobium, tantalum and protactinium from the chloroform phase into various aqueous phases

Niobium

Ammonia	0.5	1	2	4	6	10
% Back-extracted	44	74	91	96	100	100
Hydrogen peroxide*	1	2	4	6	7	
% Back-extracted	77	83	91	97	100	

Tantalum

Ammonia	0.31	0.62	1.25	2.1	2.5	3.0
% Back-extracted	28.7	59.1	85.5	96.2	99.7	99.7
Hydrogen peroxide*	0.25	0.5	1.0	1.5	2.0	3.0
% Back-extracted	8.1	47.8	83.3	92.0	100.0	100.0

Protactinium

Oxalic acid	0.1	0.3	0.5	0.8	1.0	1.5
% Back-extracted	38.3	66.0	87.1	94.1	100.0	100.0
Tartaric acid	0.1	0.5	1.0	1.5	2.0	2.5
% Back-extracted	10.2	55.1	77.3	84.2	95.7	95.2
Hydrogen peroxide*	0.5	1.0	2.0	4.0	6.0	7.0
% Back-extracted	55.1	79.9	90.6	93.9	96.8	100.0
Hydrofluoric acid	0.1	0.2	0.3	0.4	0.6	0.7
% Back-extracted	17.8	43.1	68.7	83.4	100.0	100.0

TABLE 6 Cont'd.

The concentrations of components of the aqueous phases are given in moles litres^{-1}.

* pH adjusted to 10 to 11 with dilute ammonia. Equal volumes of the two phases were equilibrated for 15 min., data refer to single extractions.

0.2%, tantalum a 0.5% and protactinium a 1% (w/v) NBPHA solution in chloroform. The effect of time on the extraction of these three elements is recorded in table 5. At optimum fluoride ion, hydrochloric acid and reagent concentrations, the maximum extraction is obtained in 12 minutes for niobium, 9 minutes for tantalum and 6 minutes for protactinium. Solutions containing from radiotracer quantities up to at least 1 mg per ml of tantalum and 0.5 mg per ml of niobium are extracted efficiently under these conditions. It would therefore seem reasonable to expect the same extraction efficiency observed for tracer protactinium-233 would apply to solutions containing at least a few tenths of a mg of protactinium per ml.

(iv) Back-extraction of niobium, tantalum and protactinium

The data obtained on the back-extraction of niobium, tantalum and protactinium into aqueous phases of different compositions and concentrationshave been recorded in table 6. Thus, niobium requires 7 M hydrogen peroxide for a complete back-extraction from the organic phase. A separate series of experiments indicated that, with this concentration of hydrogen peroxide (7 M) the back-extraction of niobium depends very much on the pH of the aqueous phase, as at pH 9 back-extraction of niobium is negligible, 72% at pH 10 and complete at pH 11. Although large amounts of niobium are back-extracted with 2 M aqueous ammonia, complete extraction from the organic phase is obtained only at concentrations of 6 M. The behaviour of protactinium in the back-extraction with 7 M hydrogen peroxide at pH 10 to 11 is similar to that of niobium while 87% of the tantalum is back-extracted at pH 10.5 and complete extraction occurs at pH 11. The efficiency of extraction of niobium is comparatively less with aqueous ammonia than with tantalum which is completely removed from the organic phase with 2.5 M aqueous ammonia. Aqueous ammonia is not suitable for back-extraction of protactinium as hydrolysis results in losses of this element to the walls of the container. In addition, it was observed even with 6 to 7 M aqueous ammonia that only about 50% of the protactinium is back-extracted. Aqua-regia can back-extract niobium efficiently, but it does not extract protactinium and only 1% of tantalum is removed from the chloroform phase even after shaking the two phases together for 15 minutes. Hydrochloric, hydrofluoric, nitric and sulphuric acids either diluted or concentrated (except sulphuric acid > 12 M[23]) were not able to back-extract niobium from the organic phase. Oxalic and tartaric acids or ethylenediaminetetraacetic acid (EDTA) were likewise ineffective in removing niobium. Potassium hydroxide or carbonate can back-extract niobium, but solutions thus obtained contain alkali metals which are difficult to remove if that should be required. Likewise oxalic and tartaric

TABLE 7

Back-extraction$^+$ of tantalum and protactinium from the chloroform phase into various aqueous phases as a function of time.

Tantalum

(A) Ammonia (2.5 mole litre^{-1})

Time (min)	1	3	4	6	8	12
% Back-extracted	37.2	58.1	69.5	77.1	99.7	99.7

(B) Hydrogen peroxide* (2.0 mole litre^{-1})

Time (min)	1	3	6	7	12	15
% Back-extracted	19.3	56.7	77.1	91.5	99.8	99.8

Protactinium

(A) Oxalic Acid (1.0 mole. litre^{-1})

Time (min)	1	2	3	6	9	12
% Back-extracted	13.1	54.8	82.7	96.0	100	100

(B) Tartaric Acid (2.0 mole litre^{-1})

Time (min)	1	3	6	9	12	15
% Back-extracted	22.1	82.9	95.7	95.7	95.7	95.7

(C) Hydrogen peroxide* (7.0 mole. litre^{-1})

Time (min)	1	3	6	9	12	15
% Back-extracted	10.2	44.8	81.01	98.1	100	100

Table 7 (continued)

(D) Hydrofluoric Acid (0.6 mole litre^{-1})

Time (min)	1	3	6	8	9	12
% Back-extracted	48.1	68.6	89.4	94.6	100	100

* pH adjusted to 10 to 11 with dilute ammonia.

\+ Equal volumes of the two phases were equilibrated; data refer to single extractions.

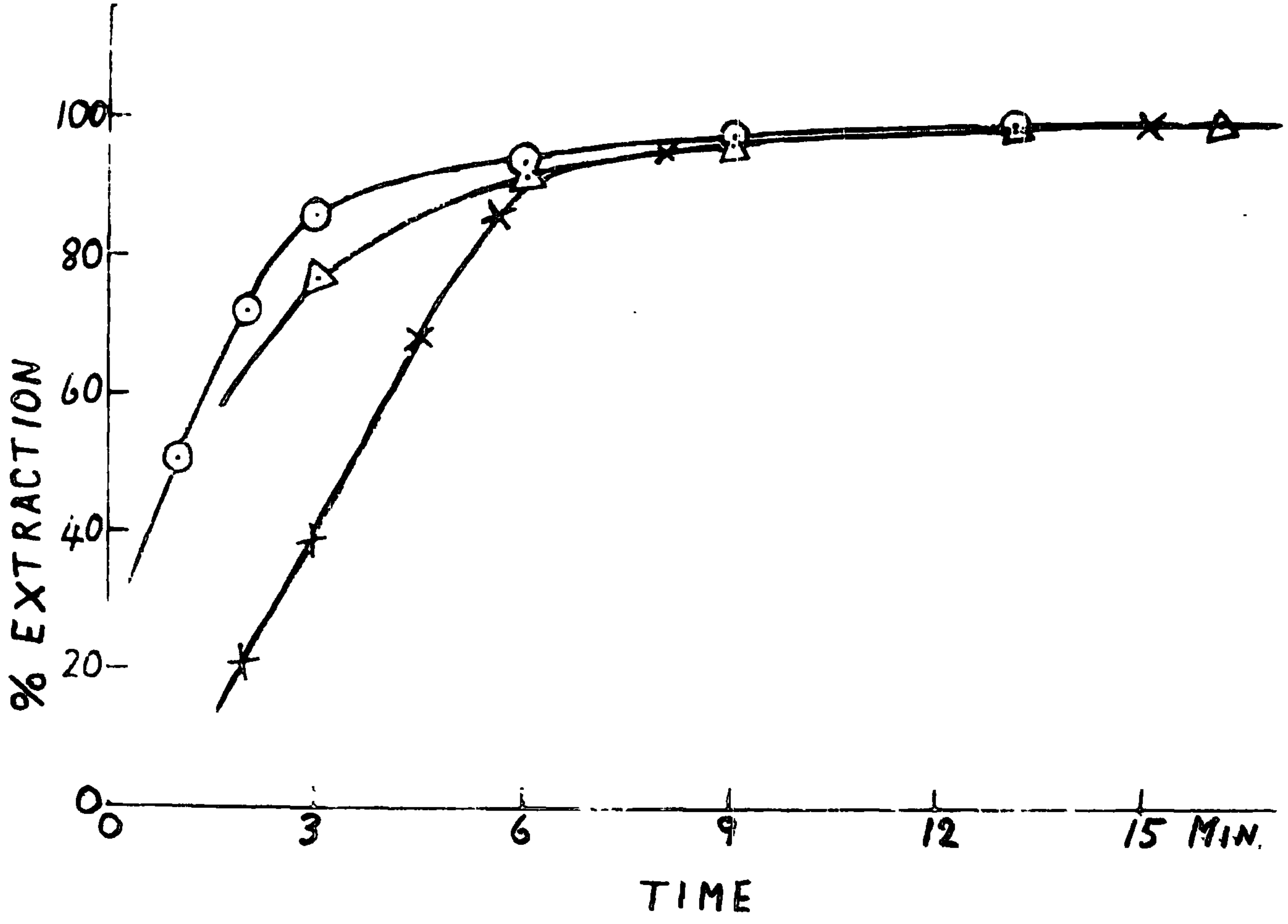

Fig.3. Back-extraction of niobium from the chloroform phase as a function of time of shaking using aqua-regia (x), 7M H_2O_2, at pH 11 (▲) and 6M aqueous ammonia (◉) as the aqueous phases.

TABLE 8

Optimum conditions for the back-extraction of niobium, tantalum and protactinium

	Element	Aqueous phase	Optimum time (min.)	% Extraction
1	Niobium	aqua regia	15	100.0
2	"	6 M ammonia	12	100.0
3	"	7 M hydrogen peroxide*	15	100.0
4	Tantalum	2.5 M ammonia	8	99.7
5	"	2.0 M hydrogen peroxide*	12	99.8
6	Protactinium	1 M oxalic acid	9	100.0
7	"	2 M tartaric acid	6	95.7
8	"	7 M hydrogen peroxide*	12	100.0
9	"	0.6 M hydrofluoric acid	9	100.0

* In all cases hydrogen peroxide was adjusted to pH 10 to 11 with dilute ammonia; other conditions as in table 6 .

acids are ineffective in back-extracting tantalum. Back-extraction of tantalum was not obtained with 0.1 M hydrochloric acid containing fluoride ions of various concentrations.

The effect of time on the back-extraction of niobium with aqua-regia, 7 M hydrogen peroxide at pH 11 and 6 M aqueous ammonia is shown in Fig. 3. Good recoveries are possible in 6 minutes or longer using any of these three aqueous phases. Table 7 records the back-extraction of tantalum and protactinium as a function of time into various aqueous phases. Aqueous ammonia seems to be more efficient in back-extracting tantalum (8 minutes) than alkaline hydrogen peroxide (12 minutes); for protactinium, tartaric and hydrofluoric acids appear to be very effective.

A summary of the optimum compositions of the aqueous phases, times of equilibration for back-extraction of niobium, tantalum and protactinium and the percentage of each of these elements extracted in a single extraction is given in table 8.

(v) Separation of niobium, tantalum and protactinium

The data from figures 1 and 2 suggest that a separation of protactinium and tantalum or protactinium and niobium may be achieved by control of hydrofluoric and hydrochloric acid concentrations. Tantalum may be separated from protactinium by extracting it from a solution 0.4 M in fluoride and 1 M in hydrochloric acid while a separation of niobium from protactinium would be possible with a solution 0.05 M in fluoride and 1 M in hydrochloric acid. It is clear that at low hydrochloric acid (about 0.01 M) and fluoride ion (0.05 M) niobium may be separated by extracting it from a mixture containing tantalum, as has been previously reported[24].

The results and observations just discussed provide the basis for the separation of pairs or all three of these elements if present together. The following schemes have been suggested[25].

(a) <u>Separation of tantalum from protactinium</u>

1. Adjust the mixture containing tantalum and protactinium to 1 M in hydrochloric acid and not more than 0.4 M in fluoride concentration.
2. Transfer the mixture to a polyethylene bottle and equilibrate with an equal volume of 0.5% NBPHA in chloroform by shaking for 9 minutes.
3. Separate the phases in a separating funnel and repeat step 2 on the aqueous phase.
4. Wash each of the separated phases twice with 10 ml portions of wash liquid; chloroform for the aqueous phase and 1 M hydrochloric acid made 0.2 M in fluoride for the chloroform phase.
5. Transfer the washings to the appropriate fractions.

Note: By this procedure tantalum is completely extracted into a chloroform solution of NBPHA, leaving protactinium in the aqueous phase. Tantalum may be back-extracted into the aqueous phase of the composition and under the conditions given in table 8.

(b) Separation of niobium from protactinium

The same steps used in the above procedure are applicable but the composition of the aqueous phase has to be 0.05 M in fluoride and 1 M in hydrochloric acid and a 0.2% NBPHA solution is used. The equilibration time is 12 minutes.

Note: Niobium thus transferred to the organic phase may be back-extracted into an aqueous phase of suitable composition (refer to table 8 for conditions).

(c) Separation of niobium, tantalum and protactinium

The conditions given above provide means of separating niobium from tantalum or niobium from protactinium. Further separations are, however, possible by making use of selective back-extraction steps for protactinium and niobium.

1. Extract niobium and tantalum from an aqueous phase 1 M in hydrochloric acid and 0.05 M in fluoride into a 0.5% solution of NBPHA in chloroform. Protactinium remains in the aqueous phase.
2. Back-extract niobium into aqua-regia by shaking the phases together for 15 minutes.

   or
3. Back-extract the niobium and tantalum into 6 M aqueous

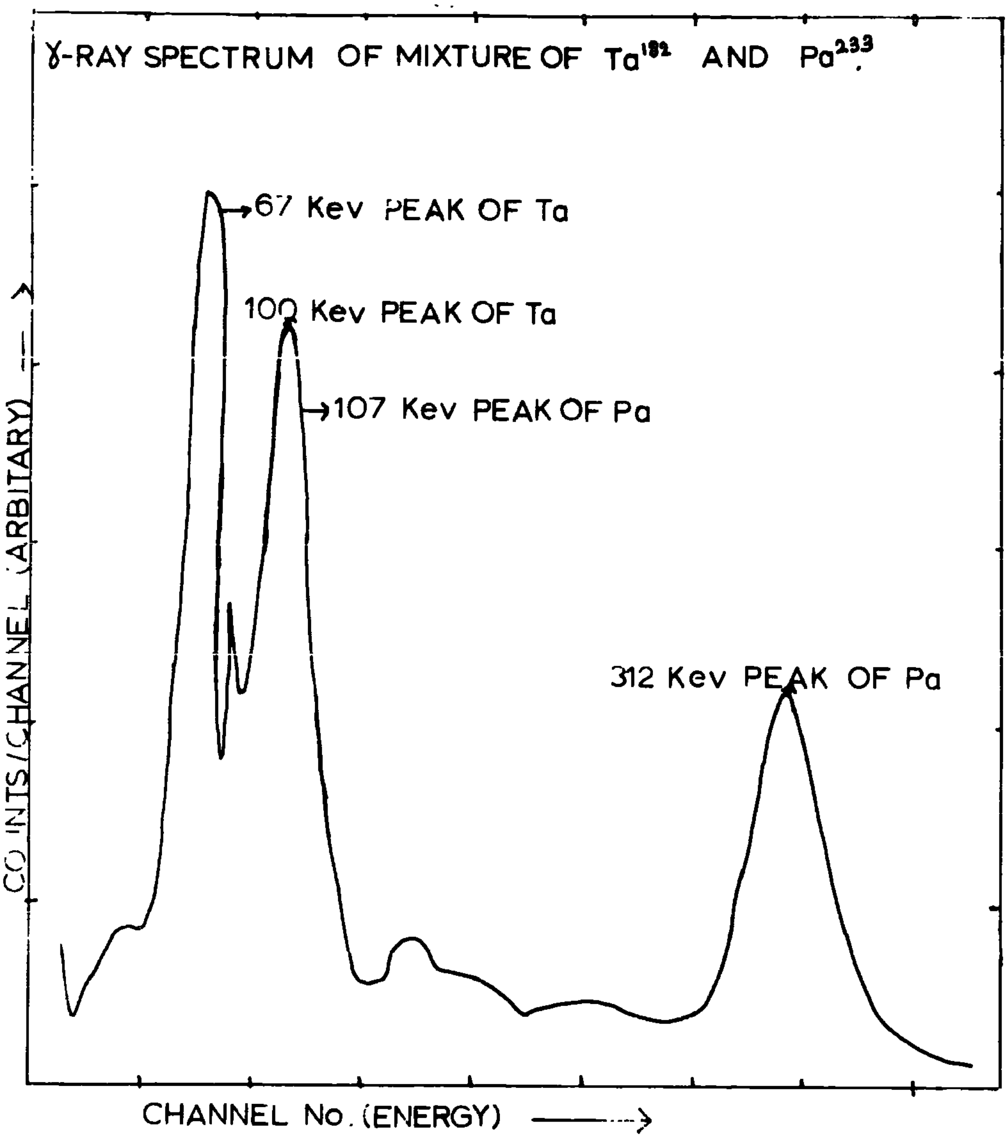
γ-RAY SPECTRUM OF MIXTURE OF Ta182 AND Pa233.
67 Kev PEAK OF Ta
100 Kev PEAK OF Ta
107 Kev PEAK OF Pa
312 Kev PEAK OF Pa
COUNTS/CHANNEL (ARBITARY)
CHANNEL No. (ENERGY)

Fig. 4

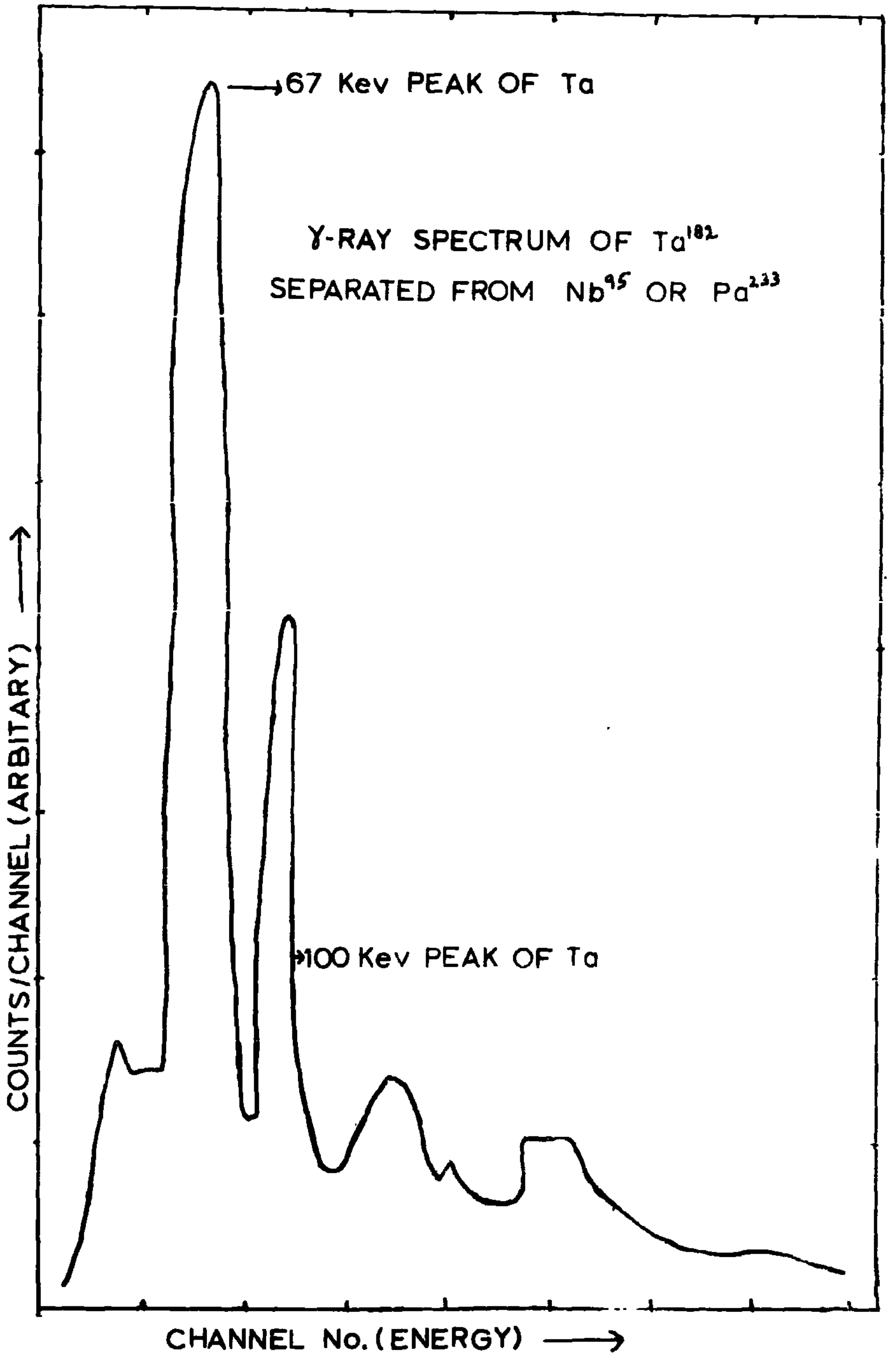
67 Kev PEAK OF Ta
γ-RAY SPECTRUM OF Ta182
SEPARATED FROM Nb95 OR Pa233
100 Kev PEAK OF Ta
COUNTS/CHANNEL (ARBITARY) →
CHANNEL No. (ENERGY) →

Fig. 5

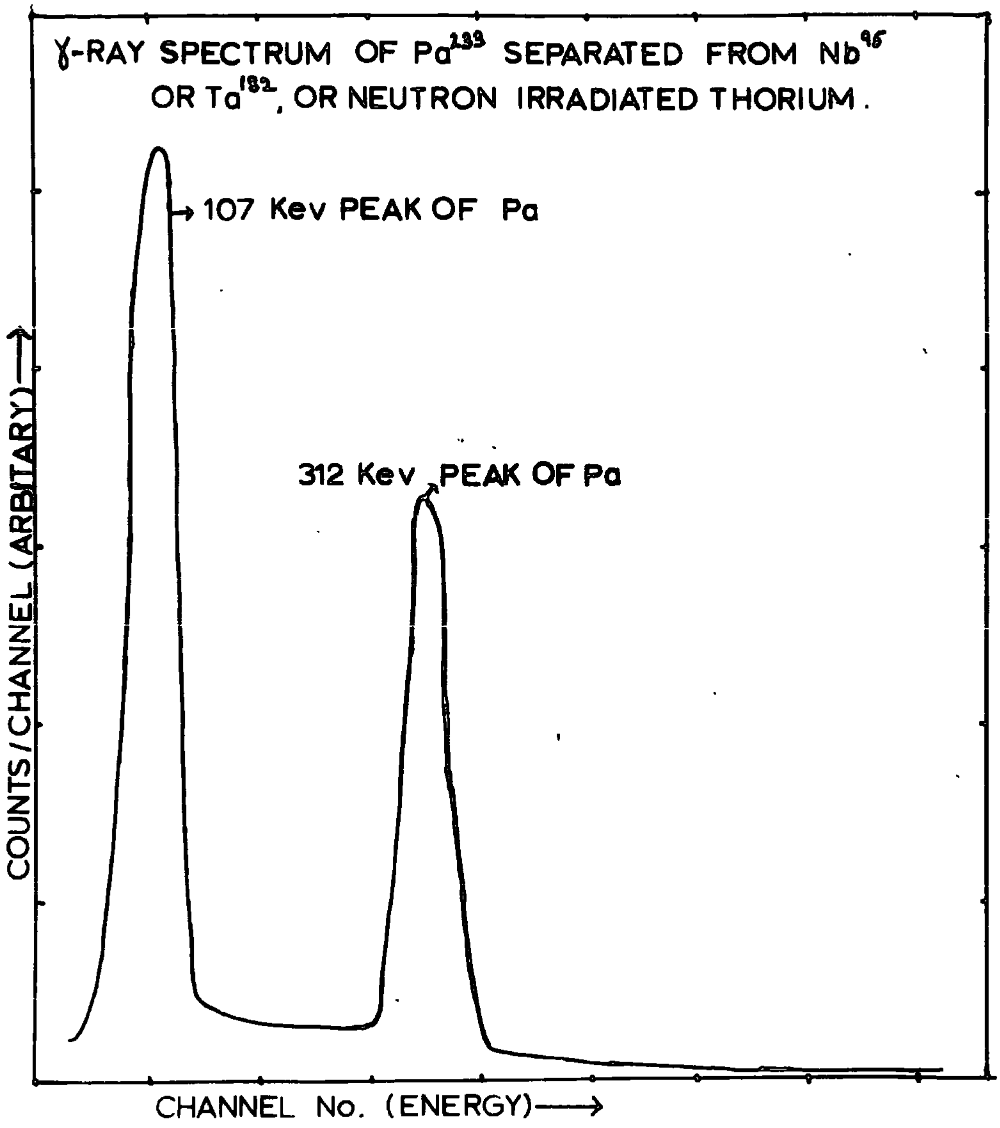
γ-RAY SPECTRUM OF Pa^{233} SEPARATED FROM Nb^{95} OR Ta^{182}, OR NEUTRON IRRADIATED THORIUM.
107 Kev PEAK OF Pa
312 Kev PEAK OF Pa
COUNTS/CHANNEL (ARBITARY)
CHANNEL No. (ENERGY)

Fig. 6

ammonia and adjust the acidity of the extract to 0.01 M with hydrochloric acid, make 0.05 M in fluoride and separate the niobium into 0.2% NBPHA (this gives a more efficient separation of niobium from tantalum than 2).

4. Protactinium is separated from niobium and tantalum by extracting all three elements into NBPHA in chloroform followed by a selective back-extraction into oxalic, tartaric or hydrofluoric acid under the conditions set out in tables 6 and 8.

The efficiency of the separations discussed above was checked by obtaining γ -ray spectra of the pairs of isotopes together using the multichannel analyser and of the individual isotopes of niobium-95, tantalum-182 and protactinium-233 and comparing with those obtained from the fractions separated from the mixtures by the methods outlined above. Fig. 4 shows the γ -ray spectrum of the mixture of tantalum-182 and protactinium-233. (In the γ -ray spectra recorded in all the figures in this chapter the marked interval (abcissa)represents 10 channels). It shows the 67 Kev peak of tantalum-182, the combined 100 and 107 Kev peaks of tantalum and protactinium respectively and the 312 Kev peak of protactinium-233. The 100 and 107 Kev peaks of tantalum and protactinium could not be resolved even with a large flat (cylindrical) sodium iodide (thallium activated) crystal 3" in diameter and 3" deep. Figs. 5 and 6 record separately the γ -ray

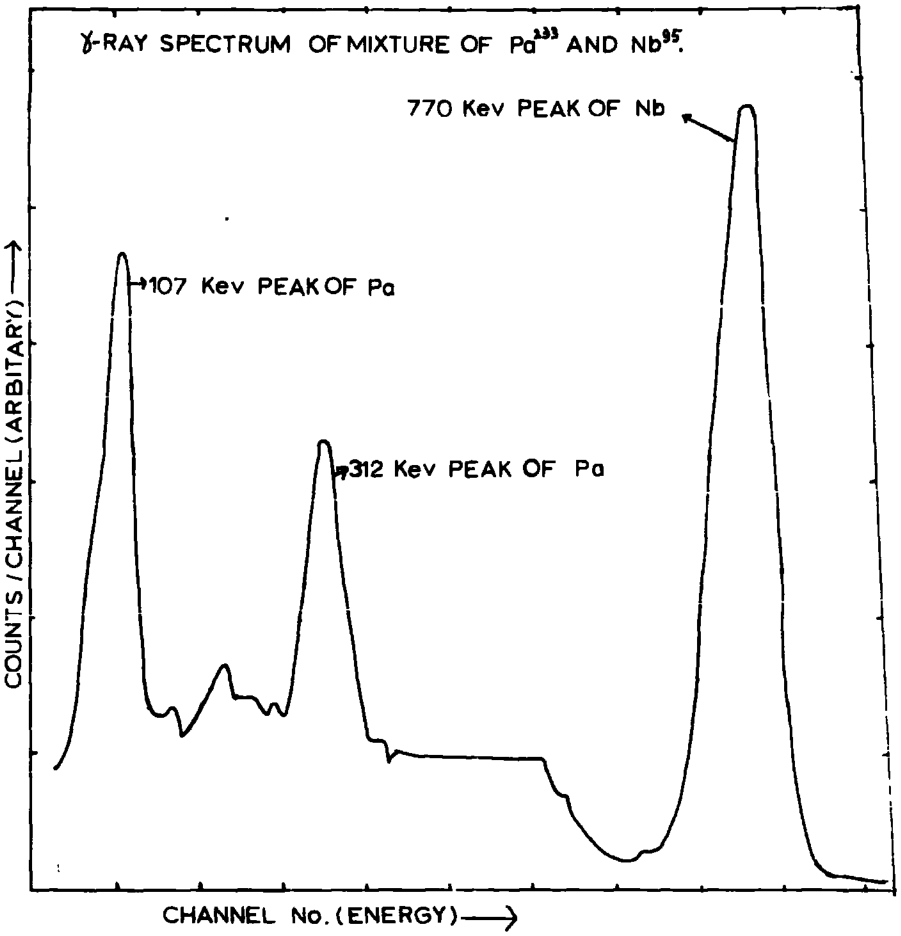
γ-RAY SPECTRUM OF MIXTURE OF Pa233 AND Nb95.
770 Kev PEAK OF Nb
107 Kev PEAK OF Pa
312 Kev PEAK OF Pa
COUNTS / CHANNEL (ARBITARY)
CHANNEL No. (ENERGY)

Fig. 7.

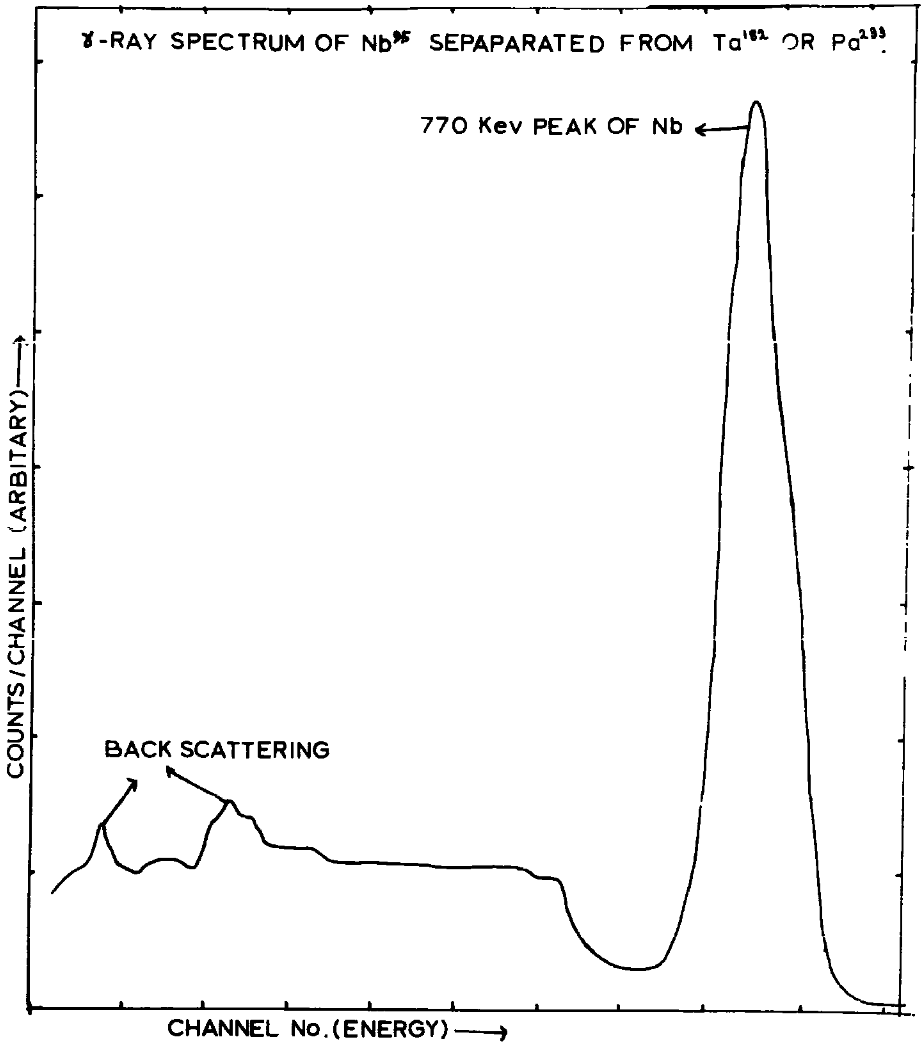
γ-RAY SPECTRUM OF Nb^{95} SEPAPARATED FROM Ta^{182} OR Pa^{233}.
770 Kev PEAK OF Nb
BACK SCATTERING
COUNTS/CHANNEL (ARBITARY)
CHANNEL No.(ENERGY)

Fig. 3

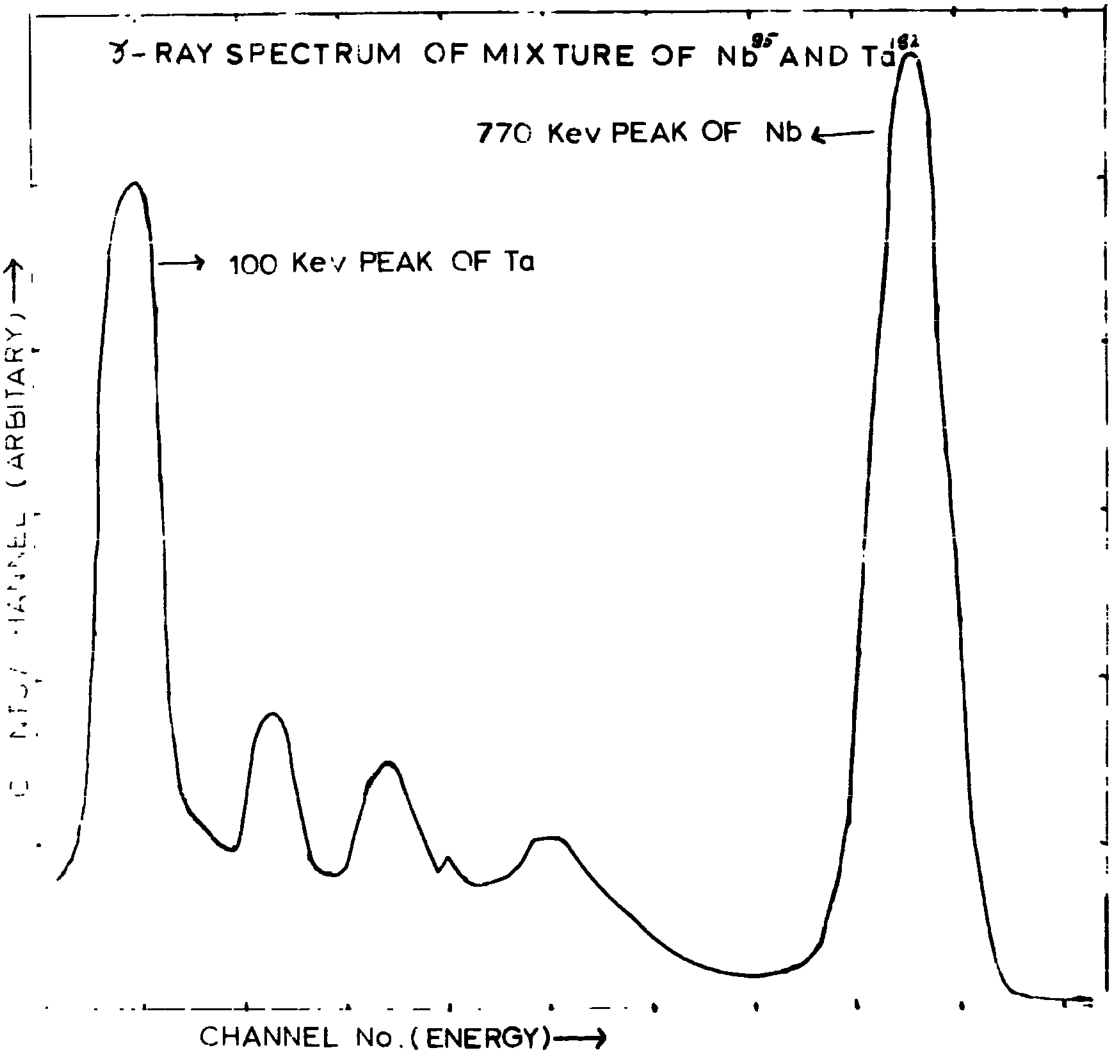
γ-RAY SPECTRUM OF MIXTURE OF Nb^{95} AND Ta^{182}
770 Kev PEAK OF Nb
100 Kev PEAK OF Ta
COUNTS/CHANNEL (ARBITARY) →
CHANNEL No. (ENERGY) →

Fig.3.

TABLE 9

Separation factors* for pairs of elements.

	Element A separated from B				System	Method of separation	Separation
1.	Ta	"	"	Pa	^{233}Pa, inactive Ta (1 mg/ml)	a	10^3
2.	Nb	"	"	Pa	^{233}Pa, inactive Nb (0.5 mg/ml)	b	10^3
3.	Nb	"	"	Ta	(1) ^{182}Ta, inactive Nb (0.5 mg/ml)	c,2	10^2
					(2) ^{182}Ta, inactive Nb (0.5 mg/ml)	c,3	10^3

* The ratio of the initial amount of B present in the mixture (A + B) to the final amount of impurity B present in the separated sample of A.

spectra of tantalum-182 and protactinium-233 separated from one another by the method (a). Neither of them show any contamination by the other. Fig. 7 gives the γ-ray spectrum of a mixture of protactinium-233 and niobium-95. The γ-ray spectrum of niobium-95 separated by method (b) is recorded in Fig. 8. The earlier two small peaks are due to back-scattering indicated by the decrease in their intensity when the shielding around the crystal was increased. The protactinium separated from the mixture gave a spectrum similar to that shown in Fig. 6. Fig. 9 is the γ-ray spectrum of the mixture of niobium-95 and tantalum-182. However, in order to include the 770 Kev peak of niobium-95, the 67 Kev peak of tantalum-182 could not be included using the same instrumental settings. By adopting method (c,3) the separated fractions gave spectra similar to those in Figs. 5 and 8.

From the above discussion of γ-ray spectra, it is clear that the separation of pairs of these elements can be effected without any evident cross contamination. However, the sensitivity of this method is limited as about 1% contamination could be detected and hence further separations were performed by using a radiotracer for one member of the pair, the other being inactive. Separations were performed and separation factors thus obtained (according to the general procedure given in chapter 2, section B, d) are recorded in table 9.

Of the interfering cations, zirconium (and also hafnium), aluminium, titanium, manganese-(II), iron-(III), rare earths and uranium and thorium should not interfere in the proposed separations. These elements have been shown previously[26-29] or during the course of this work to extract with NBPHA at (relatively) very low acidities.

B. URANIUM, THORIUM AND PROTACTINIUM

EXPERIMENTAL

(a) Radioisotopes

Thorium-234/protactinium-234 (uranium-X) was separated from 'aged' uranium-238 by an ion-exchange method[30].

Antimony-124 was obtained from The Radiochemical Centre, Amersham, England (specific activity 1c per g)as antimony trioxide in 5 M hydrochloric acid.

(b) Reagents

Reagents used are given previously in this chapter with the following additions.

Dibenzoylmethane: a solution containing 1 g of the substance (from B.D.H.) in 100 ml of 95% ethyl alcohol was used in the spectrophotometric study of uranium following the method of Yoe et al[31].

Acetic acid buffer: 80 g of anhydrous sodium acetate and 8 ml of glacial acetic acid were diluted to 1 litre. Such a solution is 0.05 M in acetic acid -acetate ions and has a pH of 5.4.

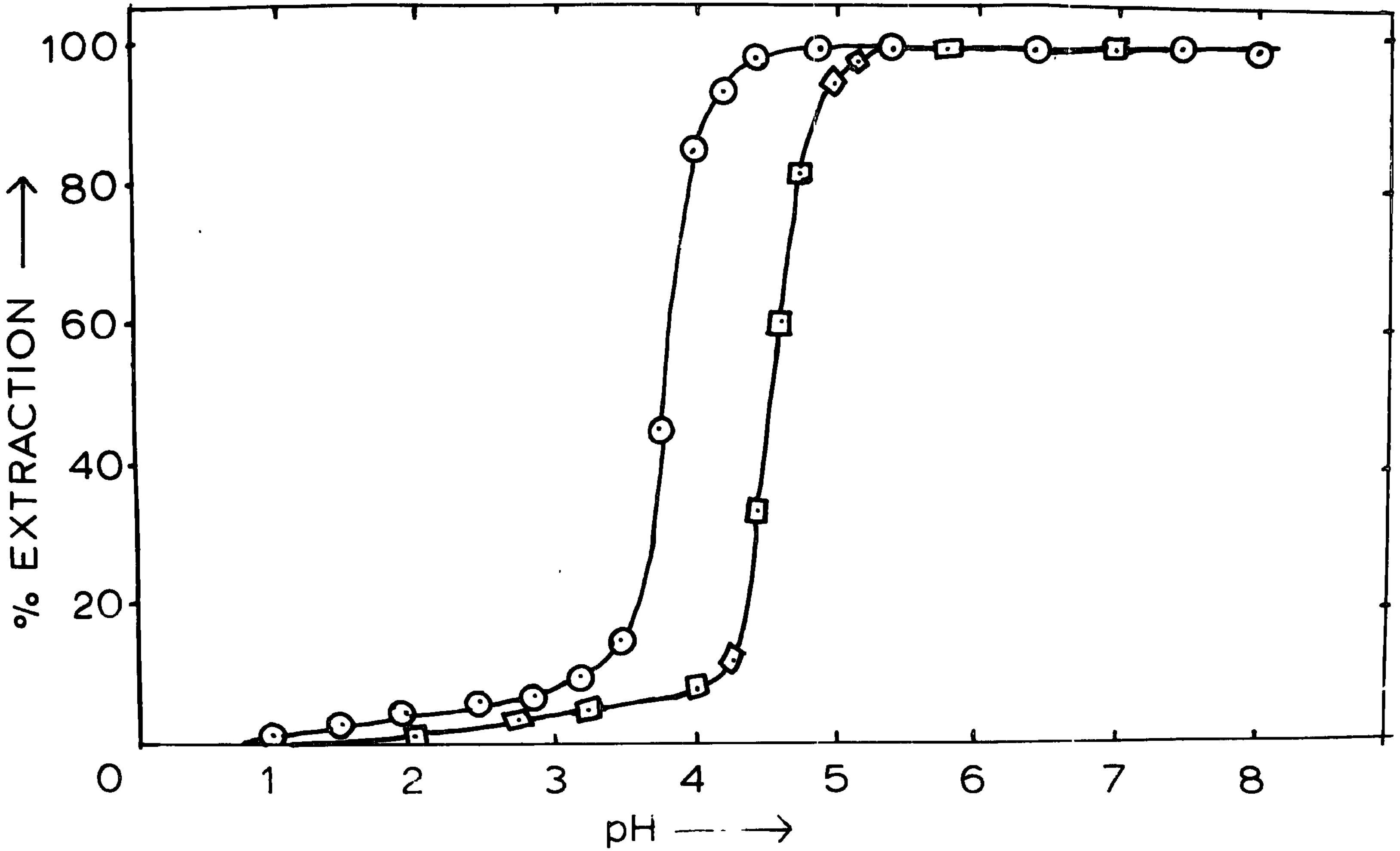

Fig.10. Extraction of uranium (⊡) and thorium (⊙) from 0.05M acetate-acetic acid as a function of pH Other conditions are given in the footnotes to Tables 10 and 11.

Uranium carrier solution: uranium-(VI) oxide was used to prepare a solution containing 5 mg of uranium per ml in 2 N nitric acid.

Antimony-124 and uranium-X were counted in a Geiger-Muller counter (chapter 2, section C, a, i). For an outline of the method of investigation refer to chapter 2, section B.

RESULTS AND DISCUSSION

(i) The effect of pH, NBPHA concentration and time of equilibration on the extraction of uranium and thorium

Extraction of uranium and thorium as a function of pH is shown in Fig. 10. The aqueous phase was 0.05 M in acetic acid + acetate ions. Uranium starts extracting at about pH 1.8 and increases with increasing pH reaching a maximum at 5.2, while thorium begins to extract at about pH 1.20 and the maximum is attained at 4.9. It is clear from the figure that uranium and thorium cannot be separated cleanly from each other using an acetate buffer system. Das and Shome[32] have described a method for the separation and gravimetric determination of uranium in the presence of thorium. They have used the magnesium salt of ethylenediaminetetraacetic acid (EDTA) to mask thorium and then they precipitated uranium at pH 5.2 using ethanolic NBPHA. But in the course of the present work it was found that about 11% of the thorium transfers with the uranium fraction when solvent extraction is practised using EDTA at pH 5.2 as

TABLE 10

Extraction of Uranium and Thorium as a function of NBPHA concentration.

S.No.	% NBPHA (w / v.)	* % Extraction Uranium	* % Extraction Thorium
1	0.05	25.1	16.1
2	0.10	36.7	31.3
3	0.20	41.8	56.2
4	0.30	56.1	83.1
5	0.50	72.5	96.7
6	0.60	89.0	99.1
7	0.80	96.2	99.1
8	0.90	99.1	99.1
9	1.0	99.1	99.1

* Equal volumes of the two phases were equilibrated for 15 min. Extraction data refer to single extractions.

The pH of the aqueous phase was 5.3 for uranium and 4.9 for thorium.

TABLE 11

Extraction of Uranium and Thorium as function of time.

S.No.	Time	% Extraction Uranium	 Thorium
1	0.5	27.3	20.0
2	1.0	44.8	39.7
3	2.0	56.4	64.4
4	4.0	75.3	90.8
5	6.0	92.1	94.6
6	8.0	95.0	99.1
7	9.0	99.1	99.1
8	12.0	99.1	99.1

* NBPHA concentration in chloroform is 0.9% for uranium and 0.6% for thorium. The data refer to single extractions. For other conditions see the footnote to Table 10 .

a masking agent and hence such a separation was found to be of little practical value. Tables 10 and 11 give the effect of varying reagent concentration and time on the extraction of uranium and thorium respectively.

(ii) A carrier-free separation of protactinium from neutron irradiated thorium

From Fig. 1 it is clear that protactinium is extracted almost quantitatively from concentrated hydrochloric acid containing 0.025 M fluoride ions into a 1% NBPHA chloroform solution. Uranium and thorium studies indicate that these two elements are not likely to interfere in the extraction of protactinium. A carrier-free separation of protactinium from uranium-233 and thorium and its daughter products has thus been devised. Elements arising from the fission of uranium-233 if it has been allowed to accumulate in the sample can be accounted for by some minor changes in the procedure.

The following scheme proposed[33] is set out for the separation of protactinium-233 from thorium irradiated for short times (several days).

1. Dissolve the irradiated thorium (metal, oxide or preferably basic carbonate) in concentrated hydrochloric acid with the addition of a little fluoride and by heating, if necessary.
2. Adjust the hydrochloric acid to at least 10 M and fluoride concentration to not more than 0.025 M. Shake

for 6 minutes with an equal volume of 1% NBPHA in chloroform.

3. Separate the two phases and again equilibrate the aqueous phase (afterwards discarded) as in step 2.
4. Wash the combined organic phases from steps 2 and 3 with equal volumes of concentrated hydrochloric acid and discard the washings.
5. Equilibrate the chloroform phase with an equal volume of an aqueous phase 5 M in hydrochloric acid and not less than 0.6 M in hydrofluoric acid.

The aqueous phase, which contains protactinium, is preferably washed with some chloroform and the washings are discarded. By step 5, niobium, if present, is retained in the chloroform phase[34]. The scheme thus outlined (excluding step 1) can be completed in about 20 minutes.

If tin and antimony are present, boric acid or aluminium chloride is added to the aqueous phase from step 5, the acidity reduced to 0.8 M and these elements are extracted with 1% NBPHA leaving protactinium in the aqueous phase, which is washed with chloroform and made strongly acid. Should boron or aluminium need to be removed repetition of steps 2-5 provides for their separation from protactinium.

Accumulation of uranium-233 in the sample undergoing irradiation results in the formation of fission products by the U-233 (n,f) reaction. Therefore such products should be taken

TABLE 12

Separation from various elements.

Separation from	system used and method of measurement	Separation factor *
Thorium	Uranium X, radiochemical	3×10^4
Uranium	Uranium-238, Spectrophotometric	$> 4 \times 10^3$
Tin	Tin-113m, radiochemical	7×10^2
Antimony	Antimony-124, radiochemical	2×10^2

* The ratio of the initial to the final concentration of the element after going through the procedure.

into account in a separation scheme in addition to thorium and its daughter products[35].

Thorium daughters which have half-lives of a few hours either do not extract at such a high acid concentration (radium-228 and 224) or begin to extract about pH 4.5 or higher (actinium-228 and lead-212[36]). Bismuth-(III), which extracts at pH 0 (see chapter 5) does not follow protactinium.

Fission products, if present, alkali metal, alkaline earth, rare earth, halogen (as halide or oxy-anion), zirconium, molybdenum-(VI), silver, cadmium-(II) and indium-(III) will not extract[34,37,38] along with protactinium. Technetium, ruthenium-(III), rhodium-(III), palladium-(II) and tellurium-(IV) or (VI) are not extracted at such a high hydrochloric acid concentration as confirmed by spot tests. About 500 mg. of each of these elements were taken through the separation procedure and the protactinium fraction examined for the elements using a sensitive spot-test[39]. Technetium was however not examined. Of the remaining fission products niobium, tin-(IV) and antimony-(III) or (V) extract partially or completely and must be taken into consideration in the separation scheme.

Separation from elements like uranium, thorium, tin and antimony which may interfere was taken into account and separation factors for all these elements (chapter 2, section B, d) are obtained and are given in table 12.

From the table it is clear that separation from uranium and thorium is good while separation from tin and antimony is less satisfactory, but these elements appear in low yield from uranium-233 fission and hence should not interfere.

No contamination by fission or daughter products of thorium was observed when protactinium was added and then recovered from natural thorium which was irradiated with 14-Mev neutrons to give about 10^9 fissions even when separation was carried out immediately after irradiation. Further, the purity of protactinium thus obtained by the method outlined above was checked by examining the γ-ray spectrum using the multichannel analyser. Thus a spectrum similar to Fig. 6 was obtained indicating a lack of evident contamination. The percentage recovery of protactinium by this method was found to be better than 80% in the presence of fission products and in their absence, about 95%. The difference in the yield was found to be due to losses of protactinium activity on the walls of the container after the addition of fluoride scavenger and the reduction of the acidity prior to the tin and antimony separation.

Elements like aluminium and iron do not extract[36] under the conditions where protactinium extracts quantitatively and hence should not interfere in the separation scheme.

C. A CARRIER-FREE SEPARATION OF NIOBIUM FROM ZIRCONIUM

EXPERIMENTAL

Details of the experimental work are given in group A of this chapter.

RESULTS AND DISCUSSION

From Figs. 1 and 2 it is clear that niobium can be extracted quantitatively even from a very low concentration of hydrochloric acid containing fluoride up to 0.05 M. On the other hand, the distribution studies of zirconium with NBPHA showed that it is not extracted at all under the conditions where niobium extracts completely. This observation has been used in devising a method for the carrier-free separation of niobium-95 from zirconium. The following steps[34] are involved in the separation method proposed.

(a) Extraction of niobium into NBPHA in chloroform

1. To the zirconium-niobium mixture add enough hydrochloric acid and hydrofluoric acid to make the final solution 1 M in the former and 0.05 M in latter.
2. Add an equal volume of a 0.2% solution of NBPHA in chloroform and shake the mixture for about 12 minutes.
3. Separate the two phases using a separating funnel; retain the aqueous phase containing the zirconium for future milkings.
4. Wash the chloroform phase twice with an acid mixture 0.05 M in hydrofluoric and 1 M in hydrochloric acids, discarding the washings.

5. Back-extract into an aqueous phase (see below).

Notes:

1. The solution before extraction (step 1) may contain 1 mg per ml of zirconium without impairing the separation.
2. The aqueous phase (step 3), if desired, can be freed from niobium at the time of extraction by washing with chloroform containing NBPHA.

(b) Back-extraction of niobium into an aqueous phase

Three procedures are applicable to the back-extraction producing aqueous solutions from which all solutes giving rise to solid matter on evaporation can readily be removed. They include treatment with aqua-regia, hydrogen peroxide and ammonia.

(i) Aqua-regia

1. Shake the chloroform phase for about 10 minutes with an equal volume of aqua-regia.
2. Discard the chloroform phase.
3. Wash the aqueous phase with 2 portions (about 10 ml) of chloroform.
4. Reduce the volume to 5 to 6 ml by evaporation.
5. Cool and extract twice with two small portions of di-iso-propyl ether to remove residual organic matter.
6. Warm to expel traces of ether.

(ii) Hydrogen peroxide

1. Shake the chloroform phase for about 10 minutes with an

equal volume of a 7 M solution of hydrogen peroxide adjusted to about pH 11 with a little dilute ammonia.

2. Repeat steps 2, 3, 4 and 5 for the aqua-regia treatment.
3. Make acid as required.

(iii) Ammonia

1. Shake for 10 minutes with an equal volume of 6 M aqueous ammonia.
2. Steps 2, 3, 4 and 5 in the aqua-regia procedure remove the organic matter and much of ammonia.

Note:

The residual ammonia in this and the previous back-extraction method may be removed by oxidation with aqua-regia and a solution is finally prepared in either hydrochloric or nitric acids.

The efficiency of the separation performed by the method outlined above was checked by adding zirconium carrier to the separated niobium fraction and precipitating zirconium with mandelic acid[40]. The precipitate thus obtained was counted for zirconium contamination in the niobium fraction. From such experiments it was established that by following this liquid-liquid extraction method the decontamination factor for niobium from zirconium was at least 10^4. Further, a solid source of niobium-95 (containing niobium pentoxide) separated by this method was prepared. This source having an initial counting rate of 2.2×10^4 c.p.m. was counted two or three times a week using an end-window gas proportional counter. The decay of the source was followed for over six months. During this period there was no evidence of contamination from zirconium and the half-life was calculated with the aid of an Elliot 803 computor and a least squares programme and found to be 34.8 + 0.4 days which is in reasonable agreement with published values[41].

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CHAPTER 4

The Application of N-Benzoyl-N-phenylhydroxylamine to the Separation of Gallium, Indium, Thallium, Germanium, Tin and Lead by Solvent Extraction

Introduction

Gallium, indium, thallium, tin and lead frequently occur together in minerals with some other common elements like iron, copper, nickel and aluminium. Separations of some of the pairs of the above-mentioned elements by precipitation methods are difficult[1]. Separation of indium from tin and lead which are precipitated as sulphides from hydrochloric acid solution leads to losses because of the tendency of indium to co-precipitate with these sulphide group elements[2]; however, this method is used sometimes[3-5] as indium losses can be reduced to a minimum by reprecipitation cycles. Alternatively, tin may be separated from indium as 'soluble metastannate' by treating the freshly precipitated hydroxide with dilute sodium hydroxide. This method, while giving better separations than are achieved by the precipitation of tin as sulphide, is not entirely satisfactory[6]. The separation of lead from indium is also difficult. Lead alloys and me tallurgical residues containing indium are sometimes digested with sulphuric acid in analysis[7]. If sulphur trioxide fumes are produced in this separation, serious contamination of lead sulphate by indium results.

Chemical separations by solvent extraction are more convenient and frequently cleaner than precipitation methods. In many cases entire separations may be carried out even with minute amounts of component which may thus be retained whereas in a precipitation process they may easily get lost through co-precipitation. From solutions made 1.5 M in potassium iodide and 0.75 M in sulphuric acid, indium is extracted and separated from gallium, aluminium, iron, beryllium, molybdenum and tungsten but tin and antimony interfere[8]. Under specified conditions extraction with di-ethyl or di-iso-propyl ethers from solutions 0.5 to 0.6 M in hydrobromic acid are used to extract indium but gallium, thallium and iron interfere[9]. Tin can be separated in a carrier-free state from 3 M hydrochloric acid using cupferron[10].

NBPHA has been used for the separation and gravimetric determination of indium[11], gallium[12] and tin[13]. The derivatives of NBPHA with these metals are soluble in benzene, alcohol, ether and chloroform. Lead with NBPHA is extracted at a high pH[14]. Qualitative tests showed that tin and thallium are extracted with NBPHA and hence the detailed study of the extraction of these two elements is reported here; further, some of the separations are of interest to radiochemists as the elements in question may be produced from neighbouring elements in the periodic table, or they may be found (with the exception of thallium) in fission products arising from the fission of certain heavy nuclei[15]. Germanium has been included in this study on these grounds.

In the partition studies of gallium, indium, thallium, tin and lead phase distributions were measured using radiotracers except in the case of lead where distributions were followed by compleximetric titration[16]. The behaviour of tin is studied in the presence of hydrochloric and perchloric acids while germanium was examined in hydrochloric acid media with chloroform alone as the second phase. Gallium, indium, thallium and lead are examined from acetic acid - acetate buffer systems since these elements only react at relatively very low hydrogen ion concentrations. Making use of the results possible separations of these elements are examined. The efficiency of separations (which have been performed according to the general procedure outlined in chapter 2, section B, d) were also determined using radiotracers except again in the case of lead for which a spot test[17], was applied. Optimum conditions of extraction for the above-mentioned elements and separation factors obtained are given in this chapter.

EXPERIMENTAL

(a) Radioisotopes

Germanium was kindly provided by Dr. D.J. Silvester of the M.R.C. Cyclotron Unit, Hammersmith Hospital, London.

It was adsorbed on alumina from which a chromatographic column was prepared and carrier-free gallium-68 milked by the method of Green and Tucker[18] using EDTA. The EDTA-gallium complex was most effectively destroyed by taking the eluate to dryness with hydrogen peroxide and heating the container to a dull red heat. The container afterwards was allowed to cool and gallium was taken into very dilute hydrochloric acid solution (0.2 M). Germanium-68 when required was obtained by desorbing it from the alumina with 8 M hydrochloric acid, extracting it into chloroform from which it was back-extracted with 2 M hydrochloric acid.

Indium-114m containing a known concentration of carrier indium was supplied by The Radiochemical Centre, Amersham, England.

Tin-113 was obtained by neutron irradiation of metallic tin in BEPO, Harwell. The 27.5 hour tin-121 was allowed to decay away before use.

Thallium-204 was obtained by irradiation of thallium in BEPO, Harwell, England.

(b) Reagents

The reagents used are mentioned in chapter 3 with the following additions:

EDTA: a 0.01 M standard solution was prepared by weighing out the disodium salt, dihydrate and dissolving it in distilled water.

Xylenol Orange (B.D.H.). A 0.1% (W/V) solution in ethanol was used.

Benzidine was supplied by Hopkin and Williams Ltd., Essex, England. A solution was prepared by dissolving 0.05 g. of benzidine in 10 ml of glacial acetic acid and diluting to 100 ml with distilled water.

Carrier solutions containing 5 mg per ml of each of these elements were prepared from reagent grade chemical substances.

(c) Measurement of radioactivity

Indium-114m and thallium-204 samples were counted in a Geiger Muller counter. Gallium-68 and tin-113 were counted in a γ-scintillation counter. For gallium-68 use was made of γ-radiation resulting from positron annihilation and for tin the 0.393 Mev γ-ray of the 1.7 hour indium daughter was employed for counting purposes. Germanium was also determined indirectly by measuring the gallium-68 after allowing sufficient time for the latter to come to equilibrium with the parent.

The details of the apparatus used are given in chapter 2, section C and for the general method of investigation the reader is referred to section B of the same chapter.

RESULTS AND DISCUSSION

(a) Effect of acids on the extraction of tin-(IV) and germanium

The effect of change in the hydrochloric and perchloric

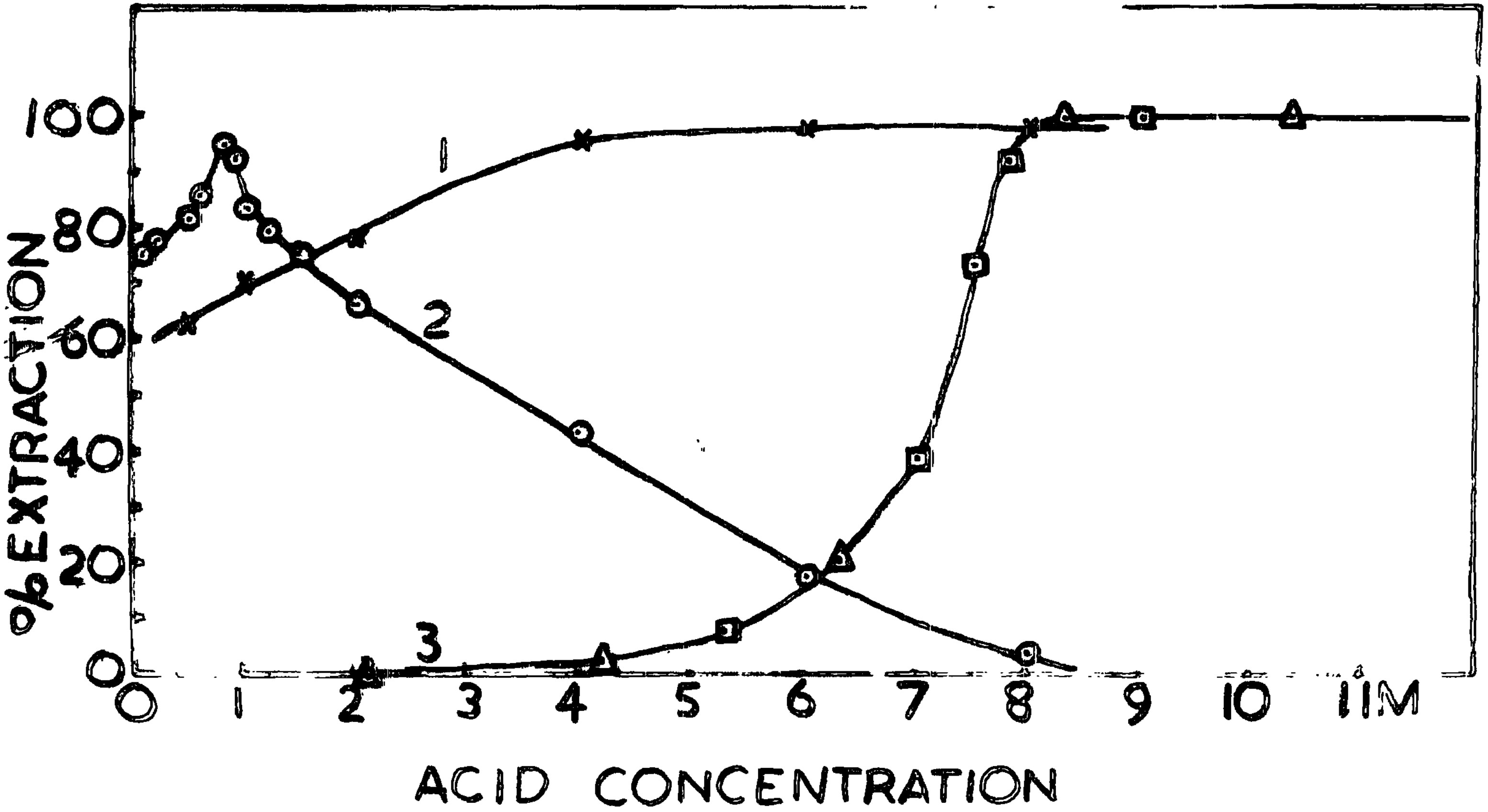

Fig.11. Extraction of tin and germanium as a function of acid concentration. Curve I, Sn from $HClO_4$; curve 2, Sn fromHCl; curve 3, Ge from HCl. ▲ values taken from BRINK et el[19], ▣ this work. Extraction conditions: 1%NBPHA for Sn, chloroform alone for Ge, equilibration time 15 min, Sn and Ge concns. were 1.3 10^{-3}M and 10^{-3}M respectively. Data refer to single extractions with equal volumes of extractant.

acid concentrations on the extraction of tin-(IV) is shown in Fig. 11. The sharp maximum at 0.8 M in the extraction from hydrochloric acid and the nature of the tin reaction with NBPHA will be discussed in chapter 5. Of the halides, only fluoride interferes considerably with the extraction of tin. With further increase in acidity the extraction decreases sharply and falls to a minimum (1%) at about 8 M in hydrochloric acid. Tin-(IV) extraction from perchloric acid shows a very different trend. The extraction increases with increase in acid concentration reaching a maximum at about 4 M. Chloroform alone extracts germanium quantitatively and some results thus obtained, together with data taken from Brink et al[19], are recorded in curve 3 of the same figure. The extraction of germanium is negligible up to about 3 M in hydrochloric acid and with further increase in acidity the extraction rises and reaches the maximum above 8 M. Germanium or tin do not extract into chloroform alone from a perchloric acid solution. Extraction was not observed (i) from a germanium solution 0.8 M in hydrochloric acid and 7 M in perchloric acid or (ii) from a 2 M hydrochloric acid solution saturated with ammonium chloride (about 6 M in chloride ion). The results indicate that germanium and tin can be separated from one another by extracting the former from a 8 M hydrochloric acid solution. Tin-(IV) may then be extracted quantitatively by neutralising the aqueous phase

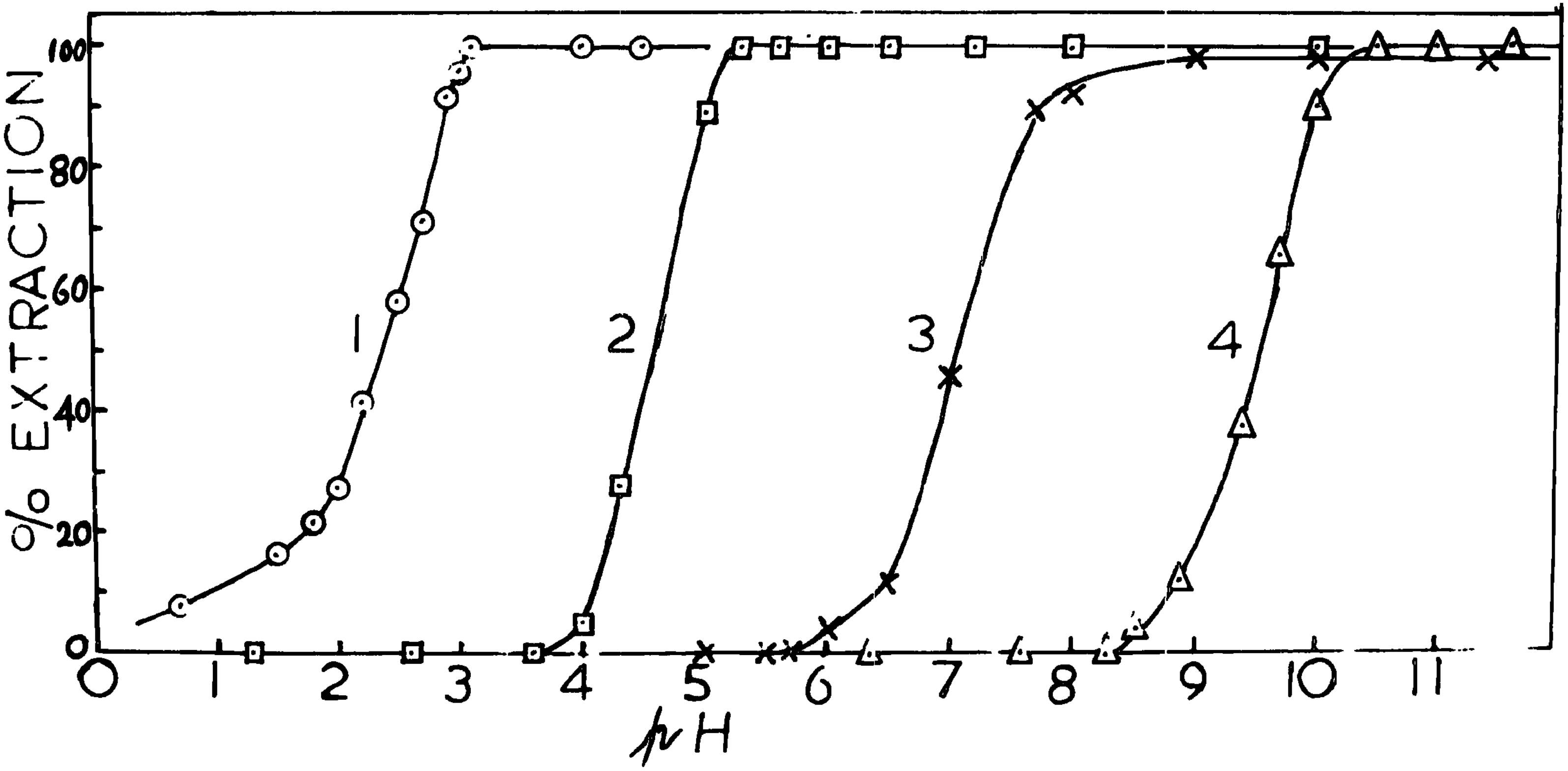

Fig.12. Extraction from 0.05 M acetate-acetic acid as a function of pH; Ga (curve I), In (curve 2), Pb (curve 3) and T^1 (curve 4). For conditions of extraction see the footnotes to Tables 13 and 14.

TABLE 12

Extraction as a Function of NBPHA Concentration.

		% EXTRACTION*				
	NEPHA Conc. (1% w/v.)	Gallium-III	Indium-III	Thallium-I	Tin-IV	Lead-II
1	0.025	-	30.2	-	-	-
2	0.05	-	50.4	-	-	-
3	0.10	21.3	69.9	55.7	17.4	31.3
4	0.20	50.1	81.1	81.9	39.9	48.8
5	0.30	60.8	84.3	86.1	58.1	60.3
6	0.40	79.3	86.7	90.8	75.3	68.9
7	0.60	88.4	90.3	95.3	84.1	82.1
8	0.70	91.7	93.1	99.7	88.3	87.7
9	0.80	94.1	96.5	99.7	90.7	90.4
10	1.0	99.4	99.2	99.7	94.4	97.4
11	1.5	99.4	99.2	99.7	94.4	97.4
12	2.0	99.4	99.2	99.7	94.4	97.4

* Equal volumes of the two phases were equilibrated for 15 minutes. Extraction data refer to single extractions. Metal concentrations:- gallium 6.0 x 10^{-3}M, indium 1.0 x 10^{-3}M, thallium 5.0 x 10^{-4}M, tin 1.3 x 10^{-3}M and lead 2.0 x 10^{-3}M.

with ammonia and making 4 M in perchloric acid or reducing the acidity to 0.8 M in hydrochloric acid with ammonia. Of these two, the first one is more advantageous if gallium is present. As in 0.8 M hydrochloric acid, with additional chloride ions or not, slight extraction (about 0.3%) of the gallium occurs along with tin.

(b) Effect of pH, NBPHA concentration and time of equilibration on the extraction of gallium, indium, thallium and lead

The extraction of gallium, indium, thallium and lead as a function of pH is recorded in Fig. 12. Acetic acid - acetate buffer systems (0.05 M in acetic acid - acetate) were used. Gallium may thus be cleanly separated from the rest of these elements by extracting it at pH 3.1 to 3.8; indium could be separated from lead and thallium-(I) at pH 5.3 to 5.6 and lead from thallium-(I) at pH 7.8 to 8.2. Thallium-(I) begins to extract above pH 8.2 and extraction is almostquantitative above pH 10.5. On the other hand thallium-(III) does not extract up to pH 9.5 from an acetate medium; precipitation of thallium hydroxide starts at about pH 9.8 and incomplete extraction is obtained. Table 13 illustrates the effect of varying NBPHA concentration in the chloroform phase on the percentage extraction of gallium, indium, thallium, tin and lead. Although indium starts extracting considerably at low NBPHA concentrations, the maximum is obtained only when the reagent concentration

TABLE 14

Extraction* of various metal ions into equal volumes of a 1.0% solution of NBPHA in chloroform

	Time (min)	Gallium-III	Indium-III	Thallium-I'	Tin-IV	Lead-II
1	1	20.8	55.6	81.2	20.0	53.1
2	3	39.9	71.3	90.4	41.8	78.5
3	6	62.1	93.6	96.5	75.3	87.3
4	8	83.7	97.8	99.7	89.1	94.4
5	10	94.3	99.2	99.7	94.4	97.4
6	12	99.4	99.2	99.7	94.4	97.4
7	15	99.4	99.2	99.7	94.4	97.4

* Expressed as a percentage of the total metal present in the system.

' Thallium extracted into a 0.7% solution.

For metal concentrations see footnote to Table 13.

TABLE 15

Optimum conditions for the extraction of various metal ions.

	Ion extracted	Acidity	NEPHA conc. (% $^{w}/v$)	Optimum equilibration time (min.)	Maximum metal ion conc. (mg./10ml.)	% extracted*
1.	Gallium-III	pH3.1	1	12	10	99.4
2.	Indium-III	pH5.3	1	10	10	99.2
3.	Thallium-I	pH10.5	0.7	8	8	99.7
4.	Germanium-IV	8M HCl	0	15	10	99.8
5.	Tin-IV	0.8M HCl 4M $HClO_4$	1 1	10 10	10 10	94.4 96.1
6.	Lead-II	pH9.0	1	10	12	97.4

* In a single extraction with equal volumes of the two phases.

TABLE 16

Separation factors* obtained for the separation of various pairs of elements.

S.NO	Element			Method of measuring	Separation factor
	A	separated from	B		
1	Ga	"	In	Radioactive B	10^4
2	In	"	Pb	Benzidine test	10^4
3	Ga	"	Pb	" "	10^4
4	Ga	"	Ge	^{68}Ga decay	10^3
5	In	"	Sn	^{113m}In decay	10^3
6	Sn	"	Ga	Radioactive B	10^3
7	Sn	"	In	Radioactive B	10^3
8	Sn	"	Pb	Benzidine test	10^4
9	Pb	"	TL	Radioactive B	6×10^2

* The ratio of the initial amount of impurity (B) present in the mixture (A + B) to the final amount present in the separated sample (A).

is 1% while the extraction reaches a maximum for thallium at 0.7% of NBPHA. Other elements require a 1% solution of the reagent for maximum extraction. Extraction as a function of time for all these elements is given in table 14. Thus they are extracted efficiently in 8 minutes or more. Table 15 summarises data on the optimum pH, reagent concentration, time of equilibration and fraction of the total metal extracted into an equal volume of NBPHA in chloroform. The maximum recommended metal concentrations for these elements when treated under these conditions are also included in this table. For back-extraction, simple adjustment of acidity was found sufficient for all except tin, for which saturated oxalic acid in 3 M hydrochloric acid was found to be adequate. As may be deduced from Fig. 11, germanium can be back-extracted into hydrochloric acid less than 4 M. It is also back-extracted into dilute perchloric acid. For all these elements, the back-extraction was almost quantitative in 3 minutes.

The results discussed above, therefore, show that by suitable choice of conditions all six elements may be separated from each other if present in the mixture and this has been confirmed by experiment. Separation factors obtained by following the procedure given in chapter 2, section B, d for pairs of elements are recorded in table 16 and this table also contains results for germanium-68 separated from gallium-68 and tin-113 from indium-113m. The decay of gallium-68 (half-life 68 minutes) and indium-113m (half-life 1.7 hour) was followed by preparing solid sources and counting them in a gas-flow proportional counter. The residual activity in each case thus provides a further check on the efficiency of separations. In the experiments with lead, a spot test with benzidine was applied to check the decontamination.

Iron-(III) which extracts[14] at pH 1 and aluminium precipitating quantitatively in the pH range 3.4 - 6.4 are likely to interfere with some of the separations. In the course of the present work the aluminium complex was found to extract readily with NBPHA. Both these elements could therefore cause interference.

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CHAPTER 5

Some Properties of N-Benzoyl-N-phenylhydroxylamine and Cupferron Systems Containing Tin, Antimony and Other Elements

Introduction

In this chapter a comparative study of the chemical behaviour of cupferron and NBPHA has been made using tin, antimony, arsenic and bismuth. Possible separations of these elements either in hydrochloric or perchloric acids are revealed by liquid-liquid extraction methods using NBPHA. The instability of cupferron at high acid concentrations led to an investigation of decomposition products since it was thought that they may have some effect on metal ion extraction. Further, an attempt has been made to obtain information on the nature of the chemical reaction between tin-NBPHA and chloride ion. In this connection a detailed study of tin extraction as a function of NBPHA, chloride and hydrogen ion concentrations has been carried out. Infra-red and nuclear magnetic resonance studies have also been used to throw additional light on the reaction and its products.

Some polarographic work in connection with the determination of tin and antimony in a mixture is also presented as a separate section (B) in this chapter.

A. SOLVENT EXTRACTION, INFRA-RED, NUCLEAR MAGNETIC RESONANCE, PRECIPITATION AND SOLUBILITY STUDIES

For elements such as tin, antimony, arsenic and bismuth which readily hydrolyse at low hydrogen ion concentrations, the use of organic reagents permitting the extraction of these elements from strongly acid media is of interest. Cupferron is introduced into the aqueous rather than the organic phase and this chelating agent, while selective in its reactions (c.f. chapter 1) is unsuitable for use in mineral acids[1]. In fact cupferron is not recommended at acidities higher than 0.5 to 1.5 M, particularly in nitric acid. On the other hand NBPHA is quite a useful reagent when in chloroform which is shaken up with highly acidic aqueous solutions; it has a clear advantage over cupferron (see chapter 1), showing good stability in systems containing hydrochloric, perchloric and sulphuric acids. However, in the course of the present work it was observed that nitric acid above about 3M attacks the reagent considerably.

It is frequently considered that NBPHA behaves in many of its chemical reactions with metal ions in a similar manner to cupferron. Ryan and Lutwick[2] have used an ethanolic solution of NBPHA for the gravimetric determination of tin from a 0.8 M hydrochloric acid solution and noted that the tin complex precipitated has the composition $Sn(C_{13}H_{11}O_2N)_2Cl_2$...(I) or $Sn(C_{13}H_{10}O_2N)_2Cl_2$... (II). The above mentioned authors claim that only one complex of composition (I) is obtained irrespective of the valency of tin in solution and that the hydrogen of the oxime group reduces tin-(IV) to tin-(II) before complex formation giving (I). In a later paper[3] the same authors are less certain on this point and even suggested that formulation (II) was more appropriate. Since then authors have variably reported that the tin in the NBPHA complex is present as tin-(II) or tin-(IV) without clear grounds for accepting one or other formulation. On the other hand, cupferron reacts[4,5] with tin from a 1 M hydrochloric acid giving two distinct products, $Sn(C_7H_5O_2N)_2$ and $Sn(C_7H_5O_2N)_4$ depending on the valency state of the tin in solution. It is reported[6] that NBPHA extracts antimony-(III) from weakly acidic solutions; while cupferron precipitates antimony-(III) quantitatively under similar conditions[7]. The precipitate obtained with antimony was found to be soluble in common organic solvents and antimony-(III) extracts into chloroform from 1 M hydrochloric solutions. Antimony-(V), arsenic-(III) and (V) do not precipitate nor extract with cupferron. Information on the behaviour of these elements with NBPHA is not available. Bismuth-(III) is extracted very well by either of these two reagents[7,8] between pH 2 to 4 into chloroform.

EXPERIMENTAL

(a) Radioisotopes

Arsenic-74. This was obtained as sodium arsenate solution of high specific activity from The Radiochemical Centre, Amersham, England.

Bismuth-210. It contained lead-210 (radium-D), bismuth-210 (radium-E) and polonium-210 (radium-F) and was also obtained from The Radiochemical Centre, Amersham, England.

For details of the other isotopes used in this work refer to chapter 3 and 4 (experimental section) respectively.

(b) Reagents

All the reagents used are mentioned in the previous two chapters with the following exceptions:

Cupferron. This was supplied by Hopkin and Williams Ltd., Essex, England.

Carrier solutions. For all the elements used these were prepared (5mg. per ml.) in hydrochloric acid from the element in question or an oxide of it.

Chloroform-d ($CDCl_3$). This was obtained (99% pure) from E. Merck AG, Darmstadt, Germany.

Deuteriumoxide (99.5% D_2O). It was supplied by Koch-Light Laboratories Ltd., Colnbrook, England.

(c) Measurement of radioactivity

Antimony, arsenic and bismuth samples were counted in a Geiger-Muller counter (see chapter 2, section C,a,i). For details of the method of counting the tin see Chapter 4. Although bismuth contains isobaric lead and polonium isotopes in this counting device only bismuth is counted and therefore separation from the last two elements mentioned was not found to be essential.

The outline of the general method of investigation is given in chapter 2, section B. Reduction of these elements to their lower oxidation states when required was performed using nickel powder[9]. Higher oxidation states were obtained by the use of bromine[9] except in the case of arsenic for which hydrogen peroxide[9] was more appropriate.

In the cupferron experiments the reagent is added to the aqueous phase. The acidity recorded in these experiments are those before the addition of cupferron to the system and hence the true acid concentration in each case would be approximately lower by 0.32 M assuming a 5% solution of cupferron and no consumption of acid in decomposition reactions.

In the study of the nature of chemical reaction of tin with NBPHA, the aqueous phases were always maintained at constant ionic strength. The component whose effect was under investigation was varied while the others are kept constant. The following are the experimental details:

(i) Effect of NBPHA. The aqueous phase was 0.8 M in hydrochloric acid and 1.3×10^{-3} M in tin. The NBPHA concentration was varied from 4.6×10^{-3} to 4.6×10^{-2} M (0.10 to 1.0% W/V). For the effect of varying NBPHA concentration on the extraction of tin from perchloric acid, the tin concentration was 1.3×10^{-3}. The ionic strength was 4.0 M in perchloric acid and the NBPHA range was 2.3×10^{-4} to 3.2×10^{-2} M (0.05 to 0.7% W/V).

(ii) Chloride effect. The ionic strength was 0.28 M in perchloric acid. The chloride concentration was varied from 1.5×10^{-3} to 8.0×10^{-3} M (using hydrochloric acid). The NBPHA concentration was 1% W/V in chloroform. In 0.28 M perchloric acid 31.8% of the tin extracts with a 1% NBPHA solution which reduces the chloride range.

(iii) Effect of hydrogen ions. The following experiments were performed to investigate the effect of hydrogen ion concentrations. The ionic strength was maintained using lithium chloride and the hydrogen ion effect was studied by varying the hydrochloric acid concentration.

No.	Tin conc. (molar)	H^+ ion range (molar)	Ionic strength	NBPHA %
1	1.3×10^{-3}	0.012 to 0.10	1.0	1.0
2	7.1×10^{-3}	0.20 to 0.80	1.1	0.30
3	1.4×10^{-3}	0.49 to 4.0	6.0	0.50

(d) Study of decomposition products of cupferron

A Pye series 104 gas-chromatograph was used (chapter 2, section C,f). A known weight of cupferron solution (10%) in hydrochloric acid at a chosen concentration within the range 1 to 11.4 M was equilibrated with an equal volume of benzene for 15 minutes. The benzene layer was separated and dried with sodium sulphate and chromatographs were recorded (0.25μ l. solutions were used in all the recorded chromatographs) at 150°. The feed volume, temperature and other instrumental settings were maintained constant. Chromatographs of various known substances were recorded for comparison.

(e) Infra-red spectra

The instrumental details are given in chapter 2, section C,c.

The deuteration of the -OH group of NBPHA was carried out by the procedure of Harp and Effert[10]. 0.1 g of NBPHA were dissolved in 3 ml. of dry ether and equilibrated with D_2O (2ml.) for 30 minutes. The two phases were separated and the ether layer was again equilibrated with a fresh portion (2nd) of D_2O for 15 minutes. A third equilibration was carried out with 2 ml. of D_2O (15 minutes) and the solvent was removed by evaporation under vacuum.

(f) Nuclear magnetic resonance studies

The details of the apparatus used are given in chapter 2, section C,d.

1 M NBPHA and 0.5 M solutions of the tin complex of NBPHA in chloroform-d were used in conjunction with tetramethyl silane as a reference substance.

(g) Tin and antimony precipitations

Tin was precipitated by NBPHA according to the method of Ryan and Lutwick[2]. Further, the precipitation of this element using NBPHA was examined from hydrobromic, hydriodic, nitric and sulphuric acids (from 0.5 to 1 M) using a slight excess of NBPHA in ethanol.

(h) Solubility measurements

Tin was precipitated from 1 M hydrochloric or hydrobromic acid using radioactive tin-113. A portion of the tin precipitate was sealed in a polythene capsule and equilibrated with a 10 ml. portion of solvent in a thermostat at 25°. After equilibration, the excess of solid was separated by centrifugation or filtration of

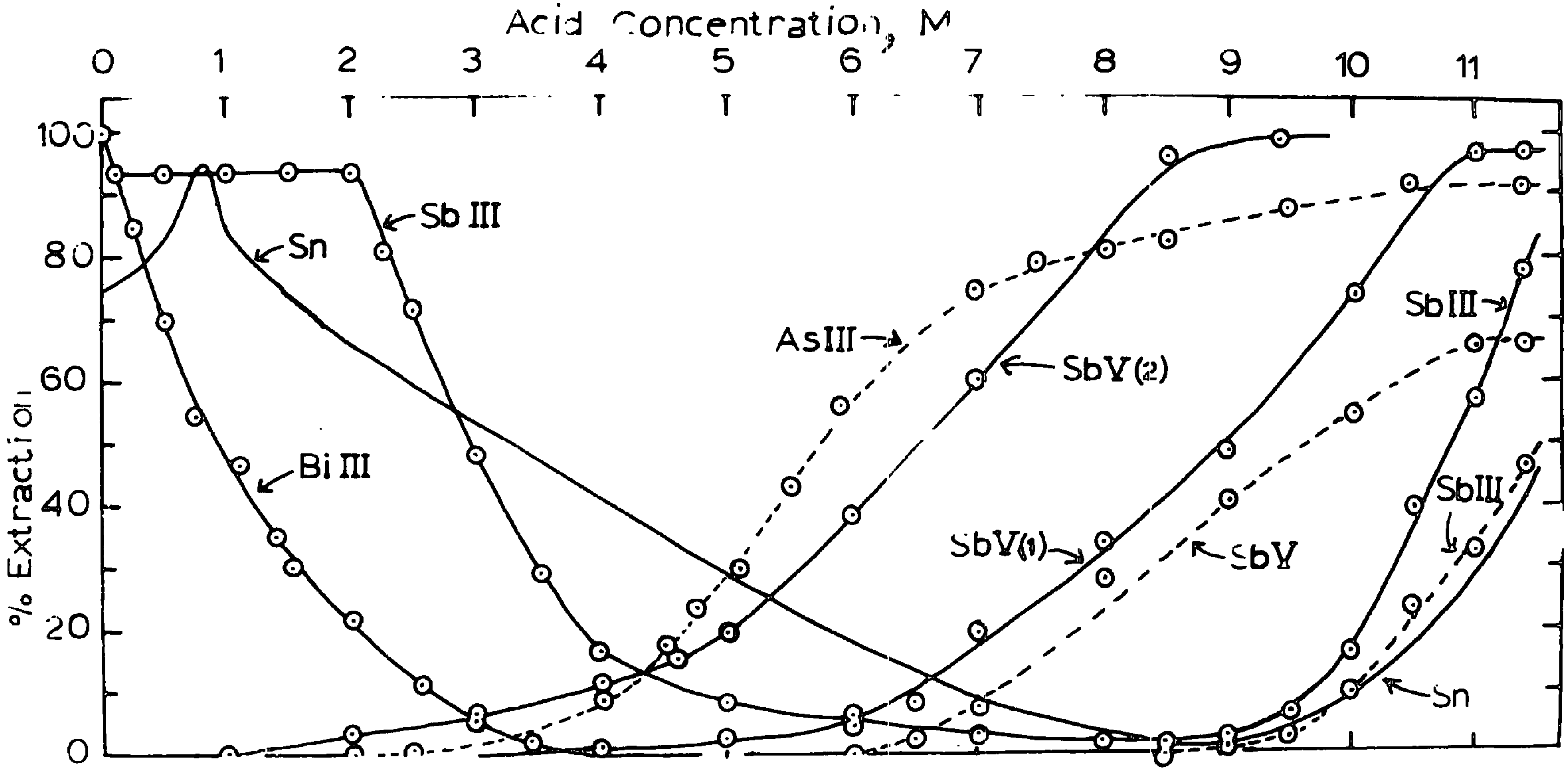


Fig.13. Extraction data for concentrations of (1 to 3) x 10^{-3}M metal ions from hydrochloric acid (except Sb-(V), curve 2, which is for a perchloric acid medium) into (a) 1% NBPHA in chloroform (full lines) and (b) into chloroform alone (broken lines).

which the former was preferred. 5 ml. of this clear solution was counted in a γ-scintillation counter.

An accurately weighted portion of the dried tin precipitate was dissolved in 1:1 V/V alcohol:water mixture and counted. The solubility X per 100 ml. was calculated using the following equation:

$$X = \frac{W\,B}{A} . 20$$

where W is the weight of tin precipitate in mg. and A the counting rate of its solution. B is the counting rate of the solution after equilibration.

RESULTS AND DISCUSSION

Fig. 13 records the effect of hydrochloric acid concentration on the extraction of these elements with NBPHA. Antimony (V) is examined from both hydrochloric and perchloric acid solutions. From the figure, it may be seen that antimony-(III) extracts almost quantitatively from up to 2 M in hydrochloric acid and with the further rise in acidity, the extraction decreases and passes through a minimum at about 8 M. Above 8 M hydrochloric acid the extraction partially due to chloroform alone, increases again. The presence of NBPHA in the chloroform phase enhances extraction by a factor of about 2 at each recorded value. Antimony-(v) on the other hand, does not extract at low hydrochloric or perchloric acid concentrations. Extraction commences in perchloric acid at about 1.25 M and in the other acid at about 4.0 M. In both acids extraction of antimony-(v) increases with increasing acid concentration and the maximum is attained at 9.4 M in perchloric and 11.4 in hydrochloric acid respectively. Chloroform alone does not extract antimony-(v) from perchloric acid while the chloroform extraction of antimony-(v) in hydrochloric acid is shown in fig. 13 (broken lines).

Arsenic-(III) extracts well into chloroform alone and the extraction is enhanced only up to 1 or 2% by the presence of NBPHA in the chloroform phase. The results presented here for arsenic are in fair agreement with those of Brink et al[11]. Only about 5% of arsenic-(v) was found to extract over the entire acid range. Hydrogen peroxide was used as an oxidant and separate experiments using other oxidants such as nitric acid and cerium-(IV) gave similar results. For bismuth-(III) extraction decreases with increase in hydrochloric acid concentrations; it does not extract above 4 M in this acid. Similarly, bismuth-(V) does not extract with NBPHA from hydrochloric acid of any concentration.

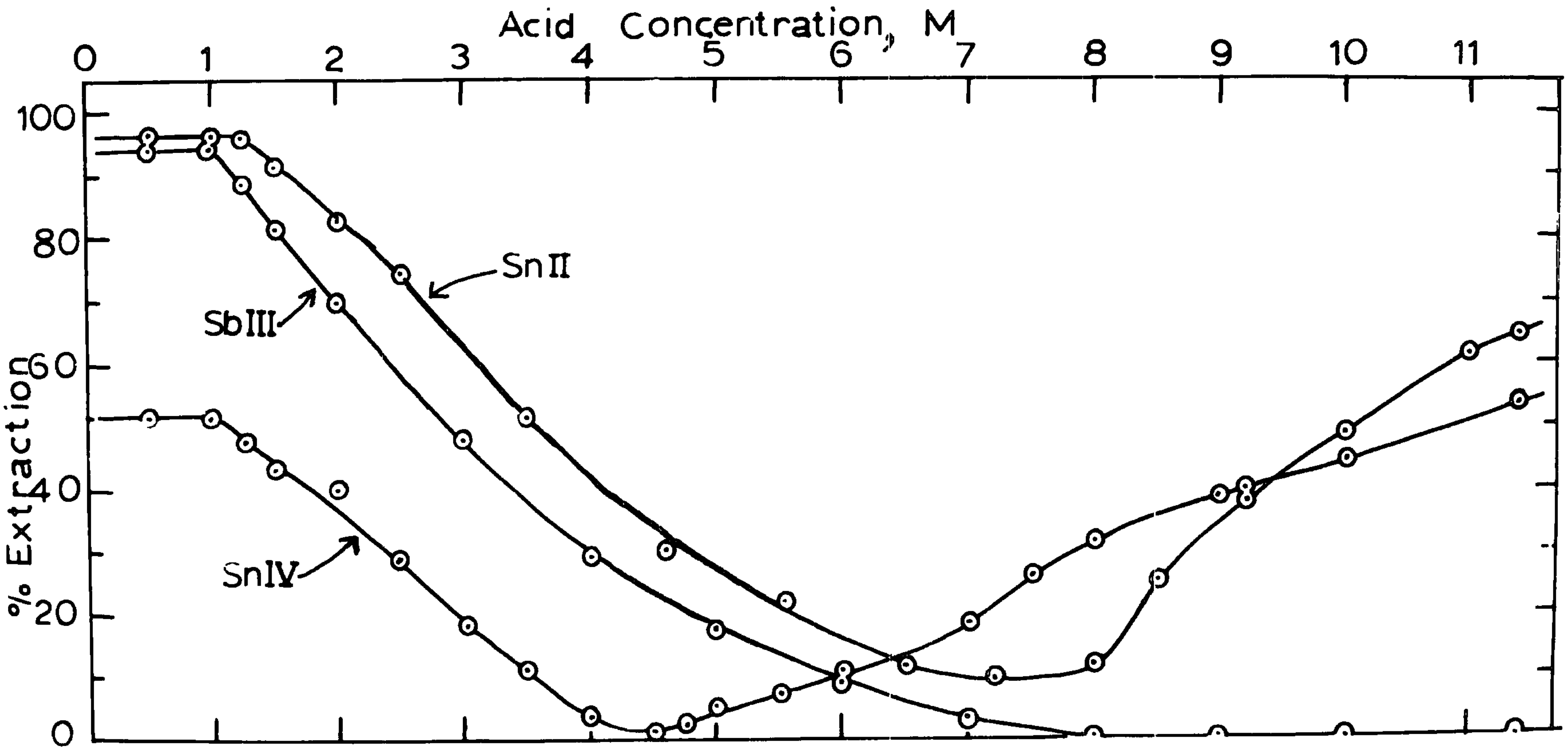


Fig.14. Extraction of (1 to 3) x 10^{-3}M metal ions from hydrochloric acid 5% in cupferron into Chloroform.

Fig. 13 also records the effect of hydrochloric acid on the extraction of tin-(IV) with NBPHA. The data is largely from figure 11 with additional results for 8 M and above in hydrochloric acid. It was observed that chloroform alone extracts tin at high acidities (8 M) with little or no contribution from NBPHA. The earlier hump was found to be due to lack of sufficient chloride ions. The tin distribution was found to be the same throughout the acid range whether the aqueous phase contained tin-(II) or (IV) to begin with.

The effect of hydrochloric acid on the extraction of tin-(II) and (IV) and antimony (III) with cupferron is shown in fig. 14. The optimum extraction range of antimony-(III) is shorter than for NBPHA (see fig. 13) in the direction of higher acidities. Cupferron extracts tin (II) very well at low hydrochloric acid concentration and extraction decreases with rise in acid. Again at high acidities chloroform extracts tin (II).

On the other hand, tin (IV) extracts only up to about 51% and behaves in the same general way as tin (II) at high acidity. Antimony (III) does not extract into chloroform at high hydrochloric acid concentrations if cupferron is present. This may be due to the fact that some of the cupferron decomposition products may be preventing the extraction of antimony-(III). Arsenic-(III) extraction at high acidities is also inhibited and a 10% cupferron solution gave about 10% and 17% extraction at 5 M and 11.4 M hydrochloric acid respectively. Cupferron does not extract antimony-(V).

The decomposition of cupferron

The mineral acid instability of cupferron has been known for a long time and various decomposition products have been reported[12]. In this work it was found that substances apparently causing inhibition of extraction of antimony and arsenic are extracted into chloroform or benzene. Further, if cupferron was added to the aqueous phase of high acidity and extracted with chloroform, the aqueous phase after two batch extractions was found to have decreased in acidity considerably. (A 10% solution of cupferron in 11.4 M hydrochloric acid decreased the acidity of the aqueous phase to about 4M after two successive chloroform extractions.) By the method outlined in the experimental section of this chapter, an attempt has been made to identify some of the decomposition products of cupferron.

In aqueous phases up to about 6 to 8 M in hydrochloric acid to begin with, the main product was found to be nitrosobenzene. With increasing acidity (from 1 to 6 or 8 M) the amount of nitrosobenzene formed also increases.

Table 17

Extraction* as a function of NBPHA concentration.

S.No.	NBPHA concn. (% w/v)	% Extraction Sb-III	Sb-V	Bi-III
1	0.05	9.3	6.8	11.3
2	0.10	28.1	15.3	20.2
3	0.15	43.6	24.7	29.8
4	0.20	50.8	37.1	40.6
5	0.30	68.3	45.0	49.4
6	0.40	79.8	58.0	66.8
7	0.45	83.1	-	77.4
8	0.50	93.1	67.1	90.8
9	0.60	93.1	75.6	99.8
10	0.70	93.1	81.3	99.8
11	0.80	93.1	88.9	99.8
12	0.90	93.1	94.4	99.8
13	1.00	93.1	98.3	99.8
14	1.50	93.1	98.3	99.8

* Equal volumes of the two phases were equilibrated for 15 min. Extraction data refer to single extractions.

Table 18

Extraction of antimony-(III), tin-(II) and tin-(IV) as a function of Cupferron concentration.

		% Extraction*		
S.No.	Cup. Conc. (% w/v)	Sb-III	Sn-II	Sn-IV
1	0.1	3.6	-	-
2	0.3	11.7	1.8	-
3	0.5	31.0	6.8	3.8
4	0.8	63.4	-	10.5
5	1.0	72.3	15.6	17.6
6	1.5	88.4	29.4	24.6
7	2.0	94.2	46.8	34.8
8	4.0	94.2	71.8	42.0
9	5.0	94.2	92.0	48.3
10	6.0	94.2	96.2	51.8
11	7.0	94.2	96.2	51.8
12	8.0	94.2	96.2	51.8

* Extraction data refer to single extractions. Equal volumes of the two phases were equilibrated for 15 min. Hydrochloric acid concentration was 1 M for Sb-(III) and 0.5 M for Sn-(II) and tin-(IV).

Table 19

Extraction* with NBPHA as a function of time.

S.No.	Time (Min)	% Extraction Sb-III	Sb-V	As-III	Bi-III
1	1	23.1	20.6	56.0	29.0
2	3	40.6	42.8	78.9	50.6
3	5	69.1	54.0	84.2	78.0
4	7	86.3	68.3	91.2	90.0
5	10	93.1	78.1	91.2	96.2
6	12	93.1	85.3	91.2	99.8
7	15	93.1	98.3	91.2	99.8
8	20	93.1	98.3	91.2	99.8

* Arsenic-(III) is extracted alone from chloroform.

For other conditions see the footnote to table 17.

Table 20

Extraction* with cupferron as a function of time.

S.No.	Time (min)	% Extraction Sb-III	 Sn-II	 Sn-IV
1	1	8.1	22.6	15.8
2	3	28.3	51.4	38.6
3	4	-	76.8	43.0
4	5	45.8	89.6	49.1
5	6	59.4	96.2	51.8
6	8	73.6	96.2	51.8
7	10	88.4	96.2	51.8
8	12	94.2	96.2	51.8
9	15	94.2	96.2	51.8

* For conditions see footnote to table 18.

Table 21

Optimum sets of conditions for the extraction of various elements.

Element	Aqueous phase		Chloroform phase	Optimum equilibration time (min)	Maximum metal cone mg/10ml.	% extracted +
*Sn-(IV)	0.8	M Hcl	1%B	10	10	94.4
	4	M Hclo4	1%B	10	10	96.1
Sb-(III)	1	M Hcl	0.5%B	10	10	93.1
Sb-(V)	9.4	M Hclo4	0.9%B	15	8	98.3
Bi-(III)	pH 1		0.6%B	10	8	99.8
Sn-(IV)	0.5	M Hcl	6%C	6	10	51.8
Sn-(II)	1	M Hcl	6%C	6	10	96.2
Sb-(III)	1	M Hcl	2%C	12	5	94.2
As-(III)	11.4	M Hcl	$CHcl_3$ only	7	12.5	91.2

B = NBPHA, C = Cupferron.

* Data taken from table 15 (chapter 2).

\+ In a single extraction with equal phase volumes.

For Cupferron systems the acidity recorded does not take into account acid consumed by the reagent.

At higher hydrochloric acid concentrations (8 M) the main product (about 80% of the total decomposition products) is different and could not be identified. Nitrosobenzene is present in very small amounts. This unidentifiable product was not phenol, nitrobenzene, phenylhydroxylamine, aniline or azoxybenzene.

Tables 17 and 18 illustrate the effect of varying the NBPHA and the cupferron concentrations respectively. Tables 19 and 20 give the effect of time on the extraction with NBPHA and cupferron. Far back-extraction simple adjustment of acidity was found to be adequate and back-extractionoccurred efficiently for all these elements within three minutes except in the case of bismuth (III) which requires 5 minutes. Optimum conditions for the extractions are summarised in table 21.

Separations

As a result of the extraction behaviour of these elements with NBPHA in hydrochloric acid, possible separations of pairs of them were investigated. The separations were performed according to the procedure given in chapter 2, section B,d.

The following separations are outlined:

Table 22

Separation factors for pairs of elements.

Element A separated from B	Method of measuring	Phases	Separation factors*
Sn-(IV) from Sb-(V)	active Sb	0.8 M Hcl/1%B	1 x 10^2
As-(III)from Bi-(III)or(V)	" Bi	conc. Hcl/$CHCl_3$	2 x 10^3
Sn-(IV) from Bi-(III)or(V)	" Bi	4 M Hclo4/1%B	9 x 10^2
Sb-(V) from Bi-(III)or(V)	" Bi	9 M Hclo4/1%B	7 x 10^2
Sn-(IV) and Sb-(V) from Bi-(III) or (V)	" Bi	9 M Hclo4/1%B	7 x 10^2

B = NBPHA

* The ratio of the amount of B present initially in A + B to the amount of B present in the separated A.

(1) It is possible to separate tin (IV) from antimony (V) by extracting (twice) the former from 0.8 M hydrochloric acid into a 1% chloroform solution of NBPHA. Antimony remains in the aqueous phase.

(2) Arsenic (III) can be separated from bismuth by partitioning the former into chloroform alone from concentrated hydrochloric acid solution.

(3) The separation of tin (II) or (IV) from bismuth may be effected by extracting the tin from a 9 M perchloric acid solution with NBPHA.

(4) On a similar basis, antimony (V) can be separated from bismuth (III) but the aqueous phase should be 9.4 M in perchloric acid.

(5) If tin, antimony and bismuth are present in a mixture, the first two elements can be separated from bismuth (III) by extracting them from concentrated perchloric acid solution into NBPHA in chloroform and back-extracting into 3 M hydrochloric acid containing 0.1 M oxalic acid. Further separation of these two may be achieved by the use of separation(1).

The above separations were performed and separation factors obtained are tabulated in table 22. In determining separation factors, the aqueous phase was extracted twice with equal volumes of organic phase and washed twice before withdrawing samples for counting.

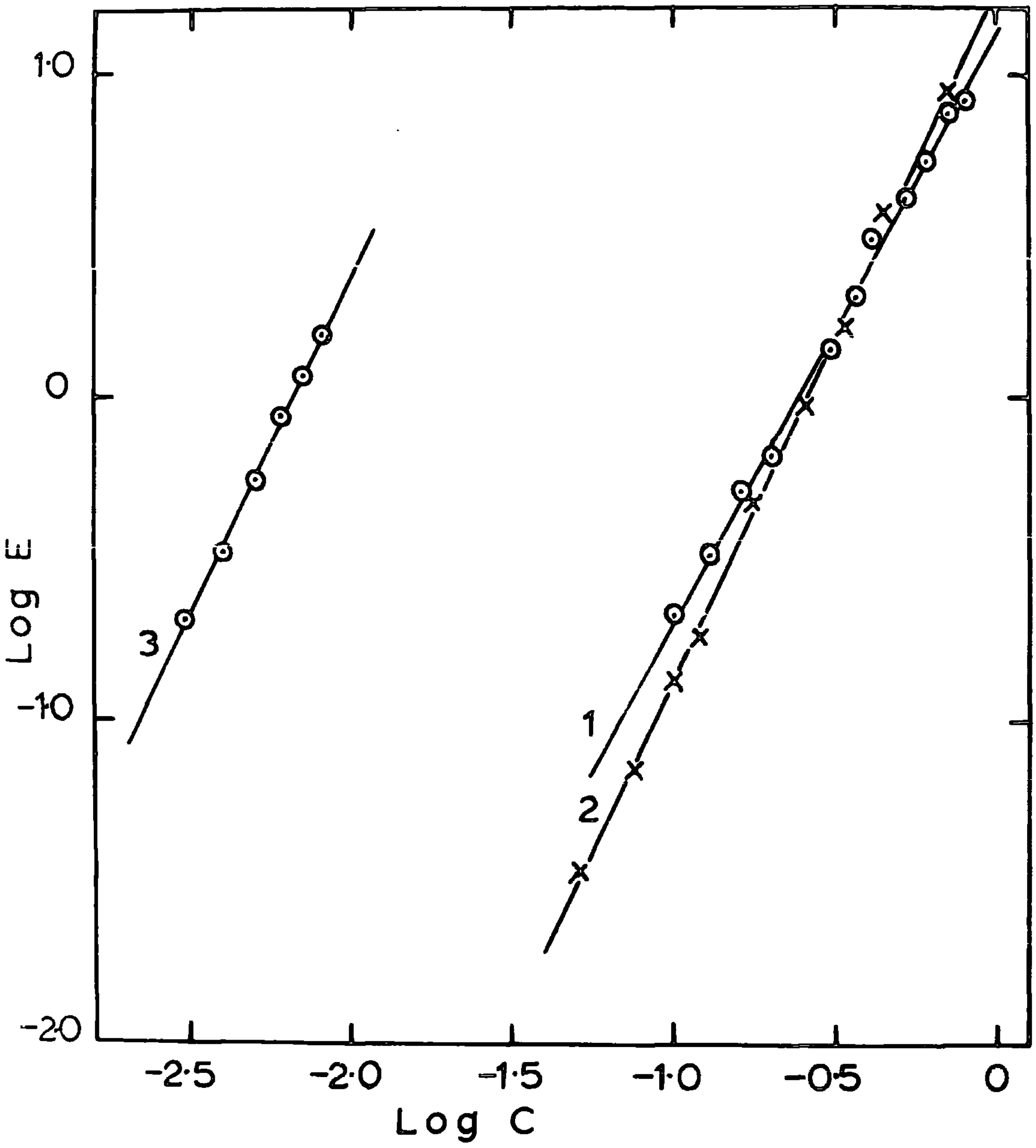


Fig.15. log E as a function of log C, the concentration of NBPHA (Curve 1 from a hydrocloric acid medium, curve 2 from perchloric acid) and as a function of Cl^- (curve 3). The slopes by the least squares method were 1.85, 2.13 and 2.08 in that order.

The nature of the tin complex with NBPHA

In order to establish the nature of the tin reaction, the study has been extended to the investigation of the effect of reagent, chloride and hydrogen ion (if any) concentrations on the extraction of tin.

(i) NBPHA and chloride dependence

Taking into consideration the presence of chloride ions in the aqueous phase equation (18) of chapter 2 may be modified to deal with the tin-NBPHA system as follows:

$$\log E = \log K^{1} - n\log[H^{+}] + n\log[HR]_{org.} + m\log[Cl] \ldots\ldots (1)$$

where HR represents NBPHA

assuming the reaction of NBPHA with tin results in proton replacement and chloride ion is also a ligand. In the derivation of this equation a number of assumptions listed below are made.

1. A known concentration of $[HR]$org. i.e. $[HR]_{aq} \ll [HR]_{org.}$
2. K_m, K_{HR} and P_{HR} are constant under the conditions used. (For definition of these terms see chapter 2.)
3. $[Sn(R)_2Cl_2]_{org.} \gg [Sn(R)_2Cl_2]_{aq.}$ i.e. $P_m \gg 1$.

If hydrogen and chloride ions are maintained constant, the effect of varying the NBPHA concentration may be studied using this relation and also if the NBPHA and hydrogen ion concentration are kept constant, the effect of varying the chloride ion may be examined. By thus following the conditions outlined in 'Experimental' a direct dependence on $(NBPHA^{-})^{2}$ and $(chloride)^{2}$ has been observed (fig. 15).

Table 23A

Hydrogen ion dependence data. $\mu = 1.0$ maintained with lithium chloride and hydrochloric acid.

S. No.	H^+ ion conc.	log H^+	% E	log E
1	0.0120	- 1.9208	61.7	+ 0.2068
2	0.0150	- 1.8239	58.2	+ 0.1437
3	0.0250	- 1.6021	52.8	+ 0.0483
4	0.0300	- 1.5229	50.0	0.0000
5	0.0320	- 1.4949	49.4	- 0.0105
6	0.0620	- 1.2076	41.6	- 0.1473
7	0.0720	- 1.1427	36.8	- 0.2350
8	0.0750	- 1.1249	34.1	- 0.2862
9	0.0820	- 1.0862	31.9	- 0.3294
10	0.092	- 1.0362	29.4	- 0.3805
11	0.1020	- 0.9914	24.3	- 0.4935

Table 23B

Hydrogen ion dependence data. $\mu = 1.1$ maintained with lithium chloride and hydrochloric acid.

S. No.	H^+ ion conc.	log H^+	% E	log E
1	0.20	- 0.6990	32.78	- 0.3120
2	0.30	- 0.5220	27.92	- 0.4119
3	0.40	- 0.3979	24.26	- 0.4945
4	0.50	- 0.3010	20.74	- 0.5824
5	0.60	- 0.2218	17.61	- 0.6702
6	0.80	- 0.0969	15.47	- 0.7375

Table 23C

Hydrogen ion dependence data. $\mu = 6.0$ maintained with lithium chloride and hydrochloric acid.

S. No.	H^+ ion conc.	log H^+	% E	log E
1	0.250	- 0.6021	71.36	+ 0.3966
2	0.492	- 0.3080	67.65	+ 0.3203
3	0.747	- 0.1267	60.01	+ 0.1764
4	0.966	- 0.0150	52.86	+ 0.0500
5	1.49	+ 0.1732	42.22	- 0.1366
6	2.00	+ 0.3010	35.26	- 0.2612
7	3.00	+ 0.4771	28.21	- 0.4057
8	4.0	+ 0.6021	23.54	- 0.5119
9	5.0	+ 0.6900	10.95	- 0.9125

(ii) Hydrogen ion dependence

The reaction between tin, NBPHA and chloride ion leading to extraction may therefore be written in one of two ways:

$$\text{Sn-(II)} + 2\text{HR} + 2\text{Cl}^- \rightleftharpoons \text{Sn(HR)}_2\text{Cl}_2 \quad .....(2)$$

$$\text{Sn-(IV)} + 2\text{HR} + 2\text{Cl}^- \rightleftharpoons \text{Sn(R)}_2\text{Cl}_2 + 2\text{H}^+ \quad .....(3)$$

Equation 2 would require that extraction was independent of hydrogen ion concentration whereas equation 3 requires an inverse square dependence. Each of the hydrogen ion dependence studies showed that with increase in hydrogen ion concentration the percentage extraction decreases. The first set of results (table 23 A) gave E approximately proportional to $1/[\text{H}^+]^{0.5}$ and the others (table 23 B and 23 C) E approximately proportional to $1/[\text{H}^+]^{1}$.

The observed hydrogen ion dependence may be explained in one of two ways depending on the conditions used in the experiments. At sufficiently high but not readily defined acid concentrations the NBPHA being weakly basic can acquire a proton and extraction may then take place by an ion-association process. For example, assuming SnCl_6^{-2} ions are present, a substance of the form $(\text{H}_2\text{R}^+)_2\text{SnCl}_2$ may extract. Such a process would require a direct hydrogen ion dependence and would be in direct opposition to the process suggested in equation(3) thus lowering the observed inverse power dependence. While from 5 M hydrochloric acid some 20% of NBPHA in chloroform acquires a proton this process does not occur significantly from 1 M hydrochloric acid or less. At these low acidities it is more likely that hydrolysis of tin is accountable for the observed results. This may be illustrated by reference to the equation below:

$$\mathrm{Sn\ OH}^{3+}\ 2\mathrm{HR} + 2\mathrm{Cl}^- \rightleftharpoons \mathrm{Sn(R)_2Cl_2} + \mathrm{H}^+ + \mathrm{H_2O} \quad ....(4)$$

which shows that the observed hydrogen ion dependence is lowered by partial hydrolysis. It may be pointed out that the study undertaken is not capable of detecting this type of competing interaction which involves the solvent[13]. Data on tin hydrolysis is very limited[14]. However, there is some direct evidence from ion-exchange studies that hydrolysis occurs below 1 M in hydrochloric acid.

To confirm that the extracted product was the same as the precipitated product (from 1 M hydrochloric acid) the following experiments were performed.

A sample of the extract from 1 M hydrochloric acid was isolated by removal of the chloroform under reduced pressure and the solid was titurated with a little water to remove a slight excess of reagent. A melting point and mixed melting point confirmed that the extracted product was the same as that precipitated by the method of Ryan and Lutwick[2]. An infra-red spectrum of the tin

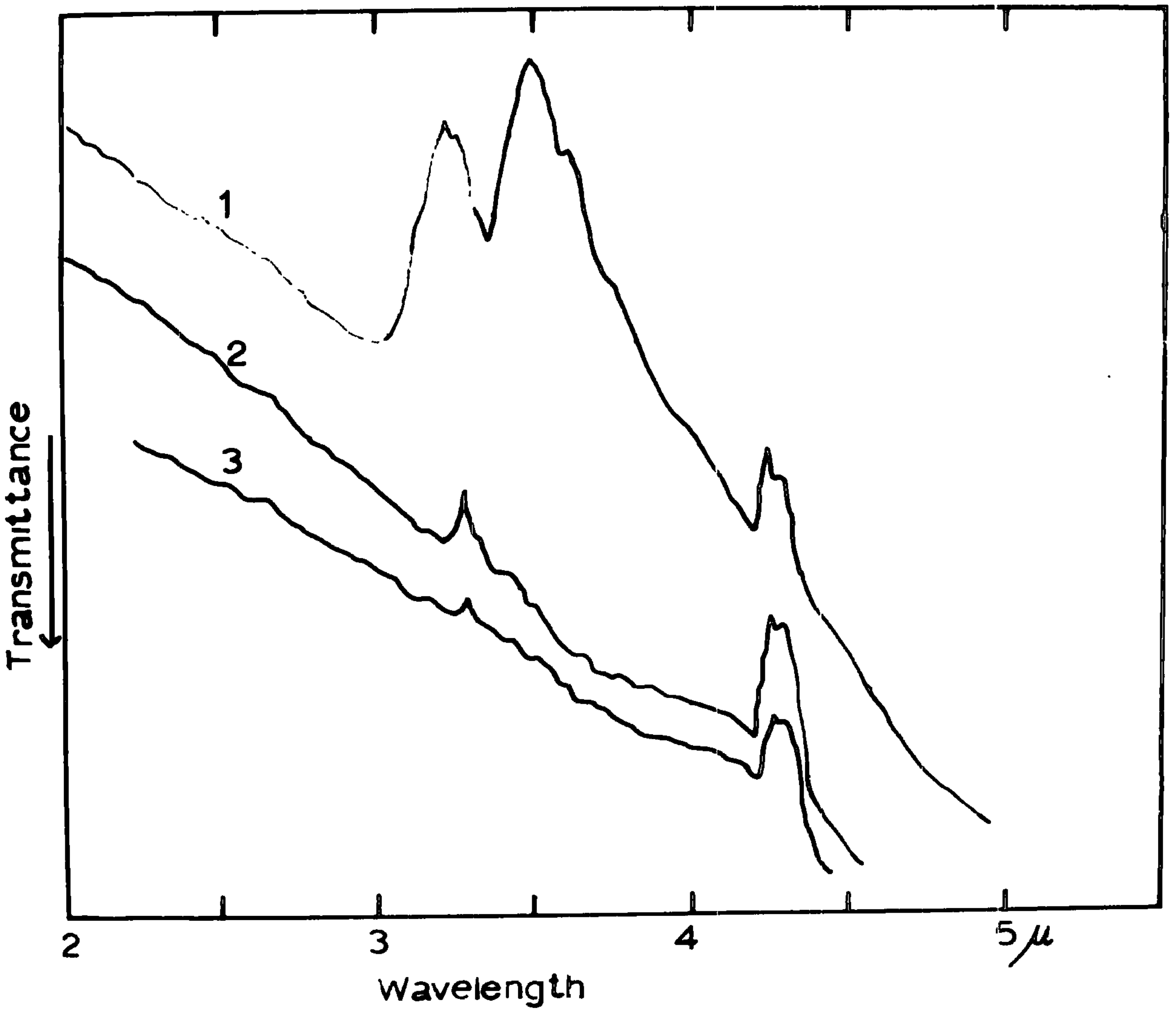


Fig. 16. Infra-red spectra of (1) NBPHA (2) $Sn(C_{13}H_{10}O_2N)_2Cl_2$ and $Sn(C_{13}H_{10}O_2N)_2Br_2$ from perfluorckerosene mulls.

compound extracted into chloroform-d supported this conclusion. On the other hand the extracted tin from a 3 M hydrochloric acid solution was found to be impure, melting and decomposing over a wide temperature range. In these extraction studies a small excess of tin was maintained over reagent.

Infra-red and Nuclear magnetic studies

The infra-red and proton magnetic resonance studies were performed on the substance prepared by the method of Ryan and Lutwick[2]. This work was intended to settle the question of the valency state of tin in the precipitated substance.

The NBPHA spectra obtained in the near infra-red region from a mull (perflurokerosene) shows (fig. 16) two peaks at 3.23 and 3.5 μ (3085 and 2890 cm^{-1}). These two peaks[15] are ascribed to the stretching mode for 'free' and hydrogen bonded -OH respectively. The spectra 2 and 3 in the same figure were obtained for the substances precipitated from chloride and bromide solutions respectively. They show only weak peaks (at 3.27μ i.e. 3090 cm^{-1}) due to the aromatic -CH stretching frequency[15]. The peaks near 4.25μ (2350 cm^{-1}) in all the three spectra are due to carbon dioxide.

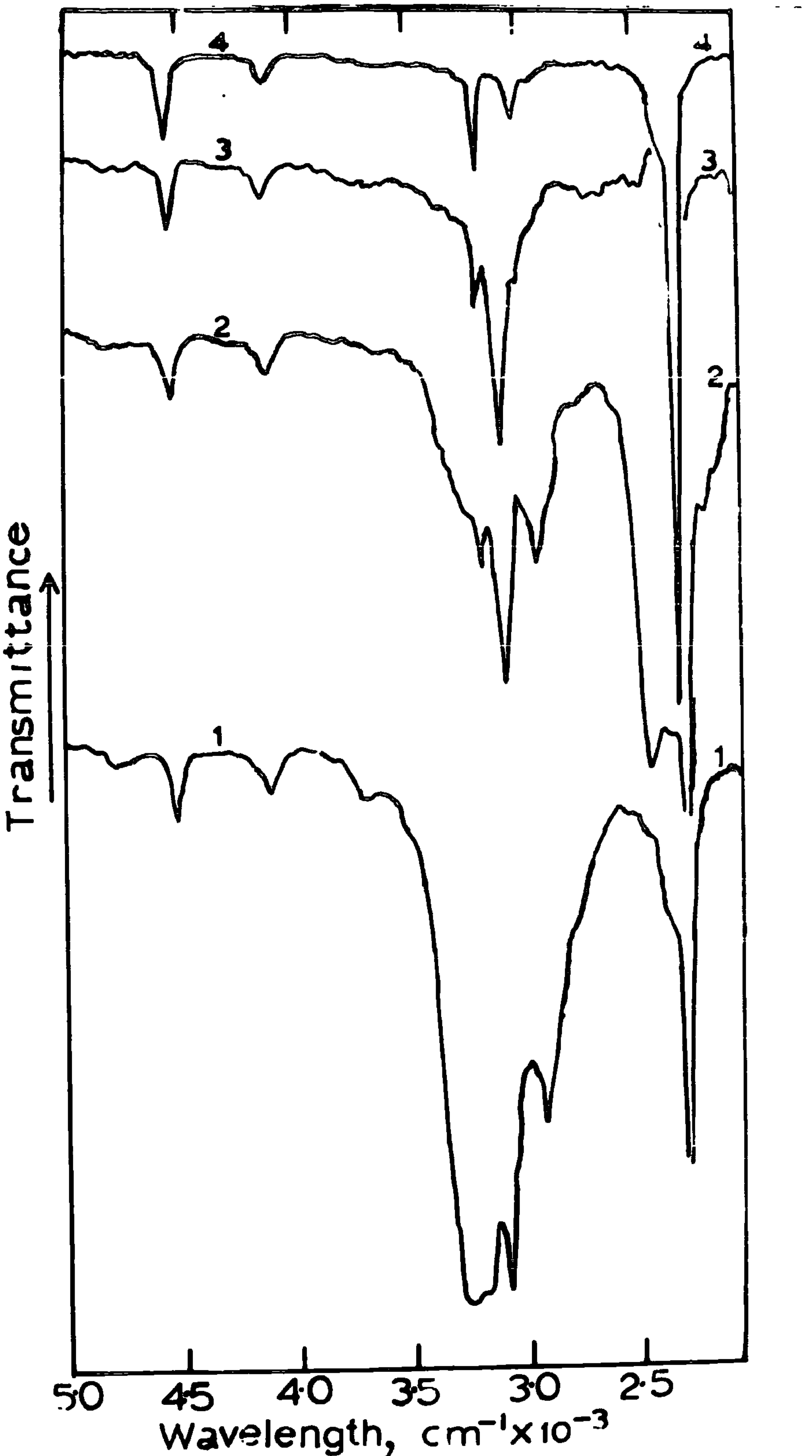


Fig.17. Infra-red spectra of (1) 1 MNBPHA (2) 1M deuterated NBPHA and (3) 0.5 M $Sn(C_{13}H_{10}O_2N)_2Cl_2$ solutions in chloroform-d (curve 4).

The spectra obtained in solution in chloroform-d are recorded in fig. 17. Curve 1 in this figure is for 1 M NBPHA, curve 2 for 1 M deuterated NBPHA and curve 4 for solvent alone. Curve 1 again, shows the two peaks due to -OH stretch (see fig. 16) but these two peaks disappear on the deutration of NBPHA thus confirming the assignment to such a group. In all the curves the peak near 3080 cm.$^{-1}$ is due to the aromatic -CH stretch[15]. The spectrum of the tin-NBPHA complex (curve 3) also shows this peak as would be expected if the hydrogen of the -OH group in NBPHA is released during the reaction with tin. If the hydrogen of the -OH group is not involved in complex formation and the oxygen of this group is bonded to the tin through a lone pair of electrons then the -OH peak will appear in the lower frequency region. No evidence for such a peak was observed in recorded spectra in the region of 4000 to 1400 cm^{-1}. It is therefore concluded that hydrogen of the -OH group is released in the tin reaction.

The absorption peak due to the stretching mode of the carbonyl group was found at 6.15μ(1625 cm.$^{-1}$). This peak is shifted due to complex formation with tin and appears at 6.6μ(1510 cm.$^{-1}$), a shift which is comparable to those reported in acetylacetone on metal complex formation[16].

The oxygen of the carbonyl is therefore bonded to the tin. It was found that infra-red spectra of the tin-NBPHA complex obtained by precipitating tin-(II) or tin-(IV) from solution gave identical spectra.

The nuclear magnetic resonance spectra shows a broad flat peak ascribable to the proton of the -OH group in NBPHA. This peak disappears in the tin complex thus providing further evidence for the release of hydrogen ion during the tin reaction with NBPHA.

Precipitation reactions and solubility measurements.

From a 1 M hydrochloric acid solution antimony-(III) is quantitatively precipitated with an ethanolic solution of NBPHA. The product thus obtained is white in colour and melts at 149°. It is soluble in acetone, alcohol and chloroform and has the composition $Sb(C_{13}H_{10}O_2N)_3$ (compare the cupferron reaction[4,17] with antimony-(III) giving $Sb(C_7H_5O_2N)_3$). The analysis of the antimony-NBPHA complex showed it to contain C,61.2%;H,3.94%. Calculated C,61.8%;H,3.96%.

Tin precipitated from 1 M hydrobromic acid also gave a white precipitate and it was found to have the composition $Sn(C_{13}H_{10}O_2N)_2Br_2$. Analysis showed that it had C,44.3%;H,289%;Br,22.3%: required, C,44.5%;H,2.85%; Br,22.8%. This complex is quite stable and melts at 155°.

Table 24

Solubility results at 25°

Substance	Solvent or solution	No. of measurements	Mean solubility mg. per 100ml.
A	water	4	2.2
B	water	3	2.9
A	1 M NaCl	3	1.6
A	1 M KBr	2	2.0
A	0.5 M HCl	2	1.3
A	0.8 M HCl	2	1.4

It is soluble in common organic solvents like acetone, alcohol, benzene and chloroform. An attempt was made to replace chloride or bromide by other anions in the tin-NBPHA reaction. The products obtained from iodide and nitrate solutions were yellow in colour and they were found to be unstable. In 1 M sulphuric acid tin precipitation with NBPHA was slow and incomplete giving a white product. The white precipitate from 9 M perchloric acid was not examined.

For solubility measurements tin was precipitated with NBPHA from a solution containing chloride (A) and bromide (B) ions and the solubility of (A) and (B) was measured in various solvents according to the procedure given in the 'Experimental' section of this chapter. The results in table 24 are recorded at 25°.

From the table it is clear that the solubility of both (A) and (B) is appreciable at 25°. However, it is lower to some extent in 1 M sodium chloride solution and hydrochloric acid. Therefore it is desirable, as recommended originally by Ryan and Lutwick[2], that the precipitation of tin be carried out under ice cold conditions which should reduce the solubility considerably.

B. POLAROGRAPHIC DETERMINATION OF TIN AND ANTIMONY WITH NBPHA

Arsenic-(III) and antimony-(III) are reduced at the dropping mercury electrode from a 1 M hydrochloric acid solution[18]. However, tin-(IV) in 1 M hydrochloric acid gives a step which is unsuitable for quantitative determination of this element[19,20]. Therefore, polarographic analysis of tin-(IV) is usually carried out[20] from a 1 M hydrochloric acid solution containing above 4 M chloride ions or in pyrogallol[21] with ammonium thiocynate as a supporting electrolyte. 3-mercaptopropionic acid[22] which avoids the use of high chloride concentrations, has been recommended for the determination of tin.

Many organic analytical reagents have been used from time to time for the polarographic determination of elements[23,24]. For example, cupferron has been used in the amperometric determination of uranium[25]. This reagent has also been used in the polarographic determination of zirconium[26], but its use is limited because of instability even in moderate acid concentrations and also because cupferron itself is reduced polarographically at a relatively low negative potential (about -0.4 volts) undergoing reduction eventually to phenylhydrazine. The use of NBPHA in polarography has not previously been reported.

EXPERIMENTAL

All stock solutions of elements were prepared from 'Analar' grade salts.

Tin-(II) - The solutions of tin-(II) were freshly prepared in 1 M hydrochloric acid using stannous chloride.

Tin-(IV) - A known weight of the metal was dissolved in concentrated hydrochloric acid containing a little nitric acid. The solution was heated to about 60°, cooled and made up to the mark.

Antimony-(III) - Antimony-(III) oxide was used to prepare a solution in 1 M hydrochloric acid.

Arsenic-(III) - The solution was prepared in 1 M hydrochloric acid using the (III) oxide of the element.

Gelatin - This was obtained in the powder form from Hopkin and Williams, Essex, England. A 0.2% solution was prepared by dispersing the required weight of the substance in boiling water and then cooling before use; the solution was prepared fresh each day.

The general description of the polarograph used is given in chapter 2, section C,g. Operating data for the polarograph are as follows:

Total height of the mercury column (cm.) = 60

Drop rate per second = 3.611×10^{-1}

Temperature = $20 \pm 2^{\circ}$

Weight of mercury per second emerging from the capillary (mg.) = 2.448

Length of the capillary (cm.) = 25

Diameter of the capillary (cm.) = 0.03 to 0.05 (according to the manufacturer's catalogue)

Potentiometer sensitivity = $^{1}/_{10}$

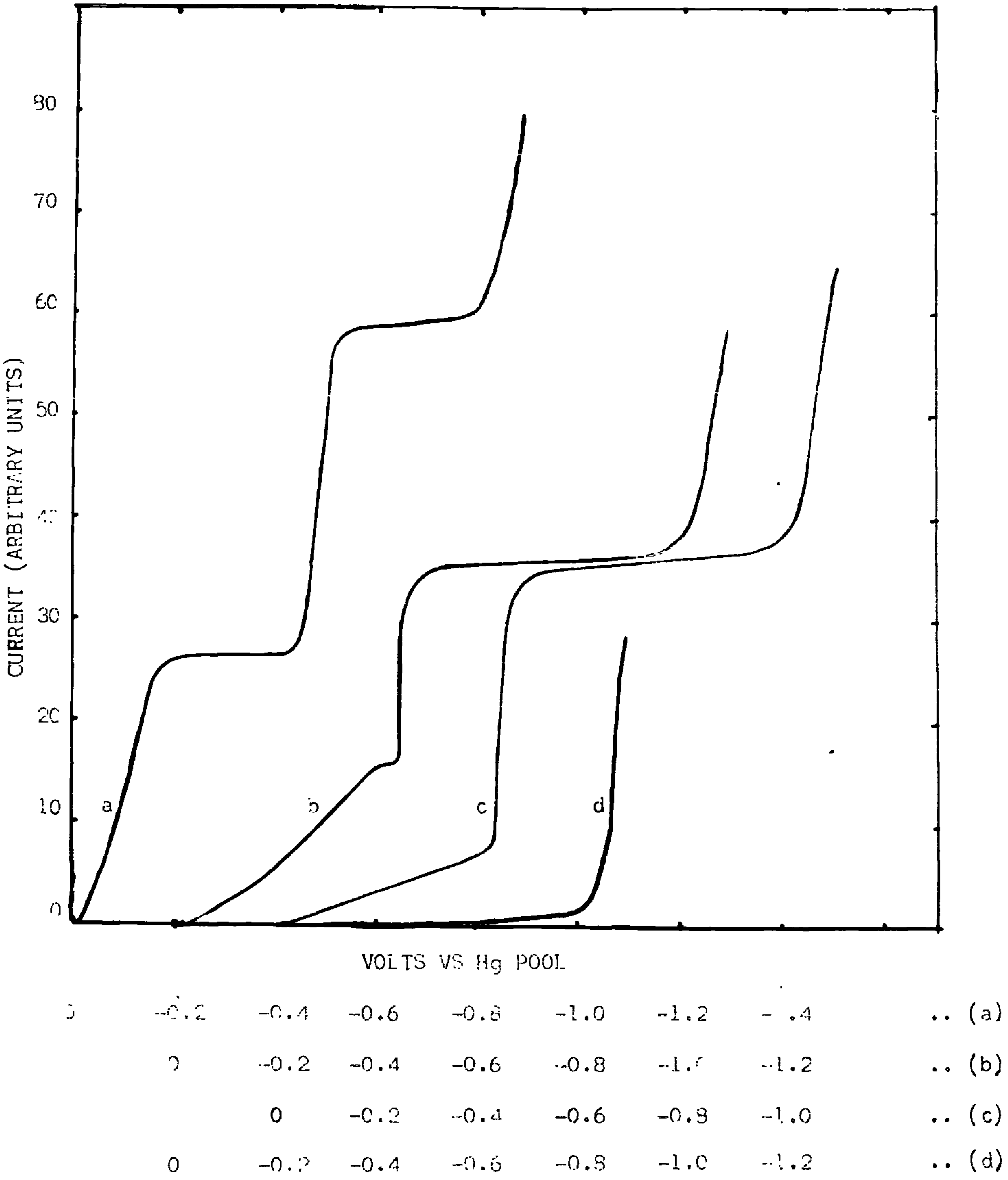
Galvanometer sensitivity = $^{1}/_{1}$

Damping control setting = 5.0

General procedure for recording polarograms

A known aliquot part of the solution of the metal ion in question was transferred to a 25 ml. standard flask containing the required volume of hydrochloric acid. This was followed by the addition of gelatin and NBPHA (when required) dissolved in ethanol. The above sequence of addition of the reagents was found essential to minimise the effects of hydrolysis. The solution was made up to the mark with distilled water so that finally it was 1 M in hydrochloric acid, 0.005 or 0.01% in gelatin and 20% ($^{V}/V$) in ethanol.

Fig. 18. Polarograms of (a) 1.15×10^{-3}M tin-(IV) containing 1.03×10^{-3}M NBPHA (Sn:NBPHA::1:2.80), (b) 6.77×10^{-4}M tin-(II), (c) 1.00×10^{-3}M tin-(IV) and (d) 3.55×10^{-3}M NBPHA in 1 M hydrochloric acid in a solution 20% in ethanol and 0.005% in gelatin.



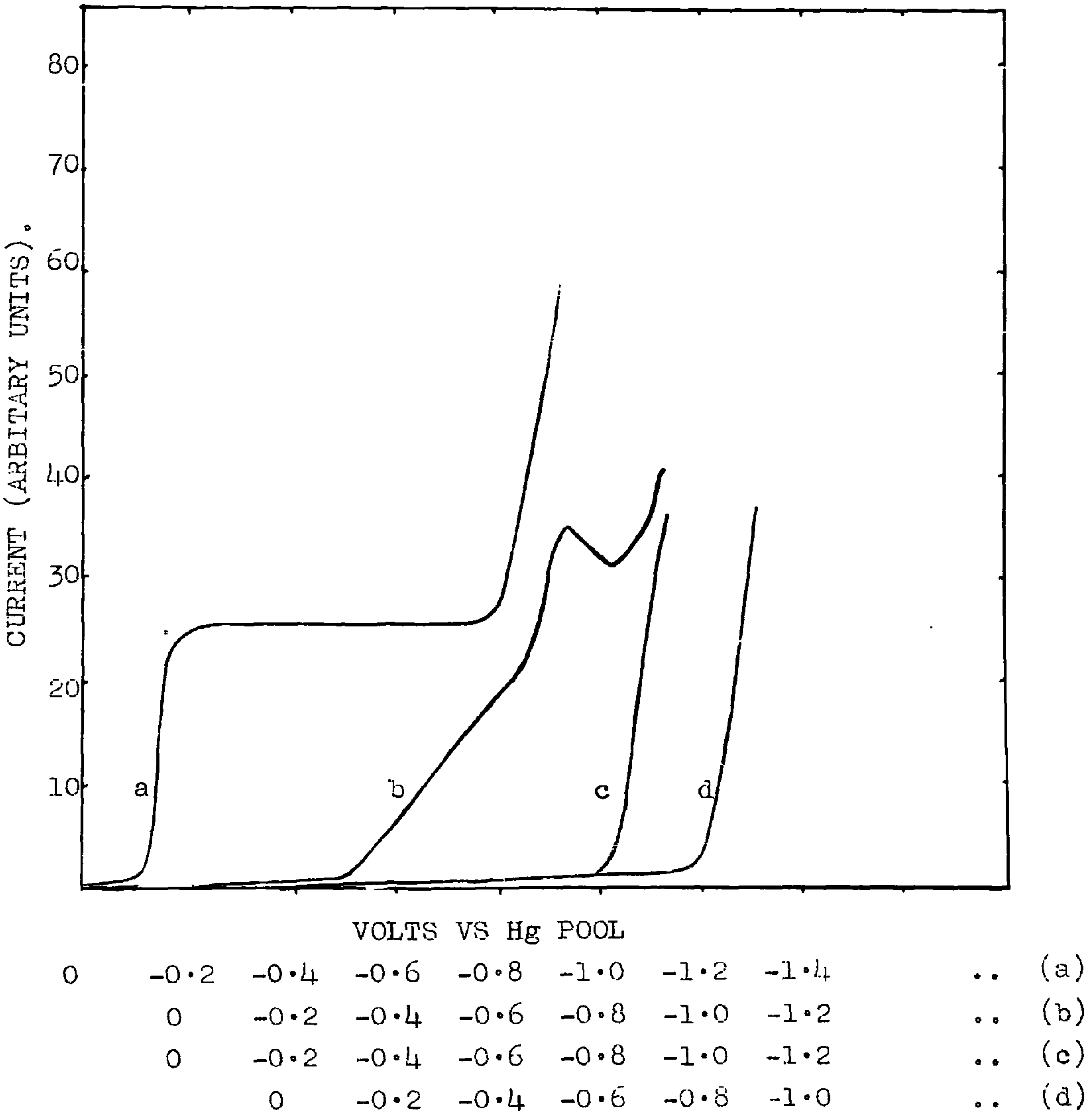
A portion (2 ml.) of this solution was transferred to the polarographic cell and deoxygenated by passing nitrogen through it for about 10 minutes. Polarograms of the elements were then recorded.

Potentials in all this work are measured with respect to the mercury pool which is not far removed from those which would have been obtained if calomel had been used. For example, the 2nd step of tin-(IV) which has a half-wave potential $E_{\frac{1}{2}} = -0.47$ v. when measured relative to the mercury pool has a similar $E_{\frac{1}{2}}$ value when measured relative to the saturated calomel electrode.

RESULTS AND DISCUSSION

Fig. 18 records the polarograms of tin-(II) and (IV) in 1 M hydrochloric acid, and tin-(IV) in the same acid concentration containing 2.8 moles of NBPHA for each mole of tin. The polarographic behaviour of NBPHA is also recorded in the same figure. Thus tin-(IV) in 1 M hydrochloric acid shows a poorly developed step while tin-(IV) under similar conditions in the presence of NBPHA exhibits a two step reduction. The first step may result (measured at -0.2 volts) from the reduction of tin-(IV) to tin-(II) and the second ($E_{\frac{1}{2}} = -0.47$ v.) from the reduction of tin-(II) to the metal. The first step appearing at -0.2 volts is ill-defined. The investigations to study the origin of this step at positive potentials were not conclusive as comparable currents are

Fig. 19. Polarograms of (a) 5·45x10^{-4}M antimony -(111), (b) 1·3x10^{-3}M arsenic -(111), (c) 4·95x10^{-4}M antimony-(V) and (d) 1·12x10^{-3}M arsenic-(V), in 1 M hydrochloric acid, in the presence of 1·88x10^{-3}M NBPHA in a solution 20% in ethanol and 0·01% in gelatin.



observed whether tin is present in the solution or not. Further, oxidation of mercury at positive potentials complicates such a study. NBPHA itself is not reduced at the dropping mercury cathode up to -0.8 volts (fig. 18). Tin-(II) in the presence of NBPHA was found to give polarograms similar to tin-(IV). A separate series of experiments revealed that in order to get optimum definition in the tin-(II)→tin reduction step, the molar ratio of NBPHA to tin must be at least 1:1.

Polarograms of antimony-(III) and (V) and arsenic-(III) and (V) in the presence of NBPHA are shown in fig. 19. From the figure it may be seen that NBPHA has no effect on arsenic-(III) and (V) or on antimony-(V). Arsenic-(V) and antimony-(V) do not reduce[19] at the dropping electrode. NBPHA shows some effect on antimony-(III), the residual current leading up to the antimony step is considerably reduced. Increasing the reagent concentrations (see fig. 19) did not show any effect on these elements, neither was any effect observed due to change in the ethanol concentration (from 10 to 50% $^{V}/_{V}$).

From figure 19 it may be concluded that antimony-(III) could be determined in the presence of antimony-(V) from a 1 M hydrochloric acid solution. The range of antimony-(III) concentrations that could be determined was found to be from 1.65×10^{-4} to 1.65×10^{-3} M while concentrations of antimony-(V) up to 8.25×10^{-3} M do not upset the antimony-(III) determination.

On the strength of the data contained in figs. 18 and 19 the following two methods are suggested for the determination of tin and antimony in a mixture.

Method I

1. Prepare two identical samples, A and B, of a tin-antimony mixture. Take a polarogram on sample A by preparing the solution according to the general procedure. The heights of both waves are measured. The first wave of height h_1 is due to antimony-(III) and tin-(IV) measured at -0.2 volts. The second wave of height h_2($E_{\frac{1}{2}}$ = -0.47 volts) is due to tin and is used for its determination in a mixture.
2. Add a little bromine (slight excess) to sample B to oxidise the antimony, then make up the solution to volume and take a polarogram as before. Measure the first step which is due to tin alone.
3. Subtract h_3 from h_1 to give the antimony step height in the mixture.

Note. By this method tin may be determined accurately in the range 1.69×10^{-4} to 1.69×10^{-3} M, but antimony-(III) could be determined only from 1.65×10^{-4} to 6.29×10^{-4} M.

Table 25

Determination of tin and antimony from various sources.

S.No.	Tin taken mg/25ml.	Tin found	Difference	Antimony taken mg/25ml.	Antimony found	difference
Synthetic mixtures						
1.	1.37	1.38	+0.01	3.75	3.58	-0.17
2.	1.49	1.45	-0.04	3.26	3.38	+0.12
3.	2.89	2.92	+0.03	1.61	1.65	+0.04
4.	1.13	1.07	-0.06	4.06	4.02	-0.04
5.	1.87	1.92	+0.05	2.47	2.38	-0.09
6.	2.16	2.16	0.00	1.75	1.74	-0.01
7.	7.53*	7.55	+0.02	2.71	2.71	0.00
8.	0.89	0.85	-0.04	7.75*	7.69	-0.06
Bronze						
1.	10.21*	10.18	-0.03	0.49	0.45	-0.04
2.	9.80*	9.77	-0.03	0.47	0.50	+0.03
3.	10.07*	10.02	-0.05	0.48	0.48	0.00
4.	9.77*	9.79	+0.02	0.46	0.42	-0.04
White metal						
1.	2.55	2.57	+0.02	5.21	5.18	-0.03
2.	1.31	1.39	+0.09	2.68	2.71	+0.03
3.	3.78	3.83	+0.05	7.73*	7.68	-0.05
4.	2.30	2.27	-0.03	4.70	4.75	-0.05
5.	3.47	3.49	+0.02	7.09*	7.11	+0.02
6.	1.87	1.82	-0.07	3.82	3.80	-0.02

* The sensitivity of the potentiometer was stepped down by a factor of two relative to that used in the other measurements quoted.

Above this antimony concentration results were low due to the residual current of antimony-(V) which increases h_3 with increasing antimony concentration.

Method II

1. To the mixture containing tin and antimony add the required reagents and take the polarogram. The total step height h_1 measured at -0.2 volts is due to antimony-(III) and tin-(IV). Determine the tin concentration in the mixture by measuring the second step height h_2. ($E_{\frac{1}{2}}$ -0.47 volts). Obtain a polarogram for tin of concentration determined by h_2 and measure its first step height (h_3) at -0.2 volts.
2. Subtract h_3, from h_1, which should give a current due to antimony-(III) only in the mixture.

The tin-(IV) range is 1.69×10^{-4} to 1.69×10^{-3} M and the antimony-(III) range 1.65×10^{-4} to 1.65×10^{-3} M.

By following method 2, synthetic mixtures of these two elements were prepared and analysed. The results thus obtained are tabulated in table 25. Further, method 2 was applied to the determination of tin and antimony in a bronze and a white metal alloy and some results of such determinations are included in the same table.

Analysis of bronze. B.C.S. 183/1 bronze was used. It has the composition: copper 84.8%; tin 5.01%; zinc 5.17%; lead 3.51%; phosphorus 0.51%; nickel 0.51%; antimony 0.24% and arsenic 0.14%.

Method. The required weight (from about 180 to 240 mg.) of the alloy was taken in a 250 ml. beaker and tin and antimony were separated from other elements by precipitating them with nitric acid[27]. The precipitate was filtered and dissolved in concentrated hydrochloric acid (5 ml.). Tin and antimony were reduced[9] using nickel powder. Finally, the solution was evaporated to about 2 ml. and made up in 1 M hydrochloric acid. Tin and antimony were determined by method 2. A single analysis required about 30 minutes to complete.

Analysis of white metal. B.C.S. 177/1 sample was used. This contains lead 84.5%; antimony 10.4%; tin 5.09%; copper 0.007%; iron 0.004%; bismuth 0.002%; arsenic < 0.005% and zinc < 0.01%.

Method. A known weight of the alloy (25 mg. to 90 mg.) was dissolved in warm dilute (2:3) nitric acid[28] and then boiled repeatedly with 10 to 20 ml. of concentrated hydrochloric acid until the alloy was completely dissolved. The bulk of the solution was evaporated to about 1 ml. and taken into concentrated perchloric acid (9.4 M). Tin and antimony were extracted with a 2.0% chloroform solution of NBPHA according to the method advocated in section A of this chapter (see under Separations, page 119). Finally, these two elements were reduced using nickel powder[9] and analysed by following method 2. The complete analysis requires about 40 minutes. Alternatively lead may be extracted twice from 0.1 M oxalic acid solution (adjusted to a pH of about 10) with a 3.0% solution of NBPHA in chloroform. The aqueous phase, containing tin and antimony was then analysed for these two elements by following method 2. This procedure was found to be comparatively lengthy and required about 55 minutes for a single analysis.

From table 25, it may be seen that the results of the two alloys analysed are satisfactory. In the determination of tin and antimony with NBPHA (method 2) elements like zinc-(II), cobalt-(II), chromium-(III) and arsenic-(V) are not likely to interfere, while copper-(II), cadmium-(II), iron-(II) and (III), lead-(II), bismuth-(III) and arsenic-(III) are likely to interfere unless separation steps are performed to remove these elements.

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CHAPTER 6

General Discussion and Suggestions for Further Work

From tables 1 and 3 (pages 10 and 21 respectively) it may be seen that cupferron and NBPHA react under similar conditions with many elements. However, the stability of NBPHA to mineral acids offers a definite advantage over cupferron. NBPHA has been known as a precipitant for metals for a long time[1]. Shome[2] has used this substance for the quantitative precipitation and gravimetric determination of elements like copper, aluminium, iron and titanium; an advantage was that the precipitates could be weighed directly. Later, Shome[3] and others extended its use to demonstrate some separations by precipitation methods[4-8]. Elements like indium, gallium, uranium and cerium are precipitated by addition of an ethanolic solution of NBPHA. As described in this thesis in chapter 5, antimony precipitates with NBPHA giving a white product from 1 M hydrochloric acid. The existing literature on antimony indicates a lack of reliable and quick precipitation methods[9] and therefore this reaction of NBPHA merits further investigation. Process of precipitation could be facilitated by a study involving homogeneous precipitation from solution. Niobium has already been studied in this way using NBPHA[10].

Colours resulting from the reaction of NBPHA with elements like iron, vanadium, chromium and titanium were noted by Bamberger[1]. Applications as a colorimetric reagent are confined to a few elements[11-13]. Attempts to use NBPHA as an indicator in titrimetric analysis have been recorded[14], but more work is needed to explore this field thoroughly. Further, apart from work described in chapter 5 (page 102) NBPHA has not been used in polarographic studies. Advantages over cupferron lies in its acid stability and also in the greater range of cathode potentials over which it is stable to reduction. Cupferron has found some application[15] in amperiometric titrimetry and therefore in view of the relatively favourable properties exhibited by NBPHA, a study of the applications of the latter in this field could lead to useful methods.

Shome[2] noted the solubility of a number of metal derivatives of NBPHA in alcohols, ketones, ethers, benzene and chloroform. But it is only relatively recently that the reagent has been used in partition studies[16], which to date have been carried out from aqueous systems containing hydrochloric, sulphuric or perchloric acids[17,18]. NBPHA has been used to separate chemically similar elements by liquid-liquid extraction methods[19-21]. Applications to the lanthanide and actinide group elements are limited[22], and might merit some investigations.

It may therefore be concluded that there is still considerable scope for the development of new methods of analysis using NBPHA.

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